THE SYNTHESIS, CHARACTERIZATION AND ACTIVATION OF SOME MULTINUCLEAR CATALYST PRECURSORS FOR OLEFIN POLYMERIZATION

by

FAZLIN WAGGIE

A dissertation submitted to the

University of Cape Town

in partial fulfillment of the requirements for the degree of

Master of Science

Supervisor : Professor J. R. Moss (UCT)
Joint Supervisor : Professor S. F. Mapolie (UWC)

Department of Chemistry
University of Cape Town
Rondebosch, 7701
South Africa

February 2003

THE SYNTHESIS, CHARACTERIZATION AND ACTIVATION OF SOME MULTINUCLEAR CATALYST PRECURSORS FOR OLEFIN POLYMERIZATION

Fazlin Waggie

University of Cape Town

2003

DECLARATION

I declare that **THE SYNTHESIS, CHARACTERIZATION AND ACTIVATION OF SOME MULTINUCLEAR CATALYST PRECURSORS FOR OLEFIN POLYMERIZATION** is my own work and that all the sources I have used or quoted have been indicated and acknowledged by means of complete references.

....

Fazlin Waggie

I dedicate this thesis to my two precious daughters, Aaliyah and Thaafirah. You two always managed to win mommies attention when I needed to sit down and write the thesis.

Love you.

☺

ACKNOWLEDGMENTS

I would like to thank everyone who contributed to the completion of this research.

- **Professor John Moss**, (UCT) for his constant encouragement, guidance and advice; and especially for his patience during my dissertation.
- **Professor Selwyn Mapolie**, (UWC) for his constant encouragement, guidance and advice; and especially for the constructive criticism throughout the research project and write-up of the thesis.
- **Mark Domingo**, (Sasol Polymers) for his constant encouragement.

Without this combination of people I would not have been able to complete the dissertation.

I would also like to thank the following institutions: Sasol Polymers (Polifin) for financial support and for the glovebox; the University of Cape Town and the University of Western Cape, for the use of the technical facilities and libraries.

Many thanks to all the technical staff at UWC, Chemistry Department, for keeping the lab clean, fully stocked with chemicals and a good supply of nitrogen gas: Gerry, Andele, Nazeem, Timmy and Ben. Thank you Prof. Mapolie for running the NMR spectra, Timmy for doing mass spectra and microanalysis, Piero for microanalysis, Ayesha for DSC of polymers, Alina for NMR of polymers, Basil and Zelda for SEM and EDS of polymers.

To my colleagues and friends, Dalene, Greg, Tracy-Ann, Zulfa, Nora, Mihaela, Sally (for proofreading); thank you for all your help and friendship.

Grant Ravenscroft (Laboratory Manager, Air Quality Monitoring, Scientific Services Department, City of Cape Town), for allowing me time off and the use of facilities needed to write the thesis.

I need to say shukran to my parents, Abduraghmaan and Ayesha, for their love and support. You always encouraged me to further my studies, without this I wouldn't have achieved what I have today.

Finally, shukran to my husband Nazeem for your love and support.

PUBLICATIONS

CONFERENCE CONTRIBUTIONS:

Poster entitled " The preparation and characterization of new allylaryl-ether dendrimers.", F. Waggie and S. F. Mapolie, presented at the 34th Convention of the South African Chemical Institute, Natal University, South Africa (1998)

Poster entitled " Zirconium alkyls as catalyst precursors for olefin polymerization.", F. Waggie and S. F. Mapolie, presented at Inorganic 99 Conference, Stellenbosch, South Africa (1999)

Poster entitled " Multinuclear catalyst precursors for olefin polymerisation." , F. Waggie and S. F. Mapolie, Catalysis Association of South Africa, Conference, Rustenburg (1999)

Lecture entitled " Zirconium alkyls as catalyst precursors for olefin polymerization." F. Waggie, FRD Technical Audit (1999)

Lecture entitled " Hydrocarbyl complexes of Zirconium as catalyst precursors for olefin polymerisation.", F. Waggie, THRIP Technical Audit (1999)

ABBREVIATIONS

Acac = acetylacetonate
Cp = cyclopentadienyl
Cp^1 = methylcyclopentadienyl
Dppe = diphenylphosphino ethane
DSC = Differential Scanning Calorimetry
Et = ethyl
FAB = Fast Atom Bombardment
FTIR = Fourier Transform Infra-Red
G = generation
GPC = Gel Permeation Chromatography
IR = infrared
MAO = methylaluminoxane
M$^+$ = molecular ion
Me = methyl
m/z = mass to charge ratio
NMR = nuclear magnetic resonance
Ph = phenyl
Pr = propyl
R = alkyl
Rp = CpRu(CO)$_2$
SEM = Scanning Electron Microscopy
tert = tertiary
THF = tetrahydrofuran
TMS = tetramethylsilane

ν = stretching vibration
γ = out-of-plane deformation vibration
m = medium intensity
$_{as}$ = antisymmetric
δ = bend or deformation vibration
s = strong intensity
w = weak intensity
$_{s}$ = symmetric

NMR spectroscopy

s = singlet
t = triplet
d = doublet
${}^{x}J$ = coupling constant over x bonds

ABSTRACT

This thesis reports on an exploratory investigation into the immobilization of homogeneous olefin polymerisation catalysts on dendritic supports.

The dendrimers employed were essentially allylaryl-ether type systems and consisted of both dendritic wedges and complete dendrimers. These materials were used as supports for homogeneous zirconocene catalysts. The zirconium moiety was attached to the surface of the dendrimer through the allyl functionality. This was done via hydrozirconation of the pendant C=C of the allyl groups on the periphery of the dendrimers.

A number of model compounds such as $Cp_2Zr\{(CH_2)_4Ph\}(Cl)$ and $Cp_2Zr\{(CH_2)_3OPh\}(Cl)$ were also prepared and their properties compared with the dendritic catalyst precursors. The supported catalyst species together with analogous mononuclear model compounds were activated using a range of activating agents. Included amongst these activating agents are, silver salts of the type AgX, (where $X = OSO_2CF_3$, ClO_4 and BPh_4); the perfluoroaryl borane, $B(C_6F_5)_3$ and MAO. The activated complexes were assessed for their polymerisation ability towards ethylene.

The dendrimers were characterised using techniques such as FTIR spectroscopy, ^1H NMR and ^{13}C NMR spectroscopy, GC mass spectrometry and microanalysis. All new organometallic compounds produced were characterised using techniques such as ^1H NMR and ^{13}C NMR spectroscopy. The polymers prepared were characterised by Gel Permeation Chromatography (GPC), Fourier Transform InfraRed (FTIR), ^1H and ^{13}C NMR spectroscopy, Differential Scanning Calorimetry (DSC) as well as Scanning Electron Microscopy (SEM).

TABLE OF CONTENTS

CHAPTER 1

INTRODUCTION TO OLEFIN POLYMERISATION CATALYSTS AND THE HETEROGENIZATION OF METALLOCENE CATALYSTS FOR OLEFIN POLYMERISATION

1.1 GENERAL INTRODUCTION TO CATALYSTS FOR OLEFIN POLYMERISATION

The polymerisation of olefins, a process that forms carbon-carbon bonds sequentially to give a range of products with different microstructures and properties, is one of the most investigated areas for both industrial and academic laboratories in polymer science.[1] Polyolefins are produced using easily available compounds (ethylene, propylene, dienes, etc), derived from crude oil and natural gas processes. Polymers with a wide range of chemical and mechanical properties are manufactured commercially in very large volume and have numerous applications such as general-purpose and engineering plastics, synthetic rubbers and elastomers. Many catalysts for polymerisation of olefins and dienes are available; some of which are discussed below.

1.1.1 HETEROGENEOUS ZIEGLER–NATTA CATALYSTS FOR OLEFIN POLYMERISATION

The first heterogeneous polymerisation catalyst emerged more than 40 years ago, when Karl Ziegler discovered that combinations of transition metal compounds of titanium (such as $TiCl_4$) and organometallic compounds of aluminium (such as $Al(C_2H_5)_2Cl$) were able to catalyse the polymerisation of ethylene at relatively low temperature and pressure.[2] A little later Guillio Natta found that these types of catalysts polymerised higher alkenes to yield stereoregular products.[3] These so-called “Ziegler–Natta catalysts” have since been used in the commercial manufacture of various polymeric materials including poly(α-olefins) and α-olefin copolymers. The majority of Ziegler-Natta catalysts consist of two components. The first component is a derivative of a transition metal, such as titanium or vanadium. Typical transition metal compounds used in Ziegler–Natta catalysts are $TiCl_4$, $TiCl_3$, $Ti(OR)_4$, VCl_4, $VOCl_3$, VCl_3, $V(acac)_3$ and $ZrCl_4$. The second component, which is referred to as the “co-catalyst”, is an organometallic compound, usually an organoaluminium compound. Typical organoaluminium co-catalysts are $Al(C_2H_5)_3$, $Al(i\text{-}C_4H_9)_3$, $Al(n\text{-}C_3H_7)_3$, $Al(C_2H_5)_2Cl$, $Al(i\text{-}C_4H_9)_2Cl$, $Al(C_2H_5)Cl_2$ and $Al_2(C_2H_5)Cl_2$. The combination of the two components results in a series of chemical reactions and some products of these reactions (called active centres of Ziegler–Natta catalysts) readily polymerise various α-olefins and dienes. Continuous efforts to increase catalytic productivity and improvement in polymer quality led to the development of special supports for the transition metal compounds. These improvements increase the catalytic activity 100 to 200 times. At present, the majority of all commercial Ziegler–Natta catalysts for the synthesis of polyolefins are supported. The most widely used supports are silica, $MgCl_2$, alumina and various polymers.[4]

1.1.2 HETEROGENEOUS PHILLIPS CATALYSTS FOR OLEFIN POLYMERISATION

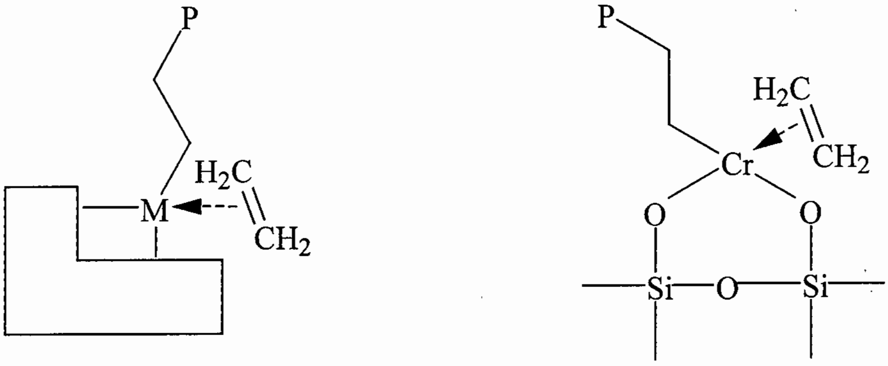
The other heterogeneous ethylene polymerisation system is the Phillips process. This process is based on the use of heterogeneous catalysts consisting of chromium compounds. Here the active catalyst is composed of isolated chromium-oxygen bridge sites (-O-Cr-O-) anchored to the surface of a support, which is usually, silica, SiO_2.[5] The products produced from this system are high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), when using ethylene as feedstock.

Other chromium-based catalysts have also been explored. Some examples are $[Cp^*CrMe]_2$, $Cp^*Cr(O)Me_2$, $Cp^*CrMe_2(THF)$, $[Cp^*CrMe(THF)_2][BPh_4]$, mixed valence dimers such as $Cp^*Cr(\eta\text{-}CH_2Ph)(\mu\text{-}\eta^3{:}\eta^6\text{-}CH_2Ph)CrCp^*$, and anionic complexes such as $[Li][Cp^*Cr(CH_2Ph)_3]$, $(Cp^* = C_5Me_5)$.[6]

Aluminium phosphate and alumina-aluminium phosphate supports are preferred for producing catalysts with high activities and polymers with relatively narrow molecular weight distribution [#].[1] Silica supported catalysts give polymers with much broader distributions.[7]

In both the Ziegler-Natta and Phillips processes, it is generally accepted that polymer chain growth occurs whilst chemically bonded to localised sites of very specific structure. There are single atoms of Cr and Ti respectively at each site and these are in oxidation states, II or III. The metal centres are also coordinatively unsaturated i.e. there are vacant orbitals which can accept pairs of electrons donated by other molecules to form co-ordinate bonds. Both a polymer chain and a monomer molecule could be bound to the metal centre simultaneously. Recently Casey *et al* reported the identification and isolation of a metal complex with both an alkyl group and an alkene monomer coordinated to the metal.[8] Figure 1.1 shows schematically the active centres of these catalysts with the growing polyethylene chain attached to the active metal atom and with the coordinated ethylene molecule positioned for insertion into the M-C bond.

[#] Molecular weight distribution: Ratio of the number average molecular (Mn) to the weight average molecular weight (Mw).



a) M = Ti, Zr **b)**

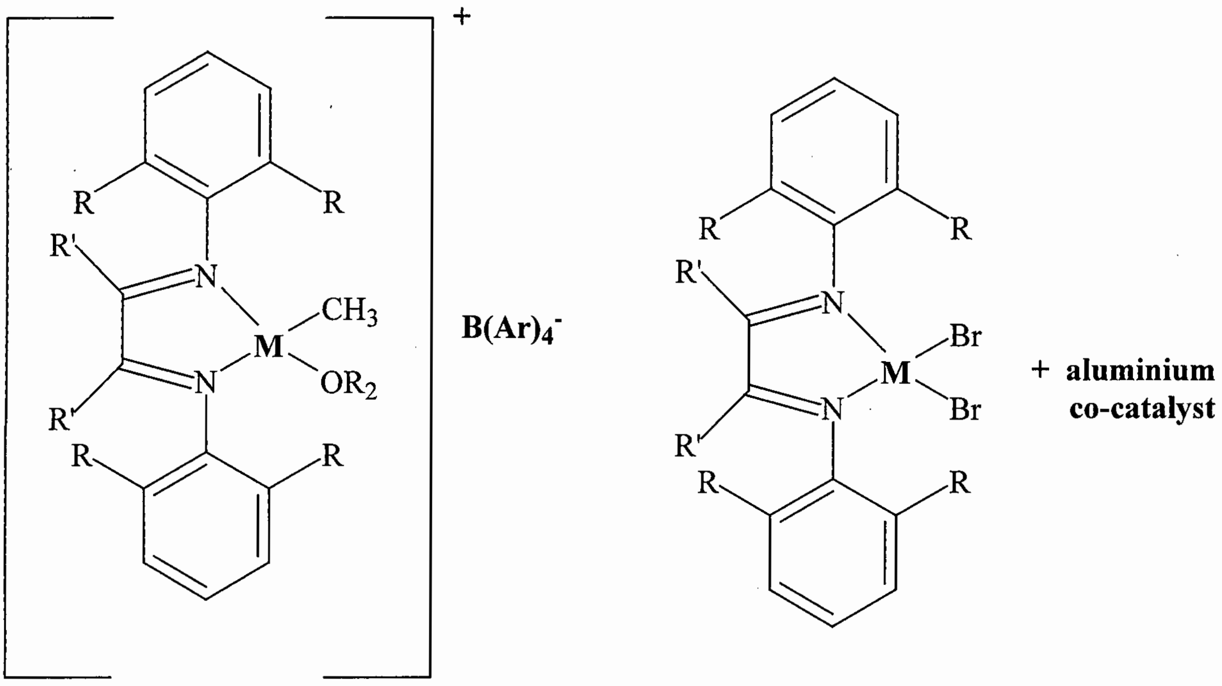
Figure 1.1. Representation of the active centre on the surface of heterogeneous polymerisation catalysts, a) Ziegler-Natta catalyst and b) Phillips catalyst.

1.1.3 LATE TRANSITION METAL CATALYSTS FOR OLEFIN POLYMERISATION

Although early transition metal catalysts currently dominate industrial polymerisation processes there has been a trend towards the development of catalysts based on late transition metal elements. Relative to early transition metal catalysts, these systems have the potential to yield polymers with different microstructures, they are less oxophilic and therefore more tolerant of functionalised monomers. In addition they also require a smaller amount of aluminium co-catalyst for their activation. Currently well defined catalysts based on complexes of rhodium[9], nickel[10], palladium[11], platinum[12], iron[13] and cobalt[14] have been reported to polymerise olefins.

Of interest is the report by Brookhart *et al*[15] of cationic Pd(II) and Ni(II) α-diimine catalysts, (Figure 1.2.), for the polymerisation of ethylene, α-olefins and cyclic olefins.

These catalysts are also capable of the co-polymerisation of nonpolar olefins with a variety of functionalised olefins.



I

II

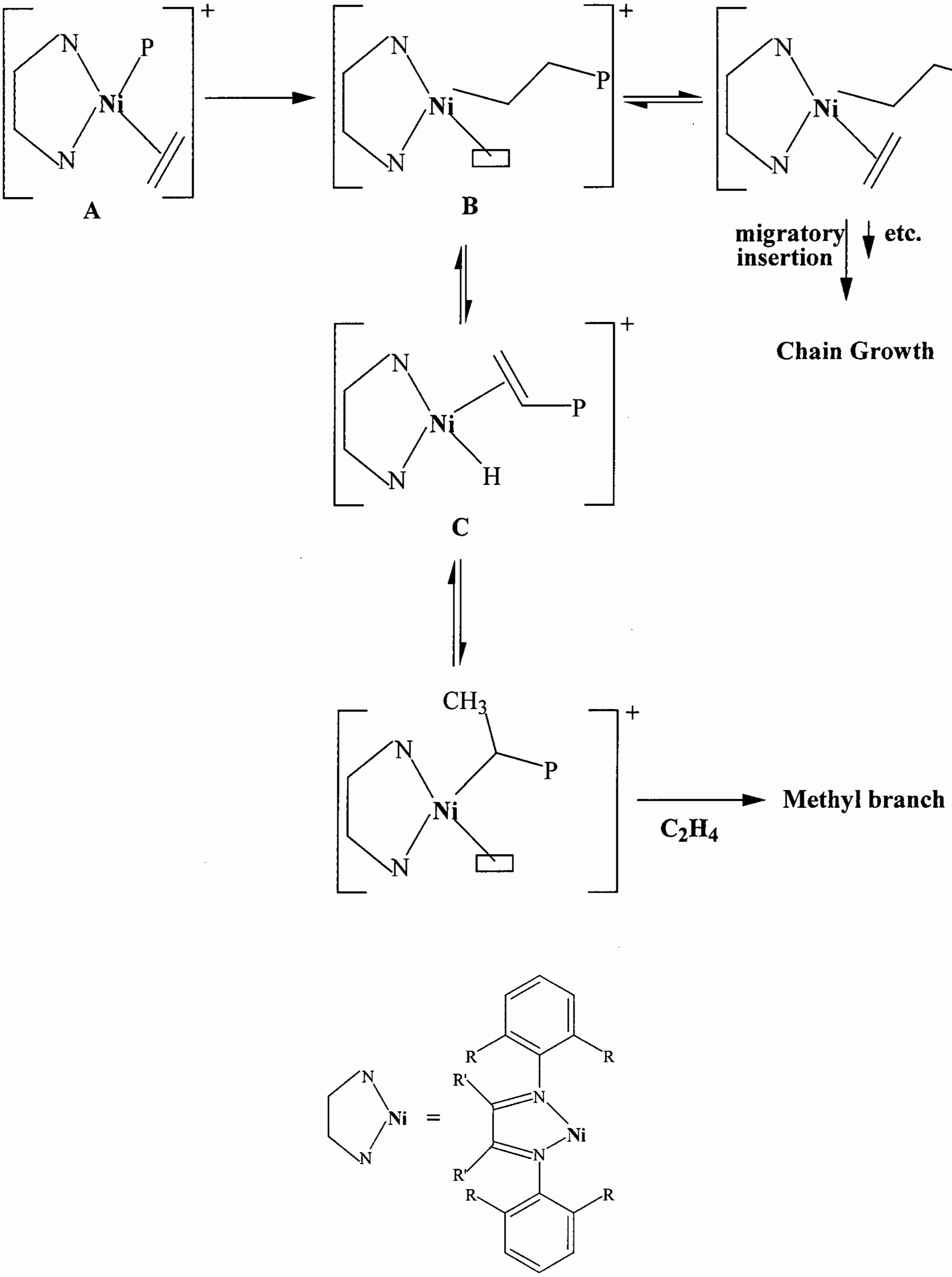
M = Ni or Pd

Ar' = 3,5-[$C_6H_3(CF_3)_2$]

Figure 1.2. Ni(II) and Pd(II) α–diimine polymerisation catalysts.

A general mechanism for alkene polymerisation has been proposed and is shown in Scheme 1.1.[10, 16] The catalyst resting state for the systems is the alkyl olefin complex A. The turnover-limiting step is the migratory insertion reaction to yield an intermediate cationic alkyl complex B. The cationic alkyl species generated following migratory insertion have been shown to have β-agostic interactions. The initially formed primary alkyl species is trapped by ethylene and then followed by insertion. This results in chain growth without the introduction of a branch in the polymer. Alternatively, prior to trapping and insertion, the agostic metal alkyl species can undergo a series of β-hydride elimination's and re-additions. This results in the metal migrating along the polymer chain. Trapping of these species followed by insertion results in the introduction of a branch into the growing polymer chain.

The Ni α-diimine catalysts may be supported on a wide range of inorganic oxide supports[17], although silica is the most widely used support. The supporting procedure generally includes the use of aluminium reagent to provide alkylation and generation of the cationic site. The nickel catalysts may also be supported on polymeric supports and clays.[18] Clays such as montmorillinite are acidic. The clay-supported catalyst does not need to be activated because the strong acidic nature of the support is sufficient to activate the catalyst.



Scheme 1.1. Proposed mechanism for the preparation of polyethylene from Ni(II) catalyst.

1.1.4 METALLOCENE CATALYSTS FOR OLEFIN POLYMERISATION

Following Ziegler and Natta's discovery of heterogeneous olefin polymerisation catalysts in the mid 1950's, efforts were directed at devising homogeneous catalyst model systems that would enable mechanistic studies to be carried out. In 1957, Natta and Breslow independently reported that the metallocene Cp_2TiCl_2 could be activated for olefin polymerisation by $Al(C_2H_5)_3$ or $Al(C_2H_5)_2Cl$.[19] Although they are useful for model and kinetics studies, these titanocene catalysts were of no commercial interest because of their low activity, propensity to decompose to inactive species and inability to polymerise higher α-olefins. Subsequent research on this and other metallocene systems with various alkyl groups has now been performed.[20] It was shown that the activity of the catalyst reaches a maximum after a short induction period then decreases continuously, due to fast ageing processes such as alkyl exchange, hydrogen transfer and reduction of the transition metal species.

A remarkable increase in activity (factor 20 to 100) was found by Reichart and Meyer[21] by adding small amounts of water in a ratio of alkyl : $H_2O = 20 : 1$ to the system Cp_2TiCl_2 / $Al(C_2H_5)Cl_2$, and by Long and Breslow[22] to the catalyst system Cp_2TiCl_2 / $Al(CH_3)_2Cl$. These workers reported a stable catalyst complex resulting from an increase in Lewis acidity. An enormous increase in activity (factor up to 1 million) was found by Kaminsky and Sinn when water was added to the catalyst system Cp_2TiMe_2/ $Al(CH_3)_3$ in a ratio of $Al(CH_3)_3 : H_2O = 1 : 2$. They also reported that the isolated product of $Al(CH_3)_3$/ H_2O, commonly referred to as methylaluminoxane (MAO) could be used together with titanocenes and zirconocenes (Cp_2TiMe_2, Cp_2ZrMe_2, Cp_2ZrCl_2) as catalysts for ethylene polymerisation.[23] Not only was the catalytic activity increased, but the average molecular weight of the polymers also increased dramatically.

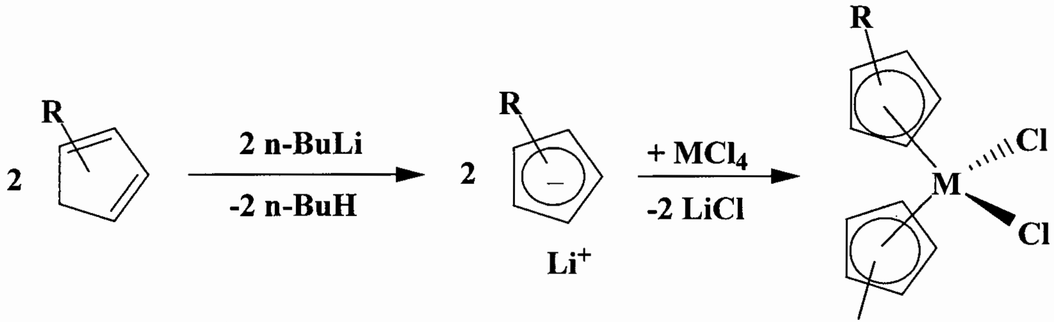
The catalysts are soluble in the reaction mixture and form a homogeneous system before precipitation of the polymer. Owing to their homogeneous nature every molecule has an active site at an identical position within the molecule and every metal atom is available for catalytic reaction. Hence they are known as single site catalysts.

1.2 PREPARATION AND ACTIVATION OF METALLOCENE CATALYSTS FOR OLEFIN POLYMERISATION

1.2.1 PREPARATION

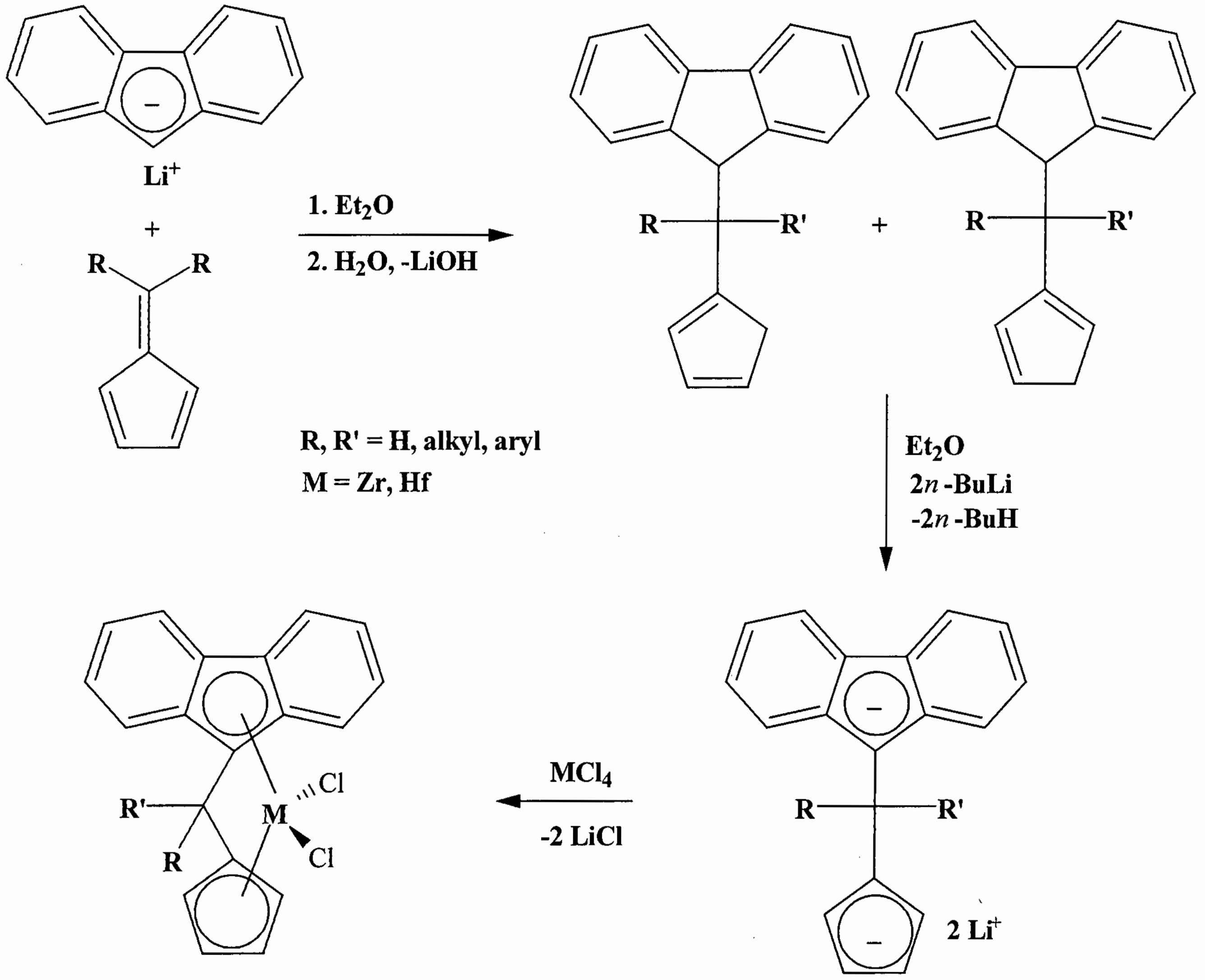
The most common catalyst precursor is a metallocene dichloride complex, Cp_2MCl_2 (where M = Zr, Hf, Ti), consisting of two aromatic five-membered ring systems that can be tethered by a bridging unit (*ansa* metallocene complexes) or not. This class of compounds are air stable but very sensitive to moisture due to the high oxophilicity of zirconium or hafnium. The two aromatic ligands at the metal can be of the same type, i.e., cyclopentadienyl, indenyl, or flourenyl. The introduction of substituents at certain positions of the two aromatic ligands and/or the bridge modifies not only the steric and electronic conditions in the molecule but also the symmetry of such a metallocene dichloride complex. Another variable parameter is the metal.

These possibilities of varying the catalytically active complex are reflected in the stereospecificity, chain branching and chain length of the polymer; specificity towards monomers and the generation of block copolymers. Hence group 4 metallocene-based catalysts can produce tailored polyalkenes for almost every possible purpose. Depending on the nature of the aromatic ligand several methods for the preparation of unbridged and bridged metallocene complexes are available (Schemes 1.2. – 1.5.).

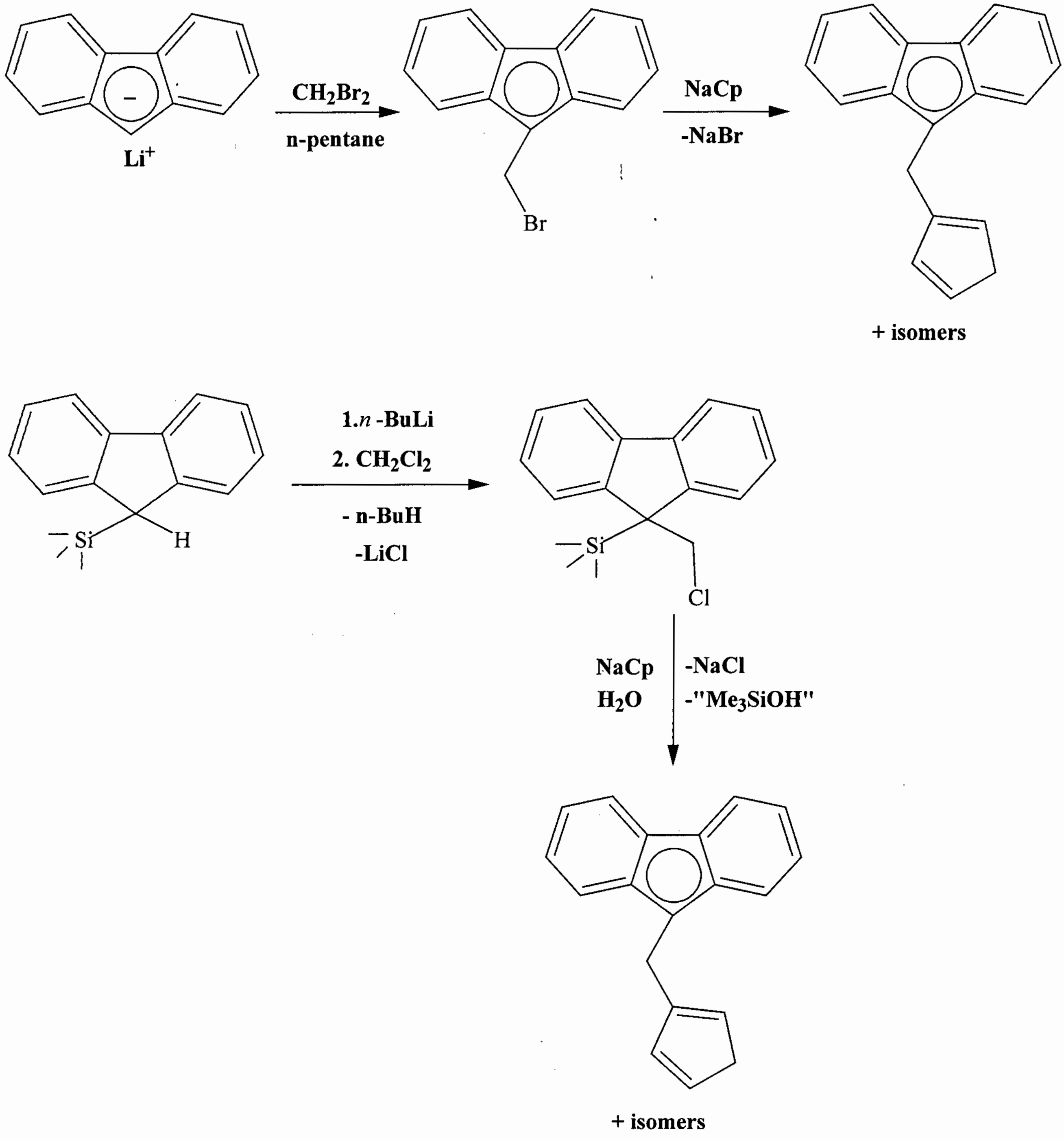


M = Ti, Zr, Hf
R = alkyl, aryl or fused ring systems (indenyl, flourenyl)

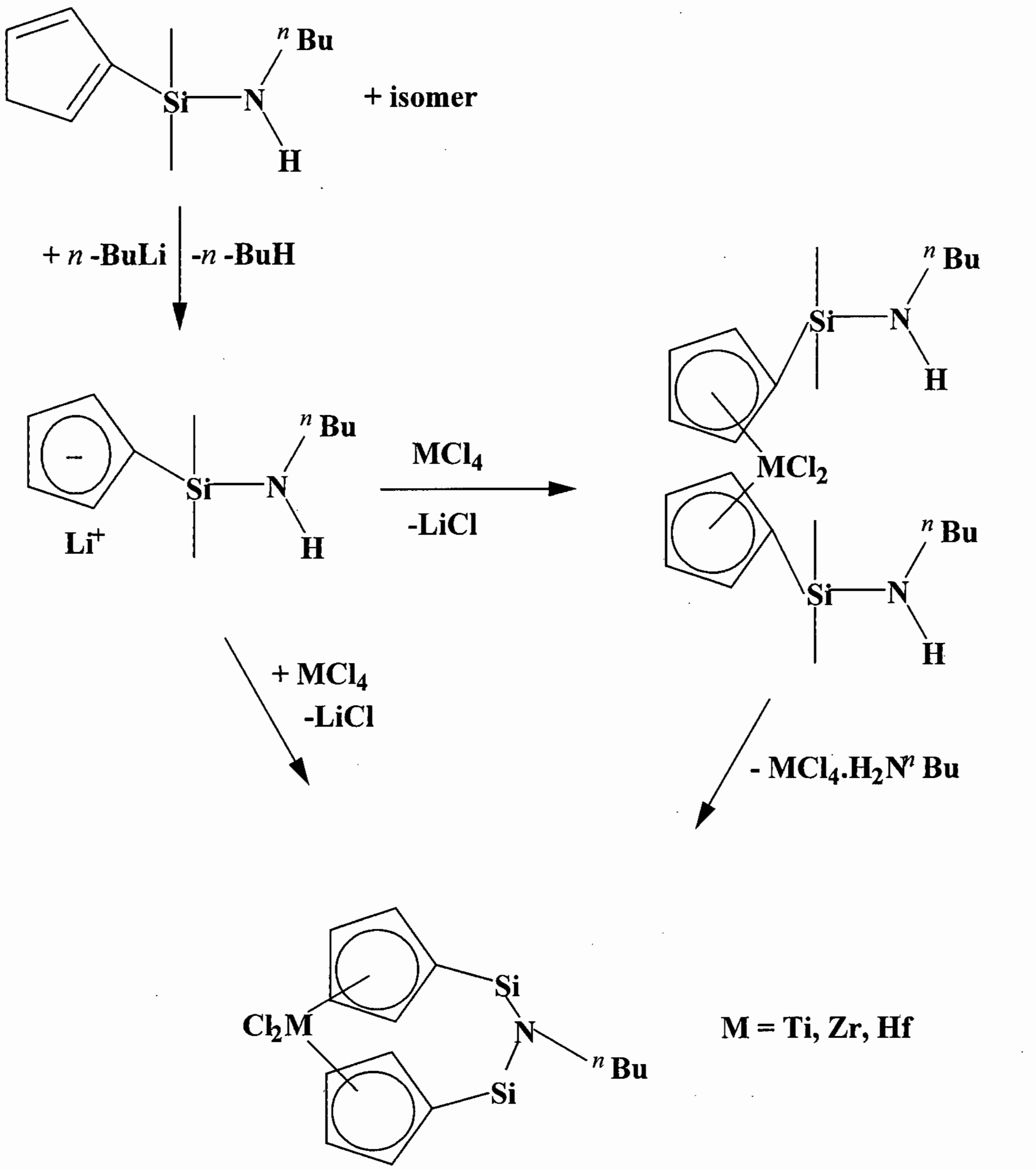
Scheme 1.2. Preparation of unbridged metallocene dichloride complexes.



Scheme 1.3. **Preparation of *ansa*-metallocene dichloride complexes via the "fulvene method".** [24]



Scheme 1.4. **C-C Coupling reactions for the preparation of ligand precursors.**[25]



Scheme 1.5. Preparation of a metallocene complex with a bridging Si-N-Si unit.[26]

1.2.2 ACTIVATION

A key to the high polymerisation activity of metallocene catalysts is the co-catalyst. Methylaluminoxane (MAO) is mostly used and is synthesised by controlled hydrolysis of trimethylaluminium. The MAO co-catalyst is believed to:

i. alkylate the metallocene;

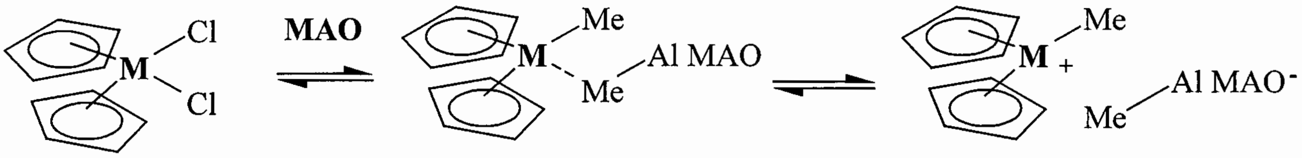
ii. scavenge impurities;

iii. stabilise the cationic centre in an ion-pair interaction and

iv. possibly prevent bimetallic deactivation processes from occurring.

Other potential co-catalysts are complexes, which show a weak coordination such as borates, flourates and silver salts.[27] One function of MAO is the alkylation of halogenated complexes. In the first step, the monomethyl complex is formed in seconds.[28] Excess MAO leads to the dialkylated species. In order for the active site to form, it is necessary that at least one alkyl group is bonded to the metallocene.[29] The second step involves the carbanion abstraction to produce a metallocene monomethyl cation as the actual catalytic species. This theory is supported by the fact that strong Lewis acids, e.g. $B(C_6F_5)_3$, abstract a methyl anion from dimethylated complexes to produce species of the type Cp_2MMe^+ that is the actual catalyst for the polymerisation of olefins.[30]

Although very extensive research has been carried out, the exact composition and structure of MAO are still not entirely clear.[31] The proposed composition of MAO is oligomers consisting of $[Al(Me)\text{-}O\text{-}]_n$ subunits, with n ranging from 5 to 20. There are different equilibria between oligomers. Amongst the different oligomers, $(CH_3)_2Al\text{-}O\text{-}Al(CH_3)\text{-}OAl(CH_3)_2$ units are important. These units can associate resulting in coordination of the unsaturated aluminium atoms. There are tri- and tetra-coordinated aluminium atoms, of which the trivalent show extreme Lewis acidity. Four of the $Al_4O_3(CH_3)_6$ units can form a cage structure resembling a half-open dodecaeder $(Al_{16}O_{12}(CH_3)_{24})$. This cage is complexed with differing amounts of trimethylaluminium. The $AlMe_3$ molecule, which is accommodated in the cage accomplishes activation by methylation of the metallocene and subsequent carbanion abstraction (Scheme 1.6.). These steps result in the generation of the catalytically active metallocene monomethyl cation. The resulting ion pair is the actual catalyst.



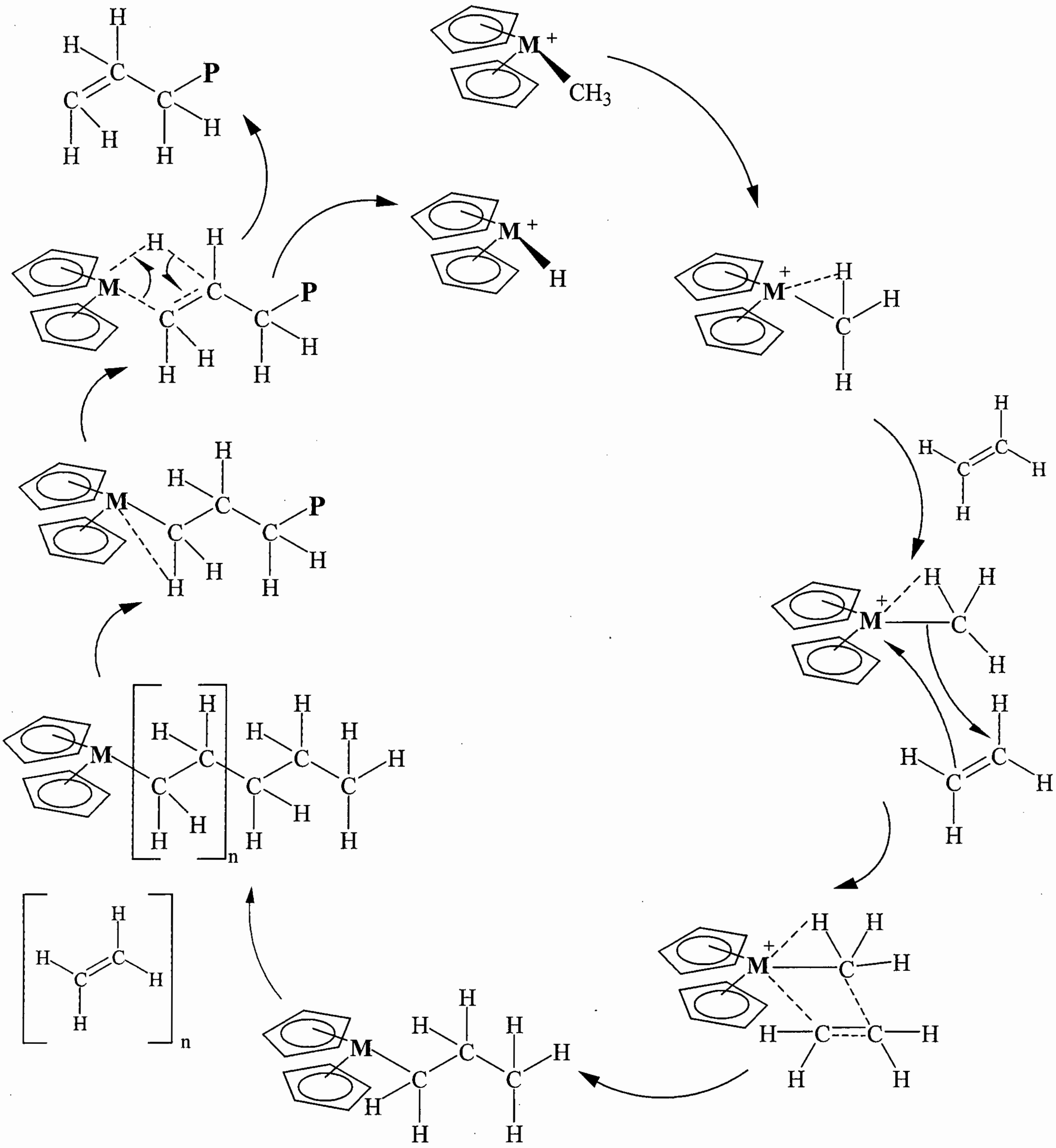
Scheme 1.6. Proposed activation of zirconocene dichloride by MAO.[1d]

1.2.3 MECHANISM

The olefin polymerisation by metallocene catalysts is believed to follow the Cossee-Arlman mechanism, which is the same mechanism followed by traditional Ziegler-Natta catalysts. The active species is a 14-valence electron cationic alkylmetallocenium ion, $CpMR^+$.

The first step in the catalytic olefin polymerisation process is the co-ordination of the olefin to the Lewis-acidic metal centre, which is confirmed by suitable model complexes such as $Cp_2Zr(PMe_3)C_2H_4$.[32] The chain propagation proceeds with a formal ethylene insertion into the M-C bond. The insertion step consists of an alkyl migration to the olefin through a four-centre transition state. At the same time, a new free co-ordination site is generated at the vacant position of the former alkyl ligand. Successive monomer addition extends the polymer chain.

Chain termination or transfer stops the polymerisation process. The main chain termination pathway is a β–hydrogen transfer reaction to the monomer. This produces a terminal olefin function at the end of the polymer chain. Chain transfer to aluminium and to the monomer can also occur.



Scheme 1.7. Catalytic alkene polymerisation as proposed by Cossee and Arlman.

1.3 HETEROGENIZATION OF METALLOCENE OLEFIN POLYMERISATION CATALYSTS

Single-site catalysts are almost all homogeneous in nature. They are soluble and active in non-nucleophilic organic solvents such as toluene and aliphatic hydrocarbons. Commercial polymerisation processes using soluble catalysts are those in which the polymers produced are soluble in the reaction diluent or which operate at temperatures above the melting point of the polymer. These products include elastomers and very low-density ethylene copolymers. In these solution processes the reaction diluent is volatilised and the polymer recovered for compounding and pelletization.

In slurry, bulk monomer or fluidised bed gas phase processes, the catalyst and polymer products are insoluble in the reactor diluent or fluidised gas stream. This is attributed to the high density or crystallinity of the polymer (eg. high-density polyethylene, linear low-density polyethylene and isotactic polypropylene). These processes are continuous and therefore require the use of morphologically uniform catalyst particles. This allows the smooth introduction of catalyst particles into the reactor without clumping. This implies fixing the solution soluble catalyst on an insoluble support.[7]

A continuous and gradual expansion of the polymer particle, especially in the early stages of polymerisation, ensures a uniform expansion. This avoids overheating of the polymer particle and melting of the polymer. This could result in the polymer particles adhering to the reactor walls and agitator to form sheets, product discharge or the formation of large chunks. The catalyst should polymerise the monomer to produce a polymer product of high bulk density, which mirrors the particle size distribution of the catalyst.[33]

Single-site catalysts have been successfully supported using numerous methods and many different types of support materials without seriously affecting polymer properties.[34] These supported catalysts have been used commercially to produce polymers with narrow particle size distribution and high bulk densities. The most widely used supports for single site catalysts are inorganic oxides, in particular silica. Silica with a wide range of particle sizes has been used.[34] Other materials for immobilising the catalysts have been reported, such as alumina, magnesium chloride, polystyrene, etc.

There are three basic methods for supporting aluminoxane-activated single-site catalysts.[35]

i. Supporting the aluminoxane, then reacting with the metal complex;

ii. supporting the metallocene, then reacting with the aluminoxane and

iii. contacting the aluminoxane and metal complex in solution before supporting.

The three methods result in different catalysts and these in turn, produce polymers with different properties. These are discussed briefly.

i. Supported Aluminoxanes

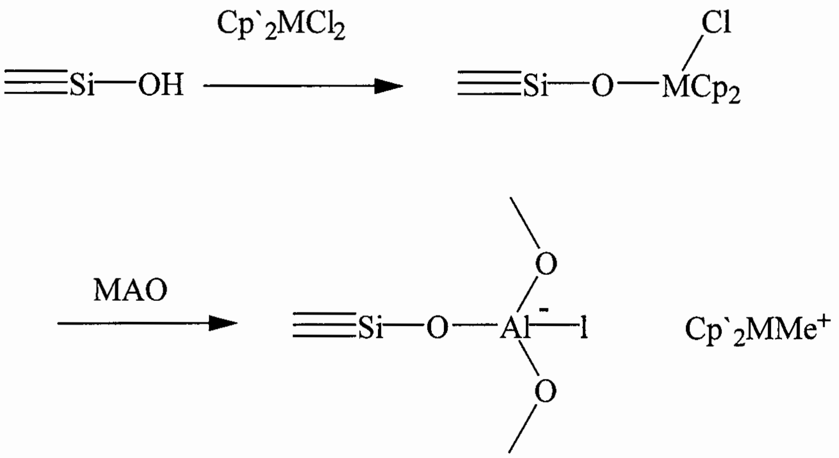
Supporting the aluminoxane first, followed by reaction with the metal complex, was among the earliest methods used for preparing heterogeneous single-site catalysts. Welborn and Takahashi reacted silica with a solution of MAO and decanted the solution to isolate the MAO-containing solids. These were reacted with $Cp`_2ZrX_2$ (Cp = substituted or unsubstituted cyclopentadienyl; X = Cl, Me) to form the catalyst. This was used for ethylene polymerisations and co-polymerisations. Subsequently, a number of metallocene complexes of the group 4 metals were supported by reaction with MAO on silica. $Et(Cp`)(NMe_2)TiCl_2$ was contacted with MAO supported on silica to form catalysts used for ethylene polymerisation.[34]

(n-BuCp)$_2$ZrCl$_2$ was reacted with supported MAO on silica and polymer growth in ethylene was examined by electron microscopy.[34] This study indicated that all the MAO is located on the particle surface of the support with no aluminium present in the pores of the particle. During polymerisation no particle fragmentation occurred and the polymer formed irregularly on the surface.

The supported MAO may be chemically modified when supported. MAO supported on silica or alumina was taken up in tetrahydrofuran (THF) and reacted with a cross-linking agent, (4,4`-isopropylidenediphenol).[34] The modified MAO support, reacted with $Et(Ind)_2ZrCl_2$, polymerises propylene to spherical polymer particles while the unmodified support forms coarse agglomerates.

ii. Supported Metal Complexes

Supporting the metal complex on the carrier first, then reacting with aluminoxane, is more common for complexes chemically tethered to the carrier and rarer for Cp_nM_{3-n} complexes. Blitz *et al* studied the adsorption of Cp_2MCl_2 complexes on bare silica, silica heated at 600^{0}C, and silica heated with dehydroxylating agent hexamethyldisilazine.[36] The order of reactivity was found to be $Cp_2HfCl_2 > Cp_2ZrCl_2 > Cp_2TiCl_2$. Metallocenes react with silica surfaces to form =Si-OMClCp`$_2$ groups, which are converted to catalytic species on reaction with MAO (Scheme 1.8.).



Scheme 1.8. Binding of a catalyst on silica.

To remove reactive surface hydroxyl groups, the support may first be treated with compounds such as aluminium alkyls. Silica treated with aluminium alkyls serves to fix metallocene complexes bearing polar substituents such as Et(2-(*t*-BuMe$_2$-SiO)Ind)$_2$ZrCl$_2$ and bis(2-tetrahydrofuranylmethyl-Cp)$_2$ZrCl$_2$.[37] Reacting the metallocene with a trialkylaluminium before supporting is reported to lead to catalysts of higher activity than when metallocene dichlorides are supported alone.

iii. Contacting the MAO and Metal Complex in solutions before supporting

The most common method of supporting single-site catalysts is to combine the metal component and aluminoxane in a solvent, then add the solution to the support material. There are several advantages to this method. The process maximises the number of active centres by activating the metal component in solution. Highly active catalysts can be produced even at low Al/Zr ratios. Techniques have also been developed to reduce the amount of solvent used. In this way the catalyst preparation process is faster and the formation of large amounts of solvent by-products is reduced.

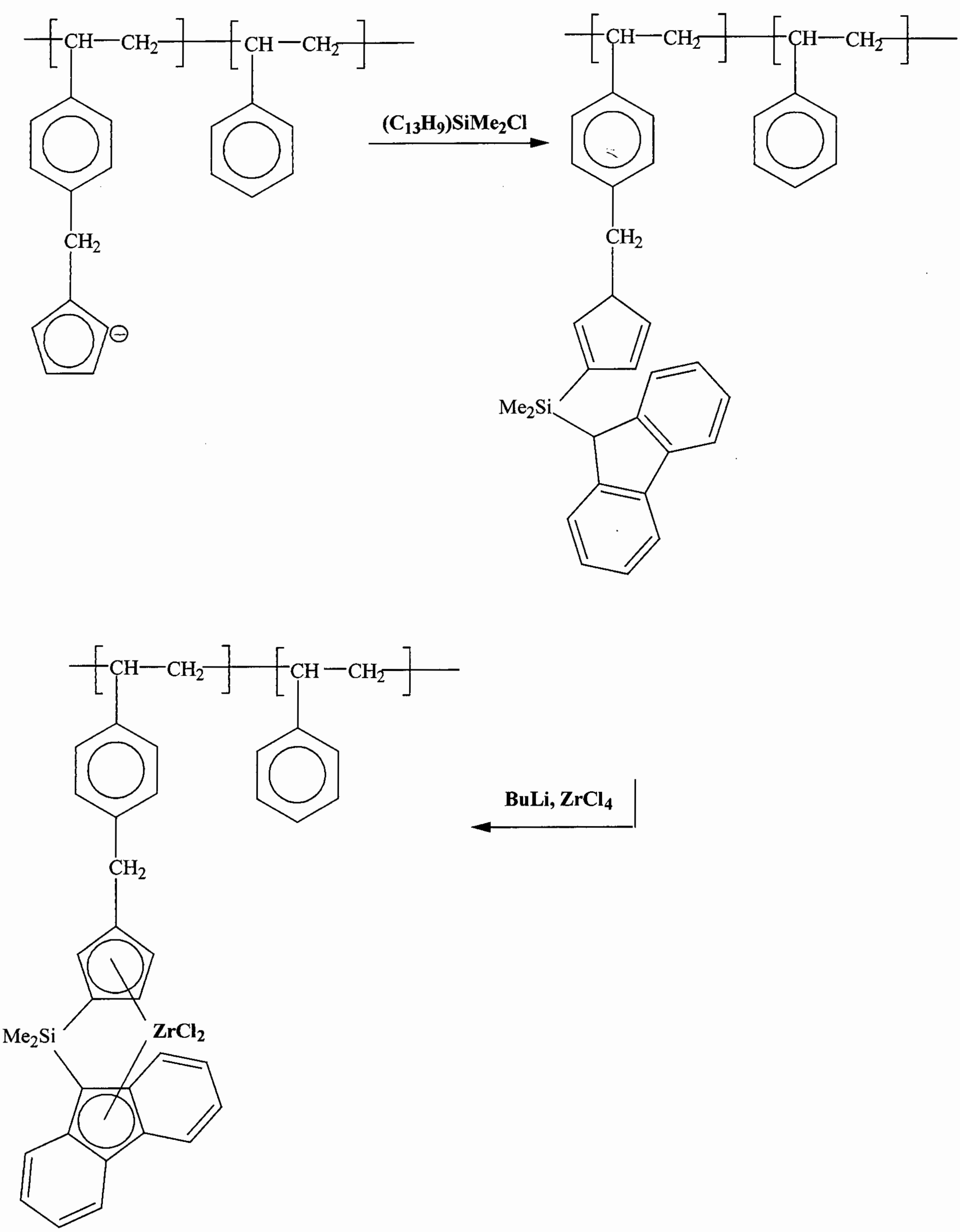
In this method, the metal component and MAO are combined in a solvent, usually toluene. Metallocenes of low solubility dissolve in MAO solutions and impurities can be removed by filtration.[20] The solution is then added to the support held at low pressure in order to improve impregnation into the pores of the support. This method is described as vacuum impregnation. In the final step the slurry is dried in a vacuum, by a nitrogen purge or by spray drying to form the finished product as a free-flowing solid.

Allowing a toluene solution of Me$_2$Si(2-Me-4-PhInd)$_2$ZrCl$_2$-MAO to stand for 18 hours before adding to the silica support is claimed to improve activity in propylene polymerisations to (193kg of PP/g of metallocene/hour). Whereas if the catalyst is added to the carrier immediately the rate of polymerisation is (103kg of PP/g of metallocene/hour).[34] Some different types of support materials are discussed briefly.

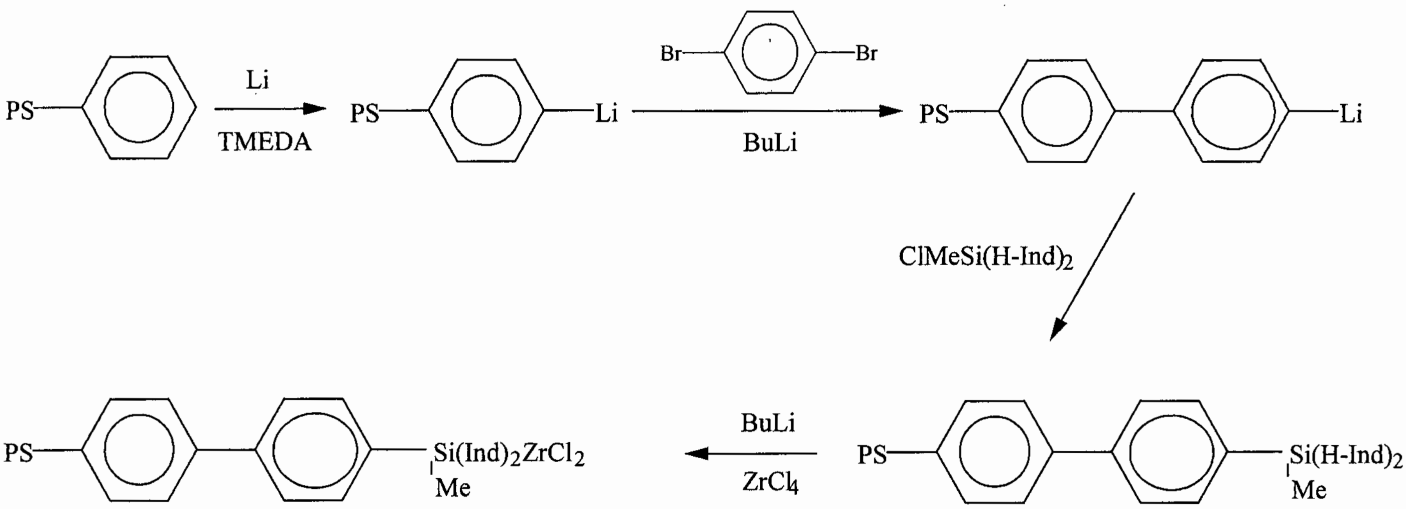
1.3.1 ORGANIC SUPPORTS

Organic materials used for supporting metallocene catalysts includes polystyrene, polyethylene, polypropylene and copolymers.[26] It is possible to fix a ligand precursor on a polymeric support and then build up the catalyst. Synthesising the metallocene on a polymeric support, can be done by reacting a chlorinated polymer, such as chloromethylated polystyrene, with cyclopentadiene. This can be deprotonated to form the polymer-bound Cp anion, which can react with $CpZrCl_3$ to form polystyrene-bound Cp_2ZrCl_2.[38] A more elaborate metallocene was constructed when the polymer-bound Cp anion is allowed to react with $ClMe_2(Flu)$, followed by deprotonation and metallation with $ZrCl_4$ (Scheme 1.9.).[34] Activated by MAO, this metallocene polymerizes ethylene in a hexane slurry.

A polystyrene-supported *rac*-$Ph_2Si(Ind)_2ZrCl_2$ was prepared by the procedure indicated in (Scheme 1.10.).[39] Combined with MAO (Al/Zr = 5000), this catalyst polymerizes ethylene at temperatures as high as 150^0C. Elemental mapping indicates that the catalyst is evenly distributed and located only on the surface of the polystyrene bead. Polymer growth then occurs only on the surface.[40]

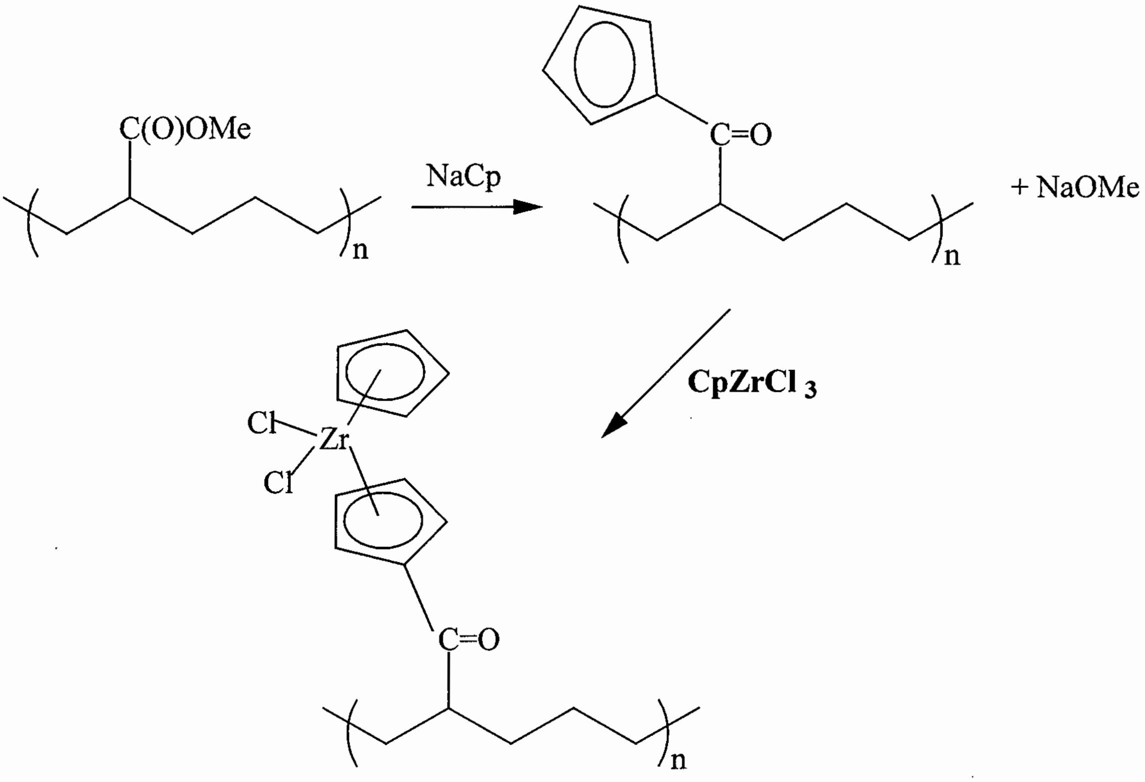


Scheme 1.9. Proposed preparation of a polymer-bound metallocene.



Scheme 1.10. Proposed preparation of polystyrene-supported metallocene.

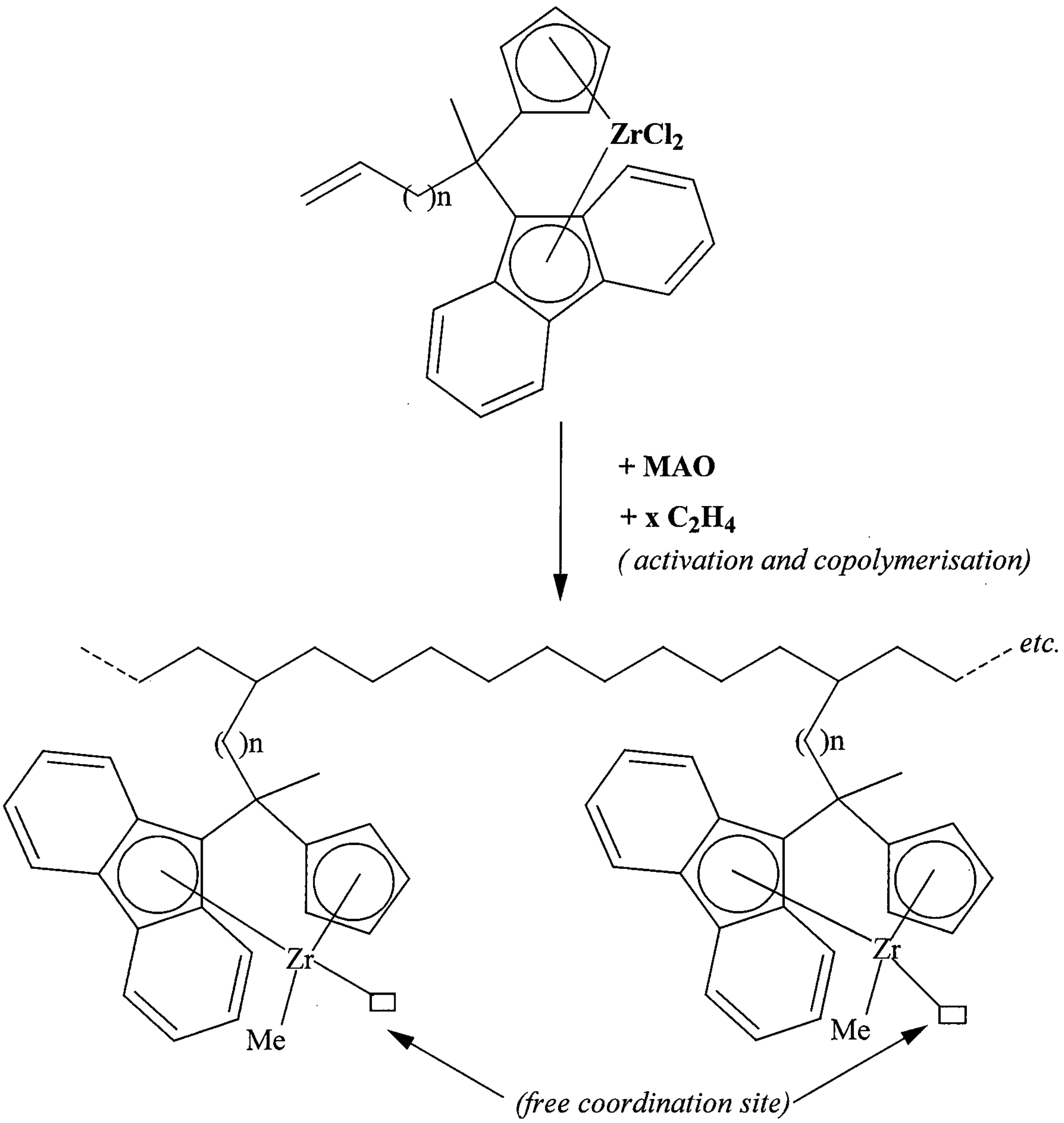
Ethylene-methyl acrylate (EMA) copolymers react with sodium cyclopentadienide yielding a polymer-bound Cp anion, which forms an EMA-bound metallocene when combined with $CpZrCl_3$ or $ZrCl_4(THF)_2$ (Scheme 1.11.).[41] Both catalysts polymerise ethylene in isobutane or toluene slurries to produce polyethylene of relative narrow molecular weight distribution (M_w/M_n=2.3 - 3.0) when activated by MAO.



Scheme 1.11. Proposed preparation of a polymer bound metallocene.

All or part of the ligand set can be homo- or copolymerised prior to metallation. 2-vinylfluorene is homopolymerised or copolymerised with styrene using 2,2`-azobisisobutyronitrile (AIBN) or $BF_3.OEt_2$ as initiator. The polymer, with a molecular weight of 5 000-20 000 daltons, is then deprotonated and reacted with $CpZrCl_3$ to form the polymeric procatalyst. The substituted styrene complex is copolymerised with styrene in the presence of AIBN yielding a polymeric ligand set. The zirconocene dichloride derived from this copolymer polymerizes propylene to syndiotactic polypropylene with relatively high stereospecificity.[42]

Polymer-bound metallocenes are also prepared by polymerizing via a substituent on the cyclopentadienyl ring or the bridge. These so-called self-immobilising catalysts, have a pendant ω-alkene group on the ligand (Scheme 1.12.). Alkenyl- and alkynylsubstituted metallocenes such as $(H_2C{=}CHCp)_2ZrCl_2$, $(H_2C{=}CHCH_2Cp)_2ZrCl_2$, $1,2\text{-}C_2H_4(H_2C{=}CH(CH_2)_nInd)(Flu)ZrCl_2$ (n=1,4), $1,2\text{-}C_2H_4(H_2C{=}CH(CH_2)_4SiMe_2Ind)(Flu)ZrCl_2$ and $Cp(2,7\text{-}(PhC{=}C)_2Flu)ZrCl_2$ can be reacted with MAO and pre-polymerised with ethylene under low-pressure conditions to form heterogeneous cross-linked metallocene polymers with or without silica as a filler. These can be used for slurry or gas-phase polymerisations free of reactor fouling.[43]

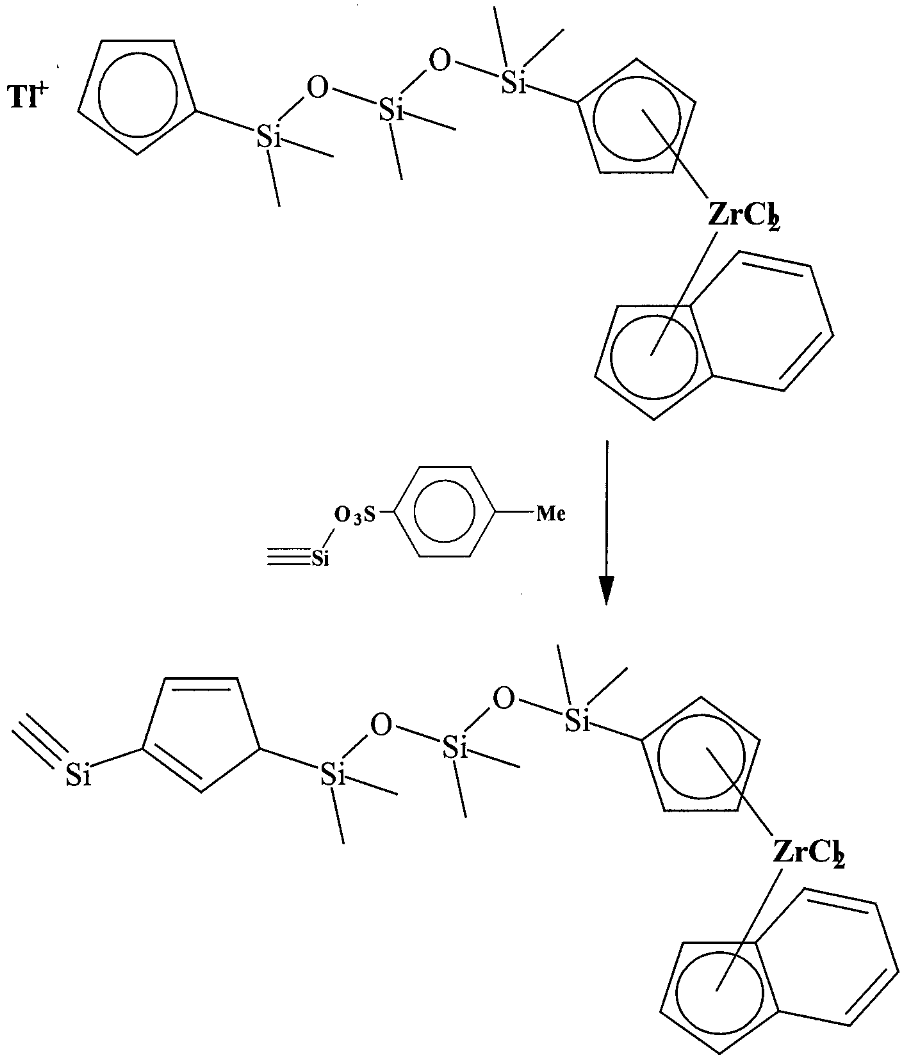


Scheme 1.12. Proposed synthetic pathway for the "self-immobilisation" of a homogeneous *ansa*-metallocene catalyst.

1.3.2 INORGANIC SUPPORTS

Inorganic support materials are widely used for Ziegler-Natta and Philips catalysts. Silica predominates amongst inorganic support materials[44], while other supports include alumina, magnesium dichloride and mixtures of the aforementioned supports. The fixation of the catalyst can either be performed by an absorption process at the surface of the solid particles or by a chemical bond.

A variety of mono- and bis(cyclopentadienyl) complexes bearing hydroxyl reactive substituents on one or two rings have been prepared. Amongst these, $(MeO)_3Si(CH_2)_3IndZrCl_3$, $((MeO)_3Si(CH_2)_3Ind)_2ZrCl_2$, $(MeO)_2MeSiCpTiCl_3$ and $((MeO)Me_2SiCp)CpZrCl_2$ have been prepared and contacted with silica to produce catalysts which are catalytically active in the presence of MAO.[29] The thallium salt of (1,5-bis(cyclopentadienyl)-hexamethyltrisiloxyl)(indenyl)zirconium dichloride reacts with *p*-tolylsulfonyl-treated silica to form a tethered metallocene with a cyclopentadiene group bound to the surface (Scheme 1.13.). This catalyst polymerises ethylene in the presence of MAO.[45]



Scheme 1.13. Zirconium supported on modified silica.

Ansa-metallocene tethered to a silica surface through the bridging group have been prepared by reacting $ClMeSi(Cp)_2MCl_2$ (M = Zr, Hf) with partially dehydroxylated silica, either by itself or modified by agents as $(MeO)_3Si(CH_2)_3NH_2$. Reaction of ClMeSi(Cp)(Flu) with partially hydroxylated silica, followed by deprotonation and reaction with $ZrCl_4$ results in an *ansa*-

metallocene attached to silica through the bridging atom. This catalyst is active for ethylene polymerisation when combined with MAO.

Silica can be modified using $(EtO)_3Si(CH_2)_3C_5H_5$ to give a cyclopentadiene-bearing silica surface. The metallocene is then assembled onto the support by deprotonation of the support with BuLi and reaction with $CpZrCl_3$. This affords the supported catalyst $=Si\text{-}O\text{-}(EtO)_2Si(CH_2)_3C_5H_4(Cp)ZrCl_2$, which is twice as active for ethylene polymerisation as a homogeneous $CpZrCl_3$-MAO catalyst.[34]

1.3.3 OTHER SUPPORT MATERIALS

Zeolites

Zeolites have begun to attract more interest as supports for single-site catalysts. Unlike silica, with its amorphous structure and wide distribution of pore sizes, zeolites have more regular structures, pore sizes and supercages. The zeolite counter-cations (Na^+, H^+, NH_4^+) can be ion exchanged. This feature allows the possibility of electronically tuning the support.

Zeolites such as NaY and HY as well as chemically modified zeolites have been studied as support materials.[46] Catalysts supported on zeolites generally show lower activity and polymer molecular weights are higher than those of the homogeneous analogue.

NaY can be treated with MAO or $AlMe_3$, then with Cp_2MCl_2 (M= Ti, Zr) to form the catalyst. The catalyst is inactive at Al/Zr = 186 and the activity is negligible when $AlMe_3$ is used. Catalyst activities are lower than the homogeneous analogues, but the polymer molecular weights are higher.[47]

Clays

Clays such as montmorillonite, hectorite and mica have also been employed as carriers for metallocene catalysts. An aqueous suspension of the clay is impregnated with a Bronsted acid such as $HNMe_2Ph^+$, then dried and reacted with $Cp'_2ZrCl_2\text{-}AlR_3$ to yield the active catalyst for olefin polymerisation. The aluminium alkyls acts as an alkylating agent for the metal component and longer-chain ammonium cations such $HNMe_2(n\text{-}C_{18}H_{37})^+$ are used.[30]

Another approach to using clay supports is the use of montmorillonite, vermiculite and hectorite. These clays are allowed to react with $AlMe_3$, followed by a $Cp_2ZrCl_2\text{-}AlMe_3$ mixture.[48] The catalyst activity is proportional to the pore volume of the support.

Miscellaneous Supports

Cyclodextrins treated with MAO or $AlMe_3$ serve as supports for Cp_2ZrCl_2-$AlMe_3$ or Cp_2ZrCl_2-MAO catalysts in ethylene polymerisation. Additional alkyl aluminium ($AlMe_3$, $AlEt_3$ or MAO) increases the activity.

Talc treated with MgR_2 complexes, then with *n*-butanol can be contacted with Cp_2ZrCl_2 to form a supported metallocene. This is activated by MAO in an isobutane slurry for the polymerisation or copolymerisation of ethylene.

Hollow $MgCO_3$ and $CaCO_3$ particles, either untreated or treated with aluminium alkyls were used as carriers for metallocene-MAO catalysts in ethylene and propylene polymerisations.

Fillers and pigments are added to polyethylene in the extrusion stage to change the colour, stiffness or magnetisability of the polymer. These same fillers (dyes, glass, ceramics or metals) can function as supports for metallocene-MAO catalysts. This improves the uniformity of the filler distribution throughout the polymer.

1.3.4 COMPARISON OF HOMOGENEOUS AND HETEROGENEOUS POLYMERISATION CATALYSTS

The most notable difference between the two is the catalyst activity. Heterogeneous catalysts generally have lower activity. This could be attributed to the following:

I) diminished diffusion of monomer into the interior pores of the supported catalyst;
II) fewer active centres present in the heterogeneous catalyst;
III) catalyst centres could be deactivated when supported or;
IV) catalytically active sites may not be generated in the metal-cocatalyst interaction.

The differences between homogeneous catalysts and heterogeneous catalysts are briefly summarised in the table below.

Table 1.1. Differences between homogeneous and heterogeneous catalysts.

Homogeneous Catalyst	Heterogeneous Catalyst
High activity	Lower activity
Difficult separation	Easy separation
Low thermal stability	High thermal stability
Well defined catalysts	Poorly defined catalysts
No diffusion limitation	Limited by diffusion processes

The molecular weight of the polymer is generally not affected or is higher for the supported catalyst. Changes in activity, molecular weight, isotacticity and polymer bulk density are more moderate for the supported catalyst than the solution catalyst.

1.4 SCOPE OF THIS THESIS

Chapter 1 - Chapter 1 gives an introduction to olefin polymerisation catalysts and the immobilisation of the catalyst precursors on support materials. Metallocene catalysts are discussed and some latest developments in the immobilisation of these catalysts on various support materials are discussed.

Chapter 2 - The convergent growth approach, based on dendritic wedges was employed to prepare a series of allylaryl-ether dendrimers. Dendrimers containing 6 and 12 allyl groups on the periphery of the macromolecule have been prepared. In the first step, 2 mol of allylbromide is condensed with two phenolic groups of the monomer, 3,5-dihydroxybenzylalcohol, under phase transfer conditions. The benzylic alcohol functionality is converted into the corresponding bromide. The resulting activated dendritic wedge is coupled to a polyfunctional core, 1,1,1-tris(4'-hydroxyphenyl)ethane to form the hyperbranched first generation dendrimer, [G-1]core containing 6 allyl groups on the periphery. The first generation bromide can be added to the monomer followed again by activation to form the corresponding bromide and finally coupling to a polyfunctional core, 1,1,1-tris(4'-hydroxyphenyl)ethane to form the second generation hyperbranched macromolecule, [G-2]CORE. The first and second generation wedges and the first and second generation dendrimers were characterised using analytical techniques such as FTIR spectroscopy, ^{1}H NMR and ^{13}C NMR spectroscopy, microanalysis and mass spectrometry.

Chapter 3 - Metallocene catalysts possess excellent activities and stereospecifties for the polymerisation of olefins but are not suitable for all technical applications. Many commercial polymerisation processes require heterogenization of metallocene catalysts. This modification is needed to avoid reactor fouling with finely dispersed polymer crystals, to prevent excessive swelling of polymers, and to produce polymer particles of a desired regular morphology. Several techniques have been developed to synthesise supported metallocene catalysts. Here we investigate the use of dendrimers as a support material for metallocene catalyst precursors. The metallation of the 6 and 12 allyl dendrimers were achieved by reaction with $Cp_2Zr(H)Cl$, resulting in hydrozirconation of the alkene moiety to form the corresponding alkylzirconium products. The model compound, $(Cl)Cp_2Zr(CH_2)_4Ph$ was prepared by reaction of 4-phenyl-1-butene with $Cp_2Zr(H)Cl$, for comparative studies to the multinuclear catalyst precursors. The new zirconium alkyl compounds are yellow crystalline solids, which are unstable in air and moisture and were characterised using the spectroscopic techniques such as ^{1}H NMR and ^{13}C NMR spectroscopy.

Chapter 4 - The multinuclear catalyst precursors together with analogous mononuclear model compounds were activated using a number of different activating agents including, silver salts (AgX, where X = OSO_2CF_3, ClO_4 and BPh_4); methylaluminoxane (MAO) and perflouroarylboranes of the type $B(C_6F_5)_3$. The activated complexes were assessed for their polymerisation ability with ethylene. The resulting polymers or oligomers were characterised using analytical techniques such as FTIR spectroscopy, ^{1}H NMR and ^{13}C NMR spectroscopy, melting points, GPC, DSC, SEM and EDS.

1.5 REFERENCES

---

1 a) H. H. Britzinger, D. Fischer, R. Mulhaupt, B Rieger, R. Waymouth, *Angew. Chem. Int. Ed. Eng.*, **1995**, *107*, 1255.

b) A. M. Thayer, *Chem. Eng. News,* **1995**, 34.

c) M. J. Bochmann, J. Chem Soc. *Dalton Trans.,* **1996**, 255.

d) W. Kaminsky and M Arndt, *Adv. in Polym. Sci.,* **1997**, *127*, 143.

e) A. L. McKnight and R. M. Waymouth, *Chem. Rev.*, **1998**, *98*, 2587.

f) R. F. Jordan, *J. Mol. Catal.*, **1998**, 128.

g) W. Kaminsky, *Metalorganic Catalysts for Synthesis and Polymerisations: Recent Results by Ziegler-Natta and Metallocene Investigations*, Springer-Verlag, Berlin, **1999**.

h) T. J. Marks and J. C. Stevens, *Topics in Catalysis*, **1999**, *7*, 1.

i) G. W. Coates, *Chem. Rev.*, **2000**, *100*, 1223.

j) G. W. Coates, *J. Chem. Soc., Dalton Trans.*, **2002**, 467.

2 K. Ziegler, E. Holtzkamp, H. Breil, H. Martin, *Angew. Chem.*, **1955**, *67*, 541.

3 G. Natta, *Angew. Chem.,* **1956**, *68*, 393.

4 a) Y. N. Kissin, *Isospecific Polymerisation of olefins with Heterogeneous Ziegler-Natta catalysts,* Springer-Velag, New York, **1985.**

b) J. C. W. Chien, *In preparation and Properties of stereoregular polymers,* **1980**, 113.

c) T. E. Nowlin, *Progress in Polymer Science,* **1985**, *11*, 29.

d) B. L. Goodall, *In Polypropylene and other Polyolefins;Polymerisation and Characterisations,* S. van der Ven, ed. Elsivier, New York, **1990**, 59.

e) J. C. W.Chien and B. M. Gong, *J. Polym. Sci.*, **1993**, *31*, 1747.

f) V. Busico, R. Cipullo, G. Monaco, G. Talarico, M. Vacatello, J. C. Chadwick, A. L. Segre, O. Sudmeijer, *Macromol.,* **1999**, *32*, 4173.

5 F. J. Karol, G. L. Karapinka, C.-S. Wu, A. W. Dow, R. N. Johnson, W. L. Carrick, *J. Polym. Sci.*, **1972**, *10*, 2621.

6 K. H. Theopold, *Chemtech.*, **1997**, *10*, 26.

7 H. G. Alt, C. E. Denner, U. Thewalt, M. D. J. Rausch, *Organomet. Chem.*, **1988**, 356.

8 C. P. Casey, J. A. Tunge, M. A. Fagan, *J. Organomet. Chem.*, **2002**, *663*, 91.

9 a) L. Wang, T. C. Flood, *J. Am. Chem. Soc,* **1992**, *114*, 3169.

b) L. Wang, R. S. Lu, R. Bau, T. C. Flood, *J. Am. Chem. Soc.*, **1993**, *115*, 6999.

c) S. Timonen, T. T. Pakkanen, T. A. Pakkanen, *J. Mol. Catal.*, **1996**, *111*, 267.

10 a) D. P. Gates, S. A. Svedjda, E. Onate, C. M. Killian, L. K. Johnson, P. S. White, M. Brookhart, *Macromol.*, **2000**, *33*, 2320.

b) L. C. Simon, R. F. de Souza, J. B. P. Soares, R. S. Mauler, *Polymer*, **2001**, *42*, 4885.

---

c) D. Yan, W.-J. Wang, S. Zhu, *Polymer*, **1999**, *40*, 1737.

11 a) A. L. Satir, B. M. Novak, .*J Am. Chem. Soc.*, **1998**, *120*, 643.

b) D. Coevoet, H. Cramail, A. Deffiex, C. Mladenov, J.-N. Pedeutour and F. Peruch, *Polym. Int*, **1999**, *48*, 257.

12 C.R. Baar, H. A. Jenkins, G. P. Yap, R. J. Puddephatt, *Organometallics*, **1998**, *17*, 4329.

13 J. Ramos, V. Cruz, A. Munoz-Escalona, J. Martinez-Salazar, *Polymer*, **2002**, *43,* 3635.

14 W. Kaminsky, *Catalysis Today*, **2000**, *62*, 23.

15 L. K. Johnson, C. M. Brookhart, *J. Am. Chem. Soc.*, **1995**, *117*, 6414.

14 C. M. Killian, D. J. Tempel, L. K. Johnson, M. J. Brookhart, *J. Am. Chem. Soc.*, **1996,** *118*, 11664.

16 S. D. Ittel and L. K. Johnson, *Chem. Rev.*, **2000**, *100*, 1169.

17 K. Sugimura, K. Yorozu, Y. Suzuki, T. Hayashi, *JP Patent 09278821*, **1996** to Mitsui Chemicals.

18 J. Heinemann, P. Reichert, R. Thomann, R. Mulhaupt, *Macromol. Rapid Commun.*, **1999**, *20*, 423.

19 a) G. Natta, P. Pino, G. Mazzanti, U. Giannini, *J. Am. Chem. Soc.*, **1957**, *79*, 2975.

b) D. S. Breslow and N. R. Newburg, *J. Am. Chem. Soc.*, **1957**, *79*, 5072.

c) D. S Breslow and N. R. Newburg, *J. Am. Chem. Soc.*, **1959**, *81*, 81.

20 a) G. W. Coates, *J. Chem. Soc. Dalton. Trans.*, **2002**, 467.

b) P. C. Mohring and N. J. Coville, *J. Organomet. Chem.*, **1994**, *479*, 1.

21 K. H. Reichert and K. R. Meyer, *Makromol. Chem.*, **1973**, *169*, 569.

22 W. P. Long and D. S. Breslow, *Justus Liebigs Ann. Chem.,* **1975**, 463.

23 W. Kaminsky, M. Miri, H. Sinn, R. Woldt, *Makromol. Chem., Rapid Commun.,* **1983**, *4*, 417.

24 a) A. Razavi and J. D. Ferrara, *J. Organomet. Chem.*, **1992**, *435*, 299.

b) H. G. Alt and R. Zenk, *J. Organomet. Chem.*, **1996**, *518*, 7.

25 S. J. Palackal, *Dissertation, Universitat. Bayreuth*, **1991**.

26 H. G. Alt, K. Fottinger, W. Milius, *J. Organomet. Chem.*, **1998**, *564*, 109.

27 a) W. E. Piers, T. Chievers, *Chem. Soc. Rev.*, **1997**, *26*, 345.

b) E. Y-X. Chen, *Chem. Rev.*, **2000**, *100*, 1391.

28 W. Kaminsky, R. Steiger, *Polyhedron.*, **1988**, *7*, 2375.

29 I. Tritto, S. Li, M. C. Sacchi, G. Zannoni, *Macromol.*, **1993**, *26*, 7112.

30 a) M. Bochmann, A. Nachr, *Chem. Tech. Lab.*, **1993**, *41*, 1220.

b) G. G. Hlatky, H. W. Turner, R. R. Eckmann, *J. Am. Chem. Soc.*, **1989**, *111*, 2728.

c) R. M. Hathorn, T. J. Marks, *J. Am. Chem. Soc.*, **1992**, *114*, 1112.

d) M. Bochmann, S. J. Lancaster, M. B. Hursthouse, K. M. A. Malik, *Organometallics*, **1994**, *13*, 2235.

31 a) C. J. Harlan, M. R. Mason, A. R. Barron, *J. Organomet.*, **1994**, *13*, 2957.

b) S. R. Srinivasa, S. Sivaram, *Prog. Polym. Sci.*, **1995**, *20*, 309.

32 H. G. Alt, C. E. Denner, U. Thewalt, M. D. J. Rausch, *J. Organomet. Chem.*, **1988**, 356.

33 H. F. Hermann and L. L. Bohm, *Polym. Commun.,* **1991**, *32*, 58.

34 a) G. G. Hlatky, *Chem. Rev.*, **2000**, *100*, 1347.

b) D. H. Lee, T. Sano, T. Uozumi, H. Nakatani, M. Terano, *Progress and development of catalytic olefin polymerization, Technology and Education Publishers*, **2000**, 137.

c) H. T. Ban, T. Arai, C.-H. Ahn, T. Uozumi, K. Soga, *Cur.r Trends Polym. Sci.*, **1999**, *4*, 47.

35 W. Kaminsky and F. Renner, *Makromol. Chem., Rapid Commun.*, **1993**, *14*, 239.

36 N. G. Dufrenne, J. P. Blitz, C. C. Meverden, *J. Microchem.*, **1997**, *55*, 192.

37 R. Duchateau, H. C. L. Abbenhuis, R. A. van Santen, S. K-H. Thiele, M. F. van Tol, *Organometallics*, **1998**, *17*, 5222.

38 M. Stork, M. Koch, M. Klapper, K. Mullen, H. Gregorius, U. Rief, *Macromol. Rapid. Commun.*, **1999**, *20*, 210.

39 S. C. Hong, H. T. Ban, N. Kishi, J. Jin, T. Uozumi, K. Soga, *Macromol. Chem. Phys.*, **1998**, *199*, 1393.

40 S. C. Hong, T. Teranishi, K. Soga, *Polym.*, **1998**, *39*, 7153.

41 H. G. Alt, *J. Chem. Soc.,Dalon. Trans.*, **1999**, 1703.

42) T. Kitagawa, T. Uozumi, K. Soga, T. Takata, *Polym.*, **1997**, *38*, 615.

43a) H. G. Alt, M. Jung, *J. Organomet. Chem.*, **1999**, *580*, 1.

b) B. Peifer, W. Milius, H. G. Alt, *J. Organomet. Chem.*, **1998**, *553*, 205.

44 J. H. Z. dos Santos, T. Uozumi, T. Teranishi, T. Sano, K. Soga, *Polym.*, **2001**, *42*, 4517.

45 D. Lee, K. Yoon, S. Noh, *Macromol. Rap. Commun.*, **1997**, *18*, 427.

46 a) M de F. V. Marques, C. A.Henriques, J. L. F. Monteiro, S. M. C. Menezes, F. M. B. Coutinho, *Polym. Bull.*, **1997**, *39*, 567

b) M de F. V. Marques, C. A.Henriques, J. L. F. Monteiro, S. M. C. Menezes, F. M. B. Coutinho, *Macromol. Chem. Phys.*, **1997**, *198*, 3709.

c) M. Mitchelotti, A. Altomare, F. Ciardelli, E. Roland, *J. Mol. Catal. A*, **1998**, *129*, 241.

d) S. O'Brien, J. Tudor, T. Maschmeyer, D. J. O'Hare, *J. Chem. Soc., Chem. Commun.*, **1997**, 1905.

47 S. Woo, Y. Ko, T. Han, *Macromol. Rapid. Commun.*, **1995**, *16*, 489.

48 T. Suzuki, Y. Suga, *Polym. Prepr.*, **1997**, *38*, 207.

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF ALLYLARYL-ETHER DENDRITIC WEDGES AND DENDRIMERS

2.1. INTRODUCTION

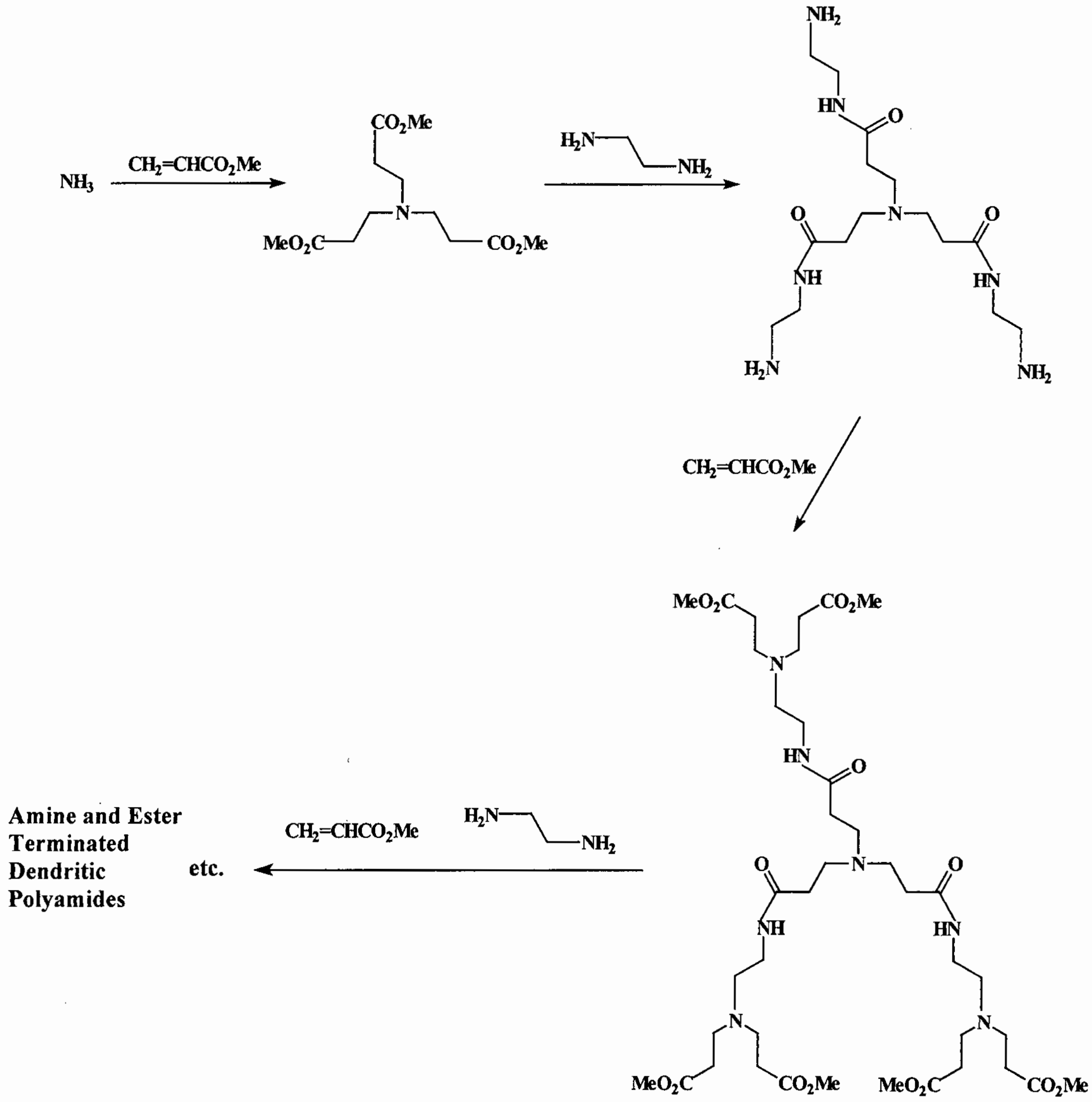
Dendrimers are hyperbranched macromolecules with well-defined three-dimensional shapes.[1] There is an increasing interest in the development of dendrimers because of the range of the applications they afford. For example dendrimers can find use in catalysis[2], molecular biology[3], material science[4] as well as electrochemical applications.[5]

Dendrimers with terminal functional groups have attracted much interest because they offer the possibility of further attachment of other functional oligomeric or polymeric groups to the periphery.[6 - 9] Of particular interest to the work presented in this chapter, are dendrimers containing alkene functionalities on the periphery.

2.1.1. SYNTHETIC METHODS FOR BRANCHED DENDRIMERS

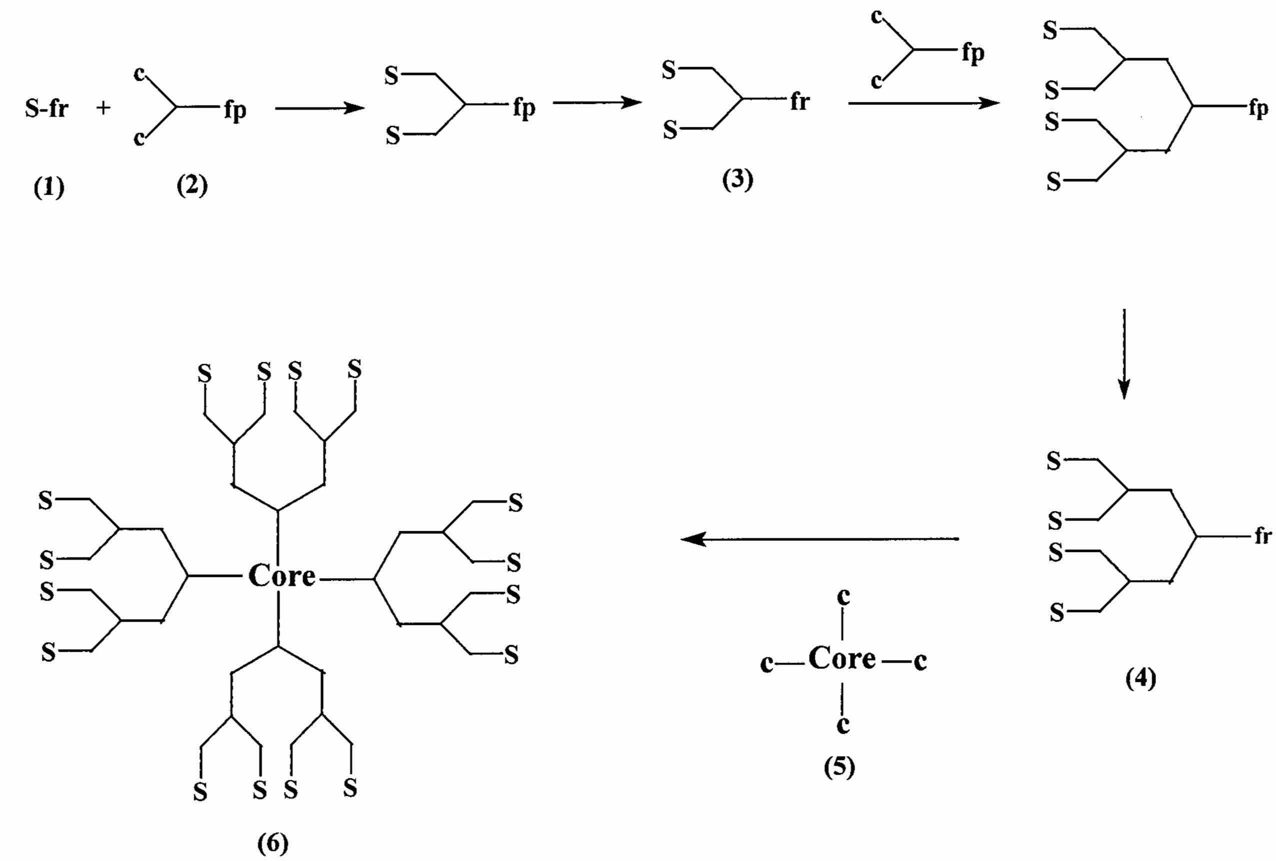
Dendritic macromolecules have been synthesised by two basic methods viz. the divergent (outward) or the convergent (inward) growth methods. These are briefly discussed below.

Divergent growth: This method, which was independently developed by Tomalia[10] and Newkome[11], involves the initial reaction of the monomer unit with a polyfunctional core, Scheme 2.1. Exhaustive activation of the terminal groups followed by coupling of the monomer affords chain growth to yield the next generation. The number of reactive groups at the chain ends increases rapidly as the generation number increases. Incomplete activation of terminal groups leads to imperfections in the next generation. Large excesses of reagents are therefore needed to force reactions to completion and this often creates purification problems.



Scheme 2.1. Illustration of divergent growth method.

Convergent growth: Hawker and Fréchet first described the convergent growth method.[12] Dendrimer growth is started at what will ultimately become the periphery of the macromolecule, Scheme 2.2. One equivalent of the growing molecule **(1)** is coupled to two sites of the monomer **(2)**. Activation of the focal point yields compound **(3)** and after repetition of the coupling and activation steps, the dendritic wedge **(4)** is obtained. Compound **(4)** can be coupled to a polyfunctional core **(5)** to provide the dendritic macromolecule **(6)**. The main advantages of the convergent growth method relative to the divergent growth method are that a limited number of reactive sites are involved at each step. There is no need for large excesses of reactants or exhaustive activation of the terminal groups. This limits side reactions which normally causes difficulties in subsequent purification. Another advantage of the divergent growth method is that the efficiency of reactions can be monitored at each individual step using various spectroscopic methods, thus preventing the occurrence of defects in the dendrimers.

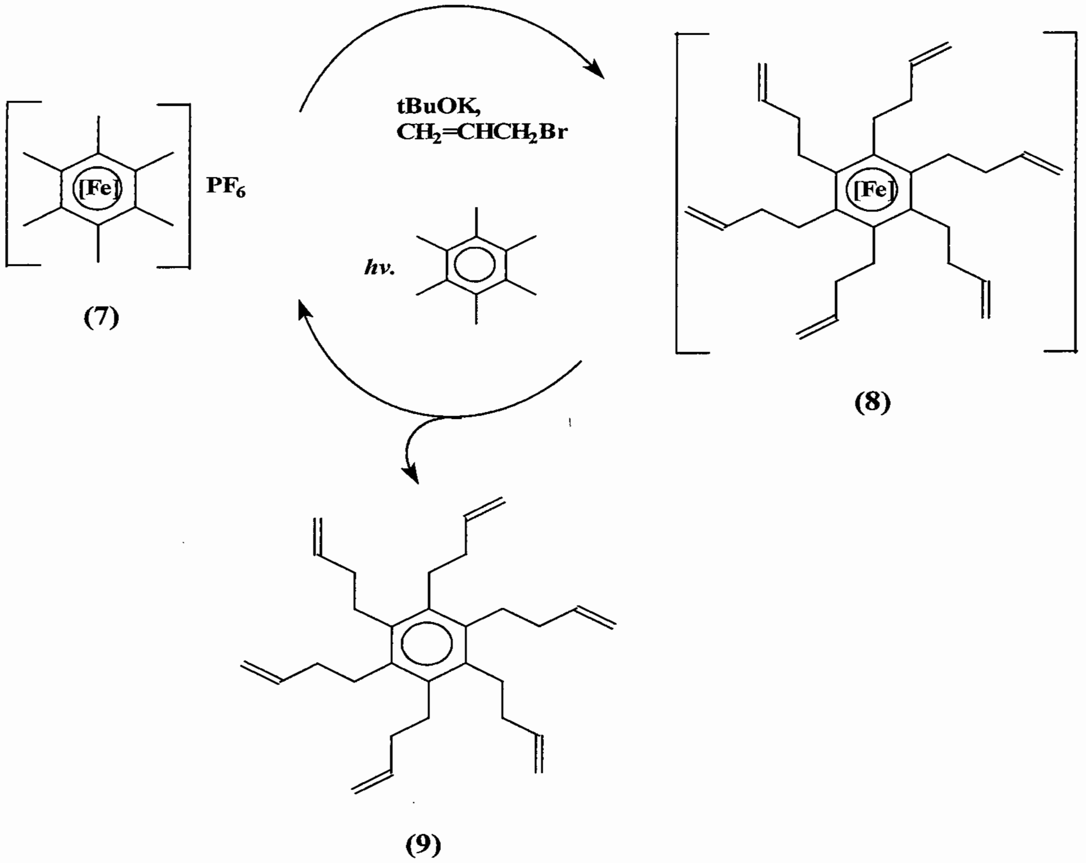


Scheme 2.2. Illustration of convergent growth method.

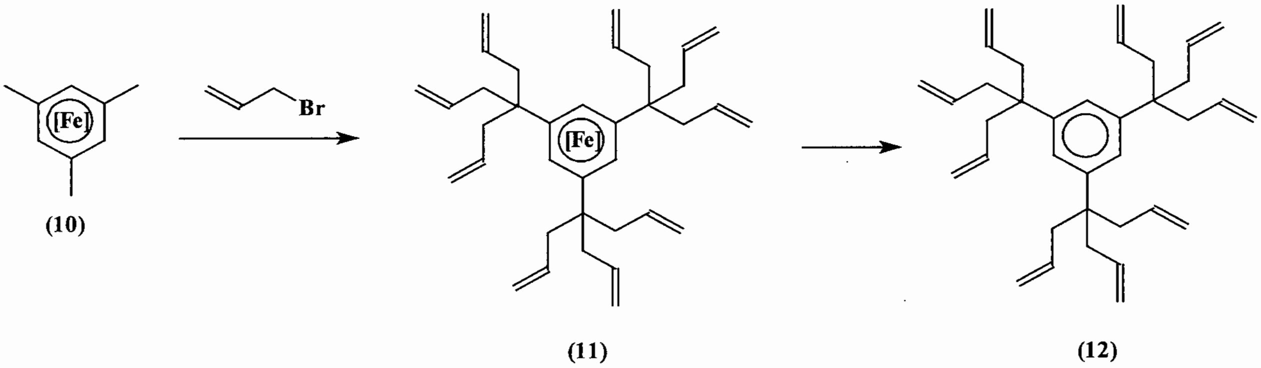
2.1.2. DENDRIMERS WITH TERMINAL ALKENE FUNCTIONAL GROUPS

Astruc and co-workers reported the synthesis of a series of dendrimers with alkene units on the periphery of the dendrimers.[13 - 18] They synthesised hexasubstituted benzene derivatives[13], by adopting a divergent approach as shown in Scheme 2.3. It was found that reaction of the readily available complex [FeCp(C_6Me_6)]PF_6, **(7)** with *t*BuOK and allylbromide in THF yields the hexakis(butenyl)benzene complex **(8)**. Demetallation of the hexasubstituted arene complex is achieved by using visible-light photolysis in the presence of C_6Me_6 in CH_2Cl_2 or using dppe in CH_3CN. In this way the new arene **(9)** is obtained.

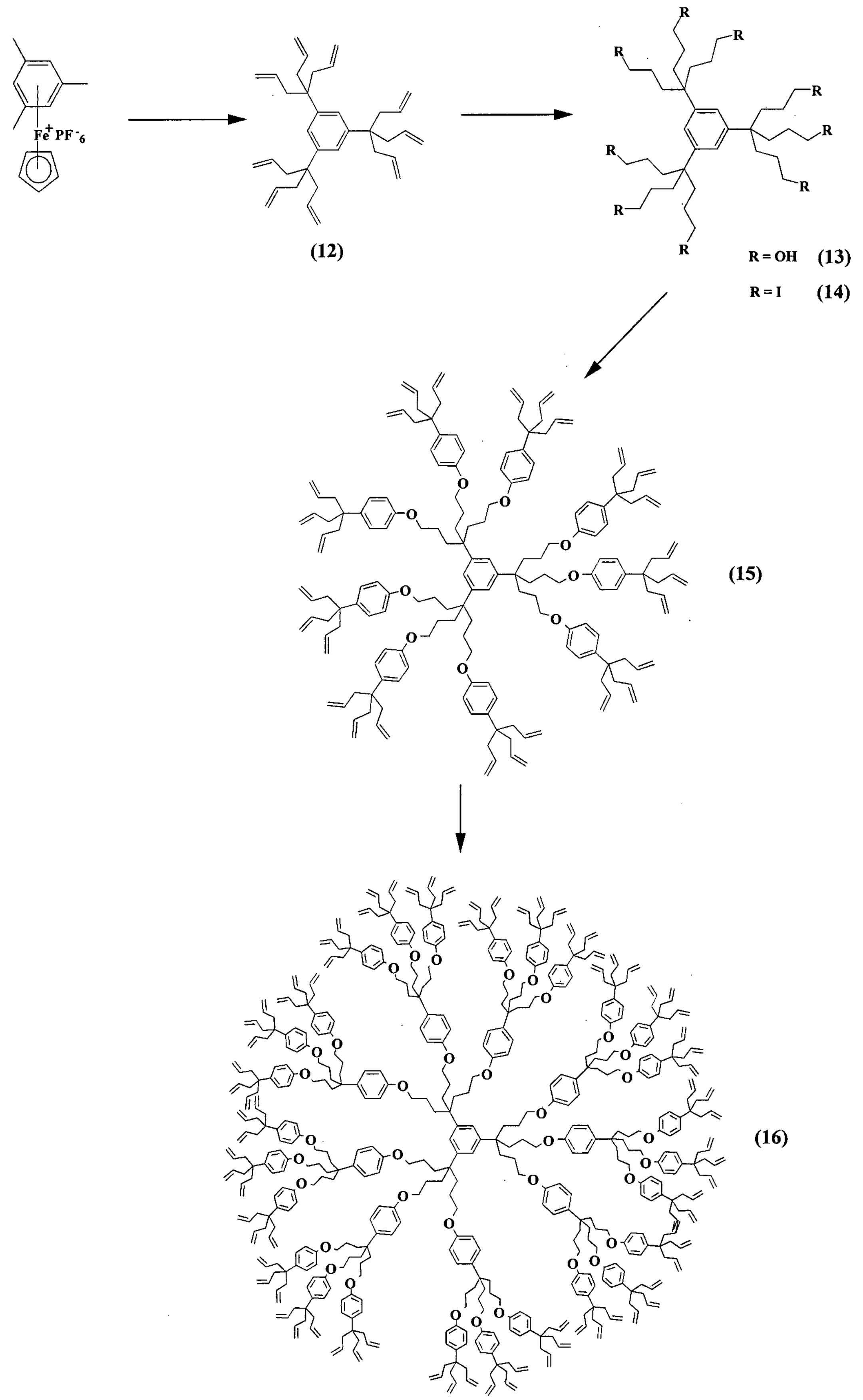
Scheme 2.4 shows the synthetic route for the compound **(12)** which has 9 terminal alkene groups.[14] Complex **(11)** is obtained by reaction of complex **(10)**, $[CpFeC_6H_3Me_3]^+PF_6$ with nine equivalents of allylbromide. Demetallation of **(11)** gave the arene compound **(12)**. Further reaction of **(12)** to form higher generations is demonstrated in Scheme 2.5.[18] Hydroboration of compound **(12)** to form compound **(13)**, followed by reaction with NaI forms the 9-iodo dendrimer compound **(14)**. Allylation of compound **(14)** is achieved by reaction with HOPhC(allyl)$_3$ to give the first generation 27-allyl dendrimer **(15)**. Repetition of the reaction sequence gives the second generation 81-allyl dendrimer **(16)**.



Scheme 2.3. Preparation of hexasubstituted benzene.[13] **[Fe] = (η^5-C_5H_5)Fe$^-$**

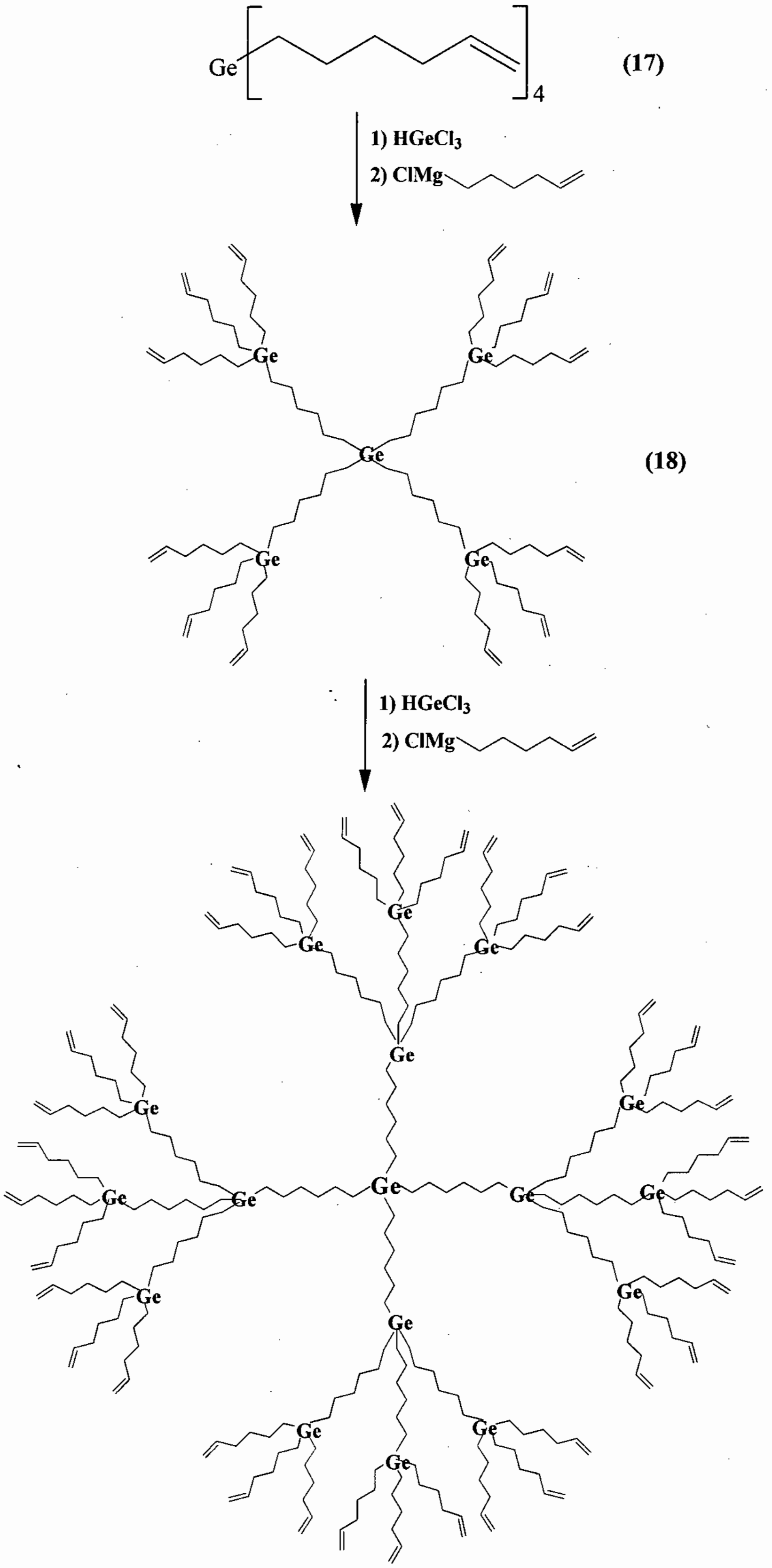


Scheme 2.4. Preparation of compound (12) with 9 terminal alkene groups.[14]



Scheme 2.5. Preparation of a second generation 81-allyl dendrimer.[18]

Mazerolles *et al* reported the synthesis of Ge-branched, alkane based, metallodendrimers (Scheme 2.6.).[19]



(17)

(18)

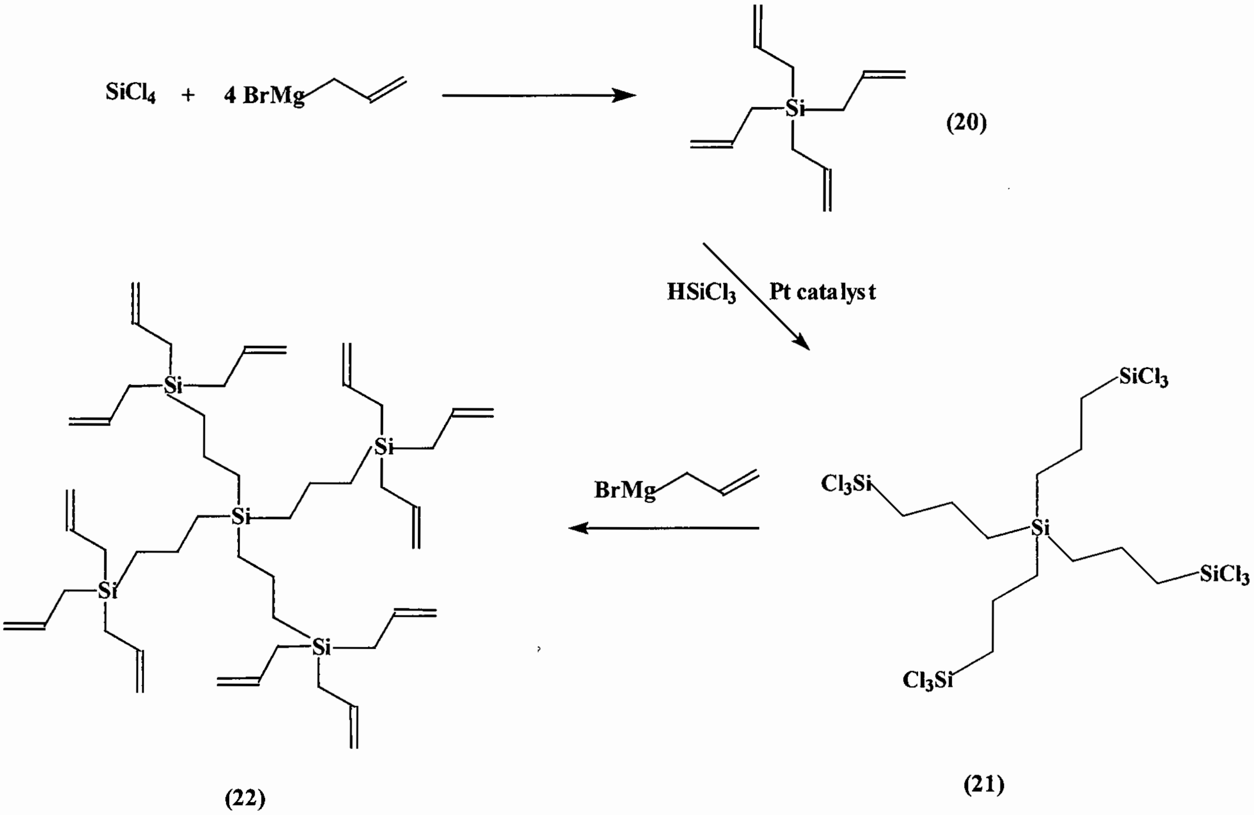
(19)

Scheme 2.6. Preparation of Ge-branched, alkane based, metallodendrimer.[19]

The first generation dodeca-alkene **18** was synthesised via both the divergent and convergent methods starting from the tetravalent core **17**. However the second generation 36-alkene **19** was only successfully obtained by a divergent approach.

Van der Made[20-21]; Zhou[22]; Seyferth[23], Lorenz[24] and Morris[25] have all independently reported a series of carbosilane dendrimers containing alkene functional groups on the periphery of the dendrimers.

One example is presented in Scheme 2.7, where Van der Made and van Leeuwen[20] report the synthesis of dendrimers up to the fifth generation by employing the divergent growth method. The synthesis of their dendrimers starts with exhaustive allylation of tetrachlorosilane using allylmagnesium bromide. The zero generation dendrimer **(20)** is formed in this way. After hydrosilylation of the four alkene groups to yield compound **(21)**, reaction with 12 equivalents of allylmagnesium bromide, gives compound **(22)**. Compound **(22)** now has 12 allyl groups on the periphery. The same reaction sequence i.e. hydrosilylation followed by allylation gave higher generation carbosilane dendrimers.



Scheme 2.7. Divergent growth of carbosilane dendrimers.[20]

Later van Leeuwen *et al* reported the synthesis of a series of diphenylphosphine ligands centred on 1,1'-bis-diphenylphosphinoferrocene. This dendrimer (Figure 2.1.) bears dendritic carbosilane substituents at the para aryl positions in a divergent manner.[21]

Another more recent report on dendrimers with alkene peripheral groups was made by Morris *et al.*[24] They report the divergent synthesis of second generation dendrimers based on polyhedral silsesquioxane cores with up to 72 terminal alkene groups at their surface. Repetitive hydrosilylation/ allylation of vinyl functionalised polyhedral silsesquioxanes produce chlorosilyl- and allyl- derivatised dendrimers respectively.

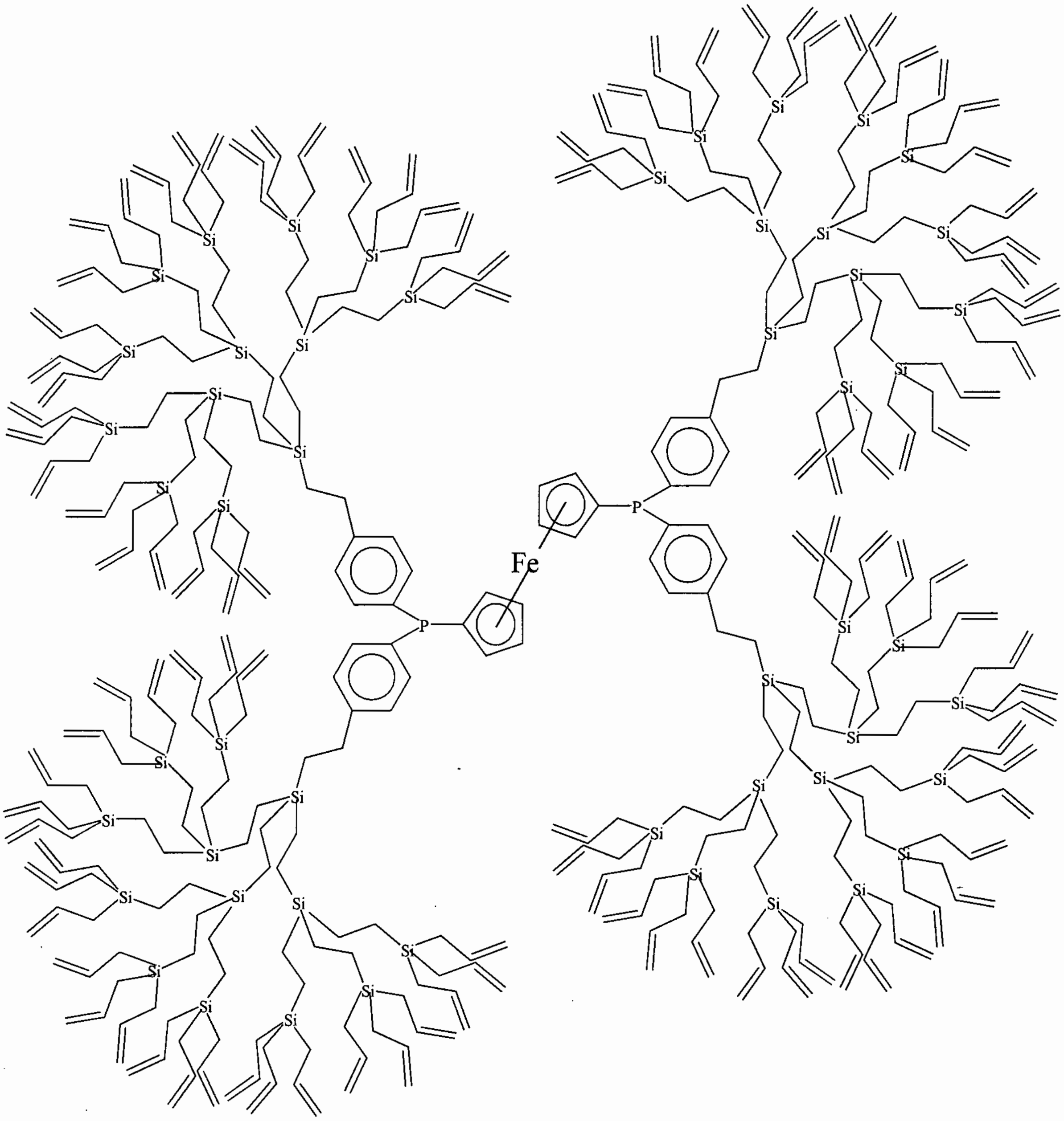


Figure 2.1. Carbosilane dendrimer prepared by van Leeuwen.[21]

2.2. SYNTHESIS OF ALLYLARYL-ETHER DENDRITIC WEDGES AND DENDRIMERS

In this chapter the synthesis of a series of organic dendritic wedges and dendrimers containing allyl groups on the periphery of the molecules are reported. The synthesis of the dendritic wedges and dendrimers are based on the convergent growth method previously employed by Hawker and Fréchet.[12] We adapted their synthetic method by reacting 3,5-dihydroxybenzylalcohol, which is used as a building block with allylbromide. The latter is used to introduce the terminal functionality. This reaction results in the formation of dendritic wedges, which have alkene functional groups exclusively at the periphery. The dendritic wedges are bonded to a polyfunctional core molecule resulting in a dendritic macromolecule. The notation used to refer to the various generations of dendritic molecules is [G-*x*]-f, in which [G-*x*] refers to the generation number (where x = 1 or 2) and f refers to the functional group located at the focal point (where f = OH or Br). The notation $[G\text{-}x]_n$ CORE is used after coupling to a polyfunctional core molecule, where n represents the number of dendritic fragments of generation *x* coupled to a core molecule.

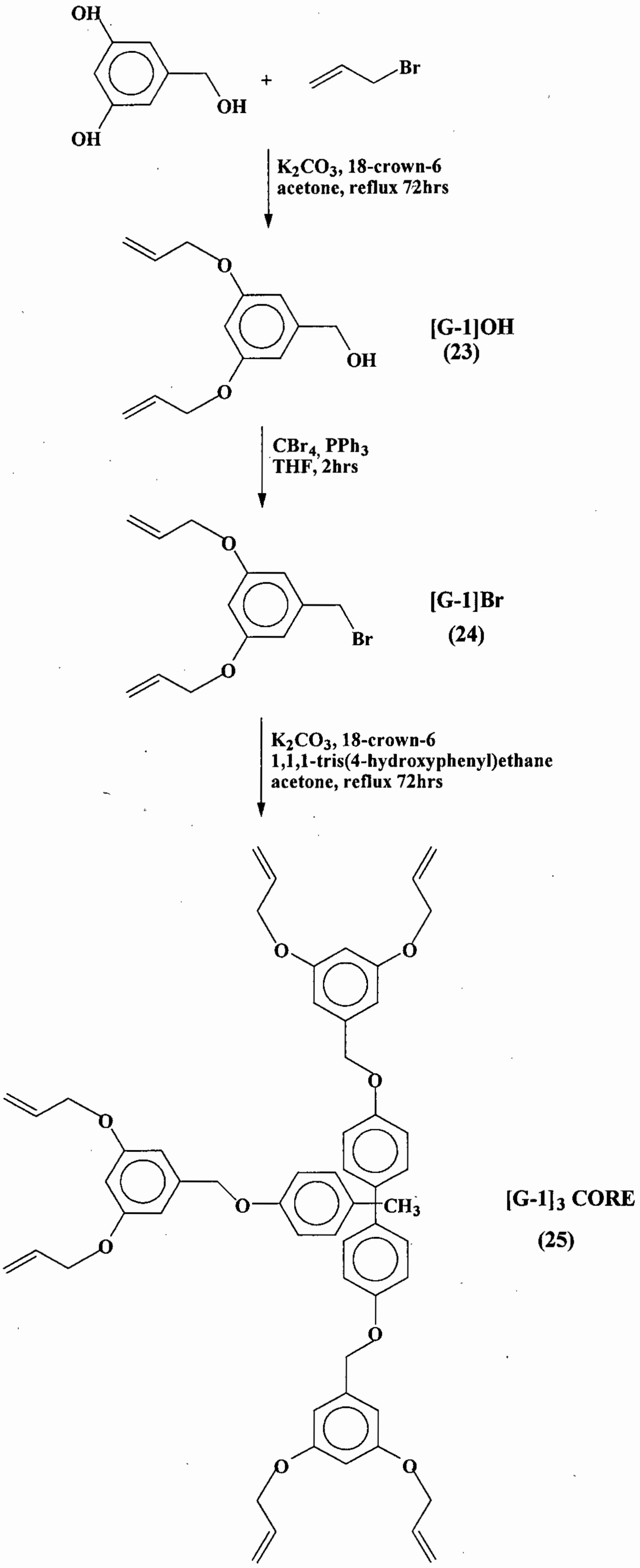
Dendrimer growth is started by reaction of two molar equivalents of allylbromide with one molar equivalent of 3,5-dihydroxybenzylalcohol in the presence of potassium carbonate and 18-crown-6 in refluxing acetone for 72 hours. The product was purified by column chromatography, eluting with initially 10 % CH_2Cl_2 in hexane followed by 50 % CH_2Cl_2 in hexane to elute the impurities and finally pure CH_2Cl_2 to give a yield of 90 % of compound **(23)** (Scheme 2.8.). Compound **(23)** is obtained as yellow oil, which is air and thermally stable. Compound **(23)** is the first generation benzyl alcohol and was characterised by standard spectroscopic methods such as NMR spectroscopy and mass spectrometry.

Treatment of compound **(23)** with CBr_4/PPh_3 in a minimum volume of THF for 2 hours yielded the benzyl bromide **(24)** (Scheme 2.8.). The product was purified by column chromatography, eluting initially with 20 % CH_2Cl_2 in hexane followed by 50 % CH_2Cl_2 in hexane to give a reasonable yield of 50 % of compound **(24)**. Compound **(24)** is obtained as a yellow oil, which is air and thermally stable. Compound **(24)** is the first generation benzyl bromide and was characterised by standard spectroscopic methods. It was found that a large excess of CBr_4/ PPh_3 is usually needed in order to achieve complete conversion to the brominated product, up to two molar equivalents is required for the reaction to proceed favourably. However using a large excess of CBr_4/ PPh_3 makes purification difficult.

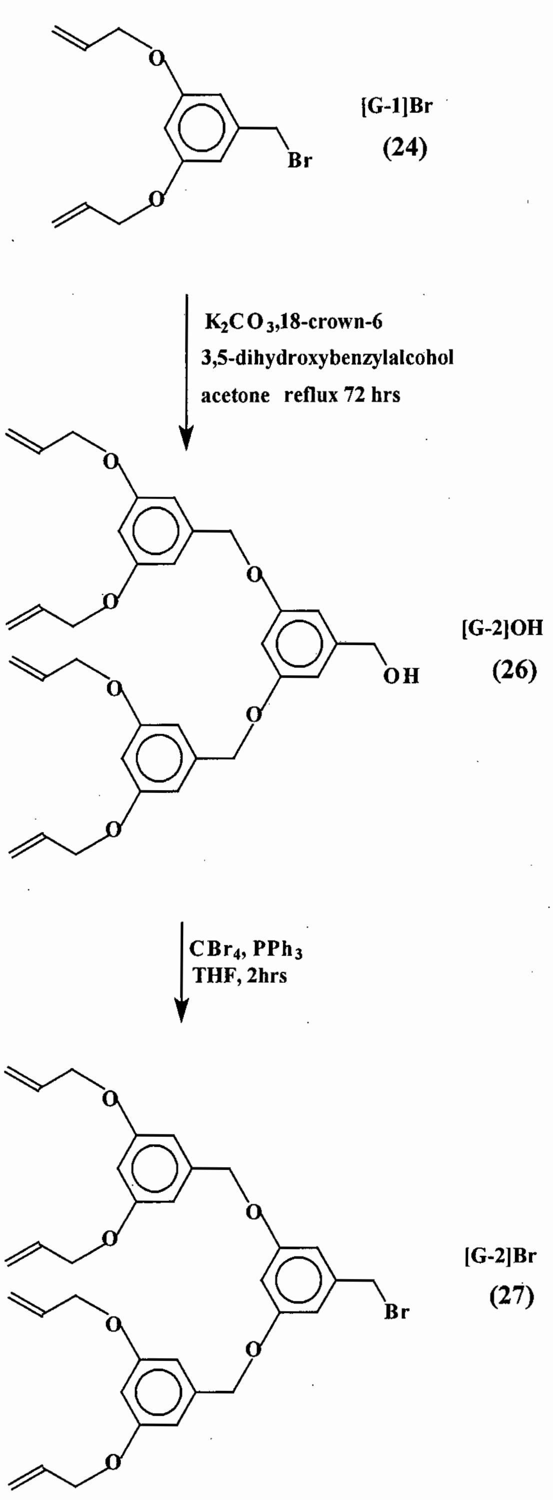
The reaction of two equivalents of **(24)** with 3,5-dihydroxybenzylalcohol forms the second generation benzyl alcohol compound **(26)** (Scheme 2.9.). Compound **(26)** was purified by column chromatography and obtained as a yellow, air and thermally stable oil in 73 % yield. Treatment of compound **(26)** with two molar equivalents of CBr_4/PPh_3 for 2 hours yielded the expected second generation benzyl bromide compound **(27)** (Scheme 2.9.). Purification by column chromatography gave compound **(27)** as sticky yellow oil in 51 % yield. Compound **(27)** is also air and thermally stable.

In the convergent approach, the dendritic wedges, containing benzylbromide functional groups can be reacted with a polyfunctional core molecule. We chose 1,1,1-tris (4-hydroxyphenyl) ethane as the core molecule. This species has three possible attachment sites. Three molar equivalents of compounds **(24)** or **(27)** were reacted independently with one molar equivalent of 1,1,1-tris (4`-hydroxyphenyl) ethane in refluxing acetone for 72 hours in the presence of potassium carbonate and 18-crown-6 to yield the first generation dendrimer **(25)** and the second generation dendrimer **(28)** respectively. (Scheme 2.8. and Scheme 2.10.) The products isolated from the reaction mixtures were purified by column chromatography, eluting with 50 % CH_2Cl_2 in hexane followed by 100 % CH_2Cl_2 in hexane to remove the impurities and finally 5 % THF in CH_2Cl_2 to collect the desired products. The first generation dendrimer **(25)**, and the second generation dendrimer **(28)** were isolated as pale yellow sticky oils in 61 % and 53 % yield respectively (Scheme 2.8. and Scheme 2.10.). After drying the oils under high vacuum they turned into sticky gums.

Purification of the second generation dendritic wedges and the second generation dendrimer was found to be difficult. This can be attributed to the fact that the dendrimers are highly soluble in most solvents and have similar solubility behavior in these solvents. They are however insoluble in aliphatic hydrocarbon solvents such as hexane and pentane. Even after repeated column chromatography and recrystallisation from CH_2Cl_2 and hexane in varying ratios and at different temperatures, traces of impurities could still be observed in the ^1H NMR and ^{13}C NMR spectra. The impurities observed in the NMR spectra are due to unreacted starting materials. The desired product peaks were however the dominant components in the NMR spectra.



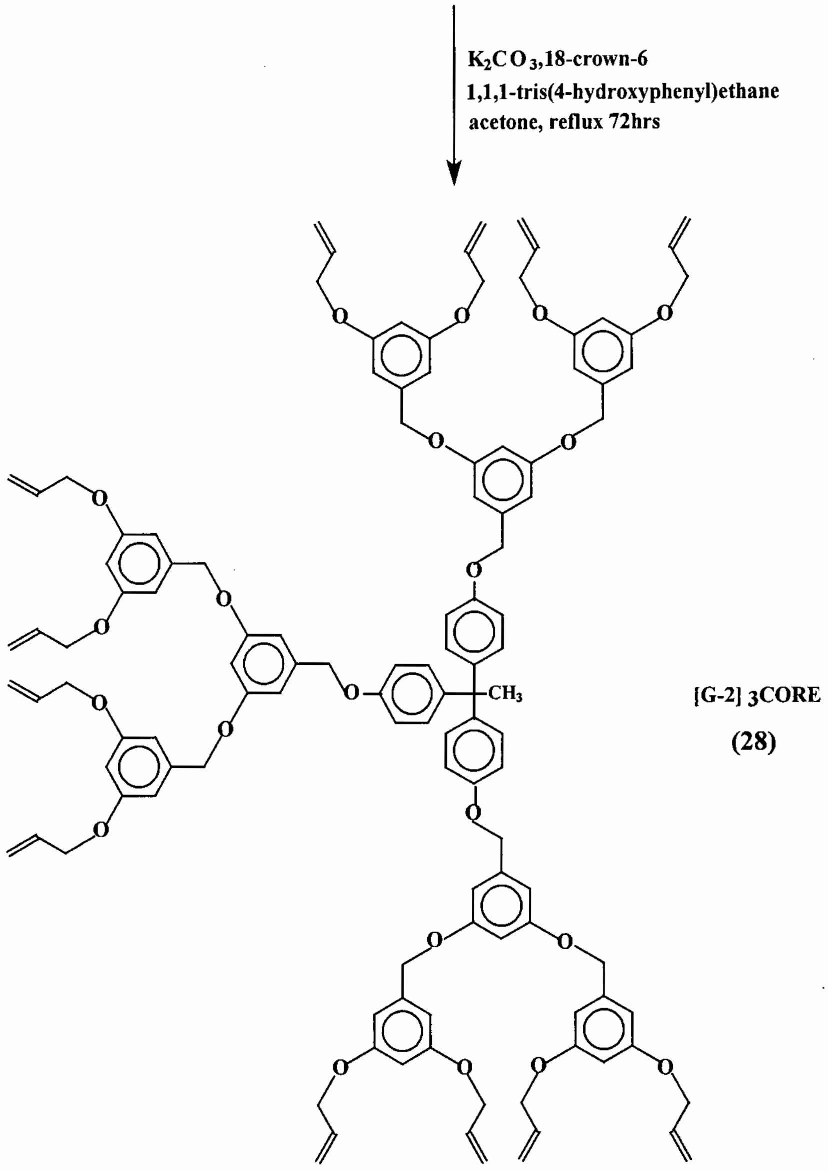
Scheme 2.8. Preparation of first generation dendrimer.



Scheme 2.9. Preparation of second generation dendritic wedge.

[G-2]Br

(27)



[G-2] 3CORE

(28)

Scheme 2.10. Preparation of second generation dendrimer.

2.3. CHARACTERISATION OF DENDRITIC WEDGES AND DENDRIMERS

The new allylaryl-ether dendrimers were characterised by standard analytical methods including IR, ^1H NMR, ^{13}C NMR, mass spectroscopy and elemental analysis. The results are discussed below and the data are presented in Tables 2.1 and 2.2.

2.3.1. Infrared Spectra

The Infrared spectra of compounds **(23)** – **(28)** were recorded as part of their characterisation. The three functional groups, aromatic, ether and alkene units, which are present in the dendrimers, give rise to several intense peaks in the regions of 800 – 1700 cm^{-1}. These peaks are fairly complex and this hinders the exact assignment of many of the functional groups. In the Infrared spectra of the first and second generation benzyl alcohols, **(23)** and **(26)**, a broad peak between 3500-3100 cm^{-1} is observed, which is due to ν(OH) of the -OH group at the focal point of the dendritic wedges. As expected this peak is not observed in the IR spectra of the benzyl bromides, **(24)** and **(27)**.

2.3.2. ^{1}H NMR Spectra

As demonstrated by Hawker and Fréchet, NMR spectroscopy is invaluable in the characterisation of dendritic compounds.[12]

The ^{1}H NMR spectral data for compounds **(23)** – **(28)** are listed in Table 2.1. The alkene functional groups at the periphery of the dendrimers give two distinct sets of resonances at δ 5.20 – 5.45 ppm (HC=C$\underline{H}_2$) and δ 5.95 – 6.18 ppm ($\underline{H}$C=CH$_2$). A doublet is observed in the region δ 4.50 - 4.53 ppm, which can be assigned to the methylene protons (-C$\underline{H}_2$O) attached to the aromatic ring. This particular signal is important, since it confirms the incorporation of the allyl group into the building block. The resonances for the aromatic protons appear in the region δ 6.42 - 6.59 ppm. Separate resonances for the aromatic protons are observed for each layer of monomer units. This is demonstrated in Figure 2.2 for the second generation benzyl alcohol **(26)**, where a triplet is observed at δ 6.42 ppm for the second layer close to the focal point ($\underline{Ar}$CH$_2$OH). A doublet plus a triplet is observed at δ 6.54 and 6.42 ppm for the first layer at the periphery for (allylO$\underline{Ar}$).

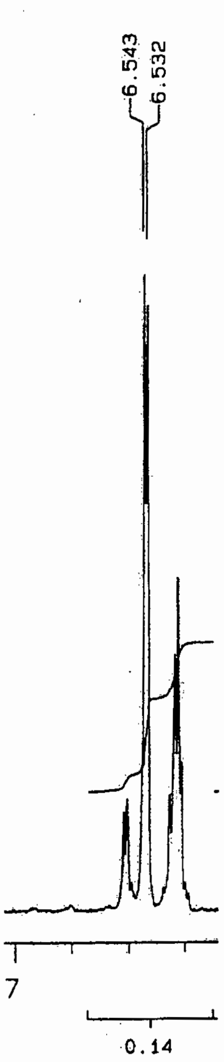


Figure 2.2. ^{1}H NMR spectrum of the second generation dendritic wedge, (26) in the region of δ 6 – 7 ppm in $CDCl_3$.

The resonances for the benzyl protons, (Ar$C\underline{H}_2$-) appear in the region δ 4.41 - 4.95 ppm. Separate resonances for the benzyl protons are also observed for each layer of monomer unit. The ^{1}H NMR spectrum of the first generation benzyl bromide **(24)** gives a singlet at δ 4.41 ppm for (Ar$C\underline{H}_2$Br) at the focal point while that of the second generation benzylbromide **(27)** shows two singlets at δ 4.95 and 4.40 ppm for (Ar$C\underline{H}_2$) close to the periphery and focal point respectively.

Figure 2.3 shows the ^{1}H NMR spectra of compounds **(23)** – **(25)** in the region δ 4 - 7.25 ppm. The most important feature in Figure 2.3 is the resonances of the benzyl protons at the focal point, where ($C\underline{H}_2$OH) appears at δ 4.62 ppm and ($C\underline{H}_2$Br) at δ 4.41 ppm. This confirms the conversion of the dendritic benzyl alcohol, **(23)** to the corresponding benzyl bromide, **(24)**. When the benzyl bromide is attached to the polyfunctional core, a shift from δ 4.41 ppm to δ 4.96 ppm is observed for the resonance of the benzyl protons. Also observed is a new resonance at δ 2.10 ppm, corresponding to methyl protons of the core molecule, as well as two distinct sets of doublets at δ 6.87 ppm and δ 6.98 ppm, corresponding to aromatic protons of the core molecule. (see Table 2.1) The integration of the resonances in all the spectra agrees well with the expected values.

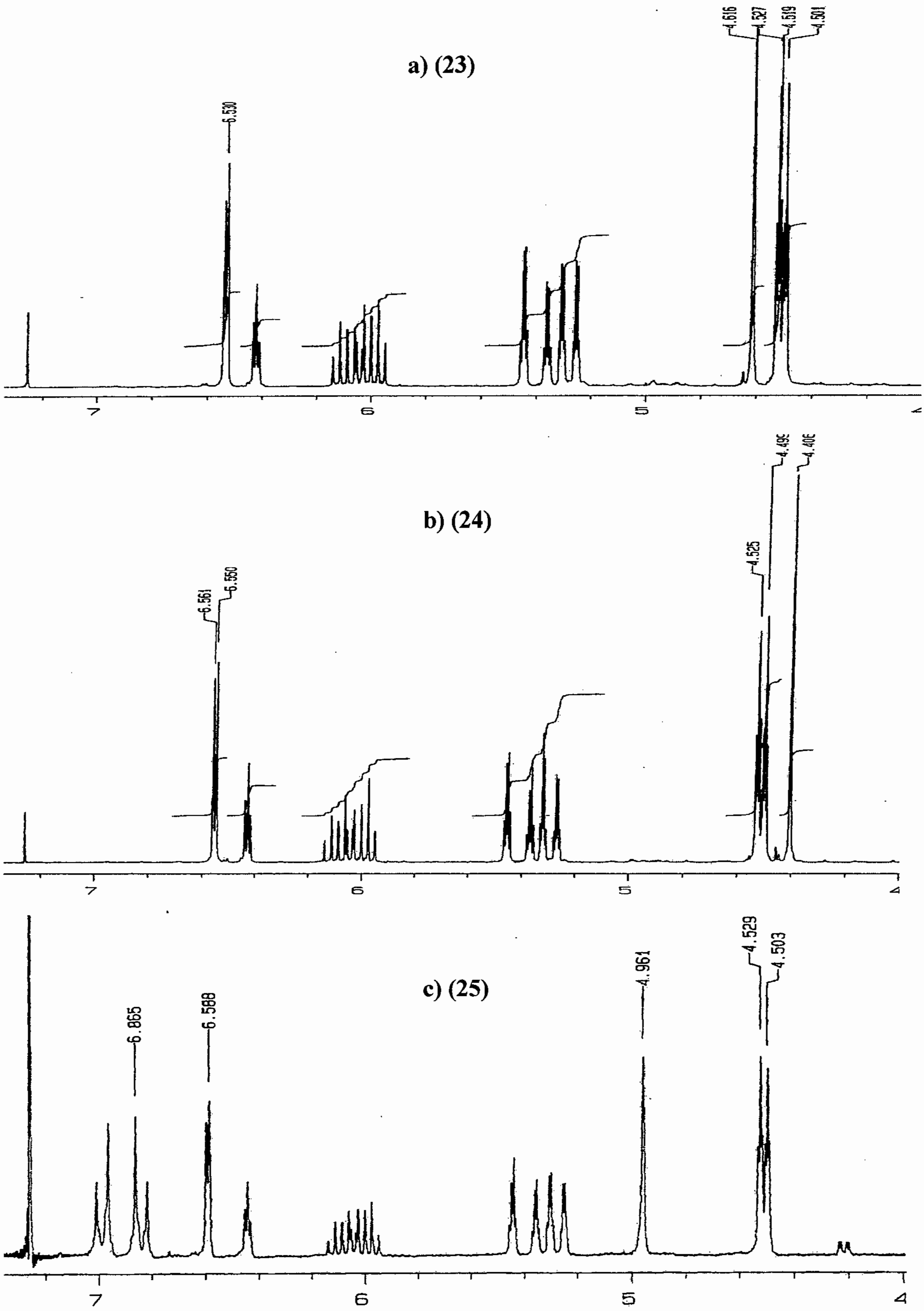
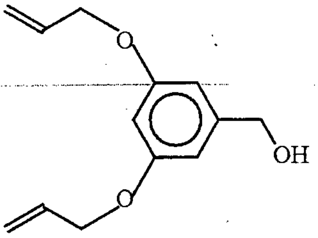
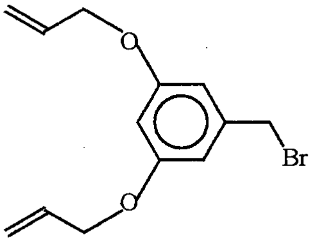
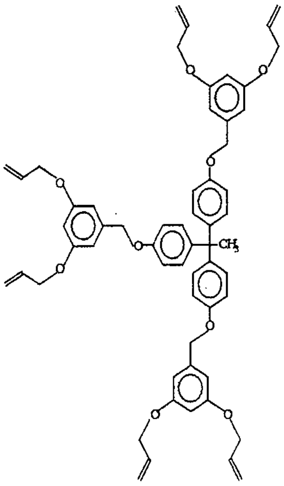


Figure 2.3. **^{1}H NMR spectra of dendrimers: a) (23) ; b) (24) and c) (25) in the region of δ 4 – 7 ppm in $CDCl_3$.**

Table 2.1. ^{1}**H NMR data for the dendritic wedges and dendrimers recorded in CDCl$_3$.**

COMPOUND NO.	STRUCTURE	CHEMICAL SHIFT[a] (δ ppm)	ASSIGNMENT
[G-1]OH **(23)**		br s , 1.68, 1H s , 4.62, 2H d , 4.52, $^{3}J_{H\text{-}H}$ = 5.2 Hz, 4H m, 5.22–5.44, 4H m, 5.95–6.18, 2H t , 6.42, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 1H d , 6.53, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 2H	$\mathrm{O\underline{H}}$ $\mathrm{C\underline{H}_2OH}$ $\mathrm{C\underline{H}_2O}$ $\mathrm{C\underline{H}_2}$= $\mathrm{C\underline{H}}$= $\mathrm{Ar\underline{H}}$ $\mathrm{Ar\underline{H}}$
[G-1]Br **(24)**		s , 4.41, 2H d , 4.52, $^{3}J_{H\text{-}H}$ = 5.2 Hz, 4H m , 5.24–5.45, 4H m, 5.95–6.18, 2H t , 6.42, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 1H d , 6.55, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 2H	$\mathrm{C\underline{H}_2Br}$ $\mathrm{C\underline{H}_2O}$ $\mathrm{C\underline{H}_2}$= $\mathrm{C\underline{H}}$= $\mathrm{Ar\underline{H}}$ $\mathrm{Ar\underline{H}}$
[G-1]CORE **(25)**		s , 2.10, 3H d , 4.50, $^{3}J_{H\text{-}H}$ = 5.2 Hz, 12H s , 4.96, 6H m, 5.22–5.44,, 12H m , 5.96–6.18, 6H t , 6.42, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 3H d , 6.59, $^{4}J_{H\text{-}H}$ = 2.4 Hz, 6H d , 6.87, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 6H d , 6.98, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 6H	$\mathrm{C\underline{H}_3}$ $\mathrm{C\underline{H}_2O}$ $\mathrm{C\underline{H}_2O}$-core $\mathrm{C\underline{H}_2}$= $\mathrm{C\underline{H}}$= $\mathrm{Ar\underline{H}}$ $\mathrm{Ar\underline{H}}$ $\mathrm{Ar\underline{H}}$core $\mathrm{Ar\underline{H}}$core

2.3.3. ^{13}C NMR Spectra

The ^{13}C NMR spectra gave further information on the structure of the dendrimers. Complete assignment of the signals in the ^{13}C NMR of the first generation dendrimers was possible. This provided further support for the structural assignments made in the ^{1}H NMR. Resonances for the alkene carbons are observed in the regions of δ 130 – 133 ppm for (H$\underline{C}$=) and at δ 115 – 117 ppm for (=$\underline{C}H_2$). These signals agree well with literature assignments of alkene groups attached to an aromatic ring.[13]

Figure 2.4 shows the ^{13}C NMR spectra of the first generation dendrimers, **(23)**, **(24)** and **(25)**. The ^{13}C NMR relative to the ^{1}H NMR shows a greater difference between the resonance of the methylene carbons of the functional groups at the focal point. The resonance for ($\underline{C}H_2OH$) appears at δ 65.29 ppm and δ 67.74 ppm for the first and second generation dendritic alcohols **(23)** and **(26)** respectively. After bromination, the resonance for ($\underline{C}H_2Br$) shifts to δ 31.63 ppm and δ 32.36 ppm respectively for compounds **(24)** and **(27)**.

On attachment of the dendritic wedge to the core molecule, the core resonances are also observed in the NMR spectrum of the dendrimer. These resonances are observed at δ 154.78, 140.08, 112.02, and 127.65 ppm and can be assigned to the aromatic carbons. The signal at δ 48.68 ppm is assigned to the quaternary alkyl carbon ($\underline{C}CH_3$) and that at δ 27.13 ppm is assigned to the methyl carbon ($\underline{C}H_3$). The assignments were compared with that of similar compounds in the literature[22, 23], and are in good agreement with these.

The second generation dendrimers give a set of resonances for each dendritic layer in the region δ 99 – 108 ppm for the aromatic carbons close to the focal point and at δ 137-160 ppm for the aromatic carbons close to the periphery. Spectral data are presented in Table 2.2.

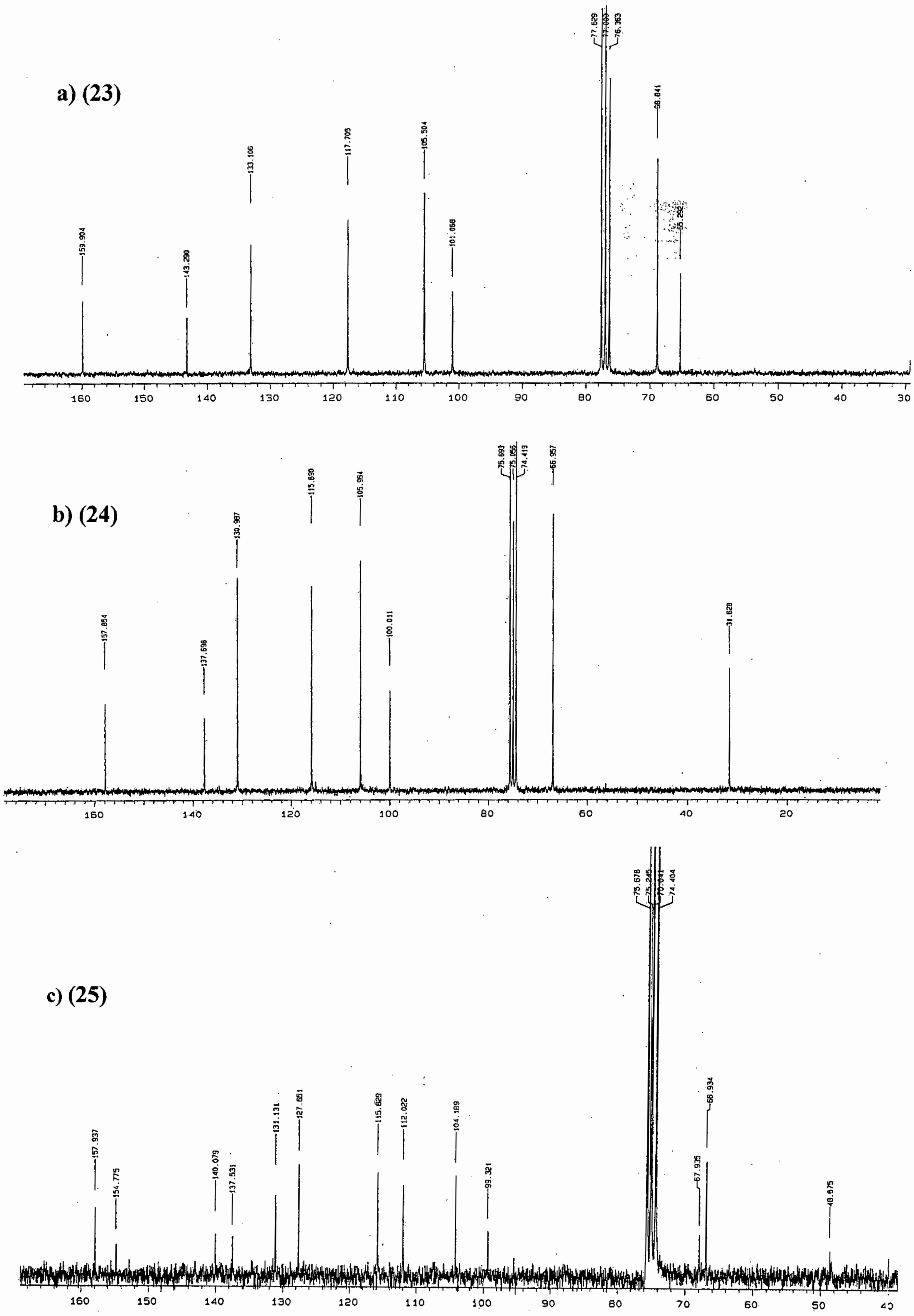


Figure 2.4. ^{13}C NMR spectra of dendrimers; a) (23); b) (24) and c) (25) as recorded in $CDCl_3$.

Table 2.2. ^{13}C NMR data of prepared dendrimers as recorded in $CDCl_3$.

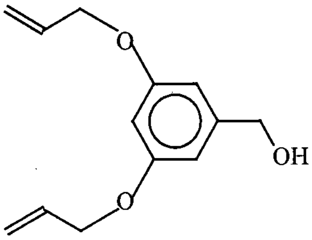
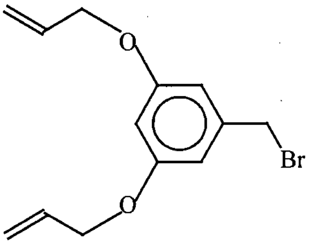
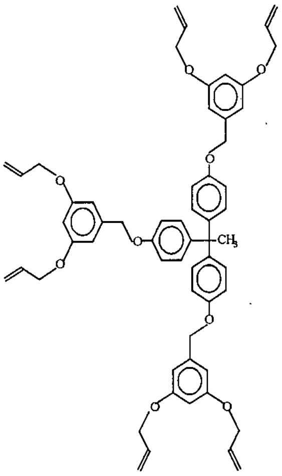
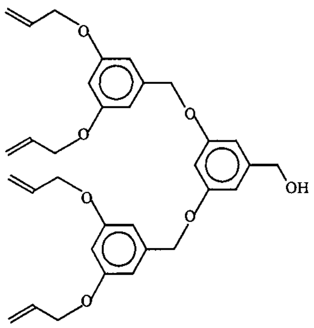
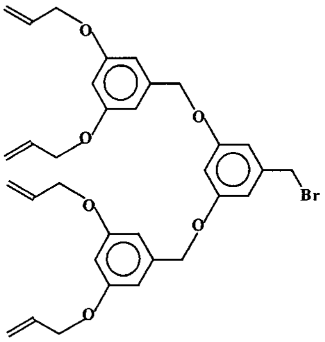
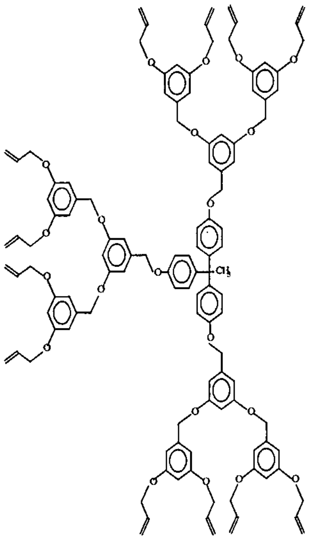
COMPOUND NO.	STRUCTURE	CHEMICAL SHIFT (δ ppm)	ASSIGNMENT
[G-1]OH (23)		159.90, 143.29, 105.50, 101.07 68.84 65.29 133.11 117.70	$Ar\underline{C}$ $\underline{C}H_2O$ $\underline{C}H_2OH$ $\underline{C}H=$ $\underline{C}H_2=$
[G-1]Br (24)		157.85, 137.70, 105.96, 100.01 66.96 31.63 130.99 115.96	$Ar\underline{C}$ $\underline{C}H_2O$ $\underline{C}H_2Br$ $\underline{C}H=$ $\underline{C}H_2=$
$[G-1]_3$ core (25)		154.78, 140.08, 127.65, 112.02 157.94, 137.53, 104.19, 99.32 66.93 67.94 131.13 115.83 48.68 27.13	$Ar\underline{C^{core}}$ $Ar\underline{C}$ $\underline{C}H_2O$ $\underline{C}H_2O$-core $\underline{C}H=$ $\underline{C}H_2=$ $C\underline{C}H_3$ $\underline{C}H_3$

Table 2.2 continued.

[G-2]OH **(26)**		108.05, 106.23, 105.82, 101.42 160.08, 143.8, 137.69 70.02, 69.63, 68.96, 53.80 67.74 133.22 117.93	ArC ArC CH$_2$O CH$_2$OH CH= CH$_2$=
[G-2]Br **(27)**		108.05, 106.26, 103.91, 101.80 160.10, 140.00, 137.69 70.02, 68.97, 66.97, 66.13 32.36 133.21 117.97	ArC ArC CH$_2$O CH$_2$Br CH= CH$_2$=
[G-2]$_3$ core **(28)**		157.95, 137.53, 104.21, 99.32 154.77, 127,67, 112.02 66.01, 66.93, 66.80 70.15 131.12 115.82 28.66	ArC^{core} ArC CH$_2$O CH$_2$O-core CH= CH$_2$= CH$_3$

2.3.4. Mass spectra and Elemental analysis

Elemental analyses and mass spectrometry were obtained for compounds **(23)** – **(25)** and the data are presented in Tables 2.3 and 2.4 below. Molecular ion peaks were observed for compounds **(23)**, **(24)** and **(25)** at m/e 220, 282 and 912 respectively.

Table 2.3. Elemental analysis for compounds (23), (24) and (25).

Compound No	Carbon (%)		Hydrogen (%)	
	Calculated	**Found**	**Calculated**	**Found**
[G-1]OH (23)	70.88	70.92	7.32	7.66
[G-1]Br (24)	55.14	55.46	5.34	5.36
[G-1]CORE (25)	77.61	77.52	6.62	6.65

Table 2.4. Mass spectra for compounds (23), (24) and (25).

Compound No	m/e	Proposed assignment
[G-1]OH (23)	220 161 105 91 41	Parent ion (M^+) $C_{10}H_9O_2^+$ $C_7H_5O^+$ $C_7H_7^+$ $C_3H_5^+$
[G-1]Br (24)	282 161 105 91 41	Parent ion (M^+) – H $C_{10}H_9O_2^+$ $C_7H_5O^+$ $C_7H_7^+$ $C_3H_5^+$
[G-1]CORE (25)	912 503 105 91 57	Parent ion (M^+) – H $C_{30}H_{31}O_7$ $C_7H_5O^+$ $C_7H_7^+$ $C_3H_5O^+$

2.4. CONCLUSION

We have successfully prepared new polyether dendrimers that contain allyl functional groups on the periphery. The first **(25)** and second **(28)** generation dendrimers contain 6 and 12 allyl functional groups on the periphery respectively. Compounds **(23)** – **(25)** were characterised by ^{1}H and ^{13}C NMR spectroscopy as well as infrared spectroscopy, mass spectrometry and elemental analysis. The second generation dendrimers **(26)** – **(28)** could not be fully purified, however the NMR data confirms that the desired products were formed.

The dendrimers **(25)** and **(28)** were investigated as synthons for multinuclear metallocene olefin polymerisation catalysts. The results are described in Chapter 3.

2.5. EXPERIMENTAL

General Experimental Procedure

Infrared spectra were recorded on a Paragon 1000 Fourier Transform Infrared Spectrophotometer as neat thin films between NaCl disks. ^{1}H NMR and ^{13}C NMR spectra were recorded as solutions in $CDCl_3$ on a Varian GEMINI 2000 spectrometer with tetramethylsilane as reference standard. The ^{1}H NMR was recorded at 200-MHz and ^{13}C NMR at 50.3-MHz. Mass spectra were recorded on a FINNIGAN MAT GCQ GC/MS. Microanalysis data were obtained from the University of Western Cape Microanalytical Laboratory and University of Cape Town Microanalytical Laboratory. TLC were performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica for flash chromatography was Merck Kieselgel 60 (230 – 400 mesh). Acetone, THF, hexane and dichloromethane were purchased from Merck. Acetone was dried over drierite. THF was dried by refluxing over sodium wire and distilled from Na-benzophenone under nitrogen. K_2CO_3 was dried at 90^0C under high vacuum for 6 hours before use.

Reaction of 3,5-dihydroxybenzylalcohol with allylbromide

To a two-necked round bottom flask was added 3,5-dihydroxybenzylalcohol (0.21 g, 1.47 mmol), K_2CO_3 (0.51 g, 3.70 mmol) and 18-crown-6 (0.15 g, 0.57 mmol). The solids were suspended in dry acetone (20 ml) and allylbromide (0.34 g, 2.8 mmol) was added. The mixture was refluxed for 72 hours. The yellow mixture was allowed to cool to room temperature, and the contents of the round bottom flask was filtered. The solvent was removed from the filtrate to give a sticky yellow oil. The oil was pre-absorbed onto silica and transferred to a silica gel column (20 cm in length). The column was eluted with 10 % CH_2Cl_2 in hexane , 50 % CH_2Cl_2 in hexane and finally 100 % CH_2Cl_2. The last fraction was collected and the solvents removed on a rotary evaporator to give pure compound **(23)** as a yellow oil, (0.36 g, 90 %).

ν/cm^{-1} 3389 (OH), 3083 (ν($HC=CH_2$)), 2975 (ν($HC=CH_2$)), 2923 (m, ν_{as}(CH_2)), 2870 (m, ν_s(CH_2)), 1701 (m, ν(C=C), 1597 (s, (C=C)), 1453, 1423 ((m, δ_{as}(CH_2)), 1362, 1294, 996 (s, γ(CH_2)), 1167, 1051 (s, ν(C-O)), 928 (m, γ($HC=CH_2$)), 833, 703, 685 (neat).

Reaction of (23) **with CBr_4 and PPh_3**

[G-1]OH **(23)** (0.15 g, 0.70 mmol) was dissolved in THF (1 ml). CBr_4 (0.24 g, 0.70 mmol) followed by PPh_3 (0.20 g, 0.7mmol) was added and the mixture was stirred for 40 minutes at room temperature. No precipitate was observed. Another batch of CBr_4 (0.14 g, 0.42 mmol) and PPh_3 (0.10 g, 0.38mmol) was added and the mixture was stirred for a further 80 minutes. After 40 minutes a yellow precipitate formed, which later changed to a green colour. After a total reaction time of 2 hours, the mixture was poured into distilled water (30 ml). The organic products were extracted with CH_2Cl_2 (3x10 ml). The organic layers was collected and dried over $MgSO_4$. The mixture was filtered and the solvent removed from the filtrate on a rotary evaporator. The resulting yellow oil was pre-absorbed onto silica and transferred to a silica gel column (20 cm in length). The column was eluted with 20 % CH_2Cl_2 in hexane followed by 50 % CH_2Cl_2 in hexane. The first pale yellow fraction was collected and the solvents removed on a rotary evaporator to give product **(24)** as a yellow oil, (0.09 g, 50 %).

ν/cm^{-1} 3083 (ν($HC=CH_2$)), 2984 (ν($HC=CH_2$)), 2922 (m, ν_{as}(CH_2)), 2865 (m, ν_s(CH_2)), 1648 (m, ν(C=C), 1596 (s, (C=C), 1453, 1422 ((m, δ_{as}(CH_2)), 1358, 1321, 1296, 991 (s, γ(CH_2)), 1170, 1053 (s, ν(C-O)), 928 (m, γ($HC=CH_2$)), 834, 690 (neat).

Reaction of (24) with **1,1,1-tris(4-hydroxyphenyl)ethane**

Compound **(24)** (0.28 g, 0.98 mmol) was dissolved in dry acetone (15 ml). K_2CO_3 (0.17 g, 1.2 mmol), 18-crown-6 (0.08 g, 0.32 mmol) and 1,1,1-tris(4-hydroxyphenyl)ethane (0.1 g, 0.32 mmol) were added. The yellow suspension was refluxed for 72 hours. The resulting orange suspension was allowed to cool to room temperature then filtered. The solvent was removed from the filtrate on a rotary evaporator to give an orange oil. The oil was pre-absorbed onto silica and was transferred to a silica gel column (20 cm in length). The column was initially eluted with 50% CH_2Cl_2 in hexane then 100 % CH_2Cl_2 in hexane to collect the impurities and finally 5 % THF in CH_2Cl_2 to collect the product **(25)** as a yellow oil. (0.17 g, 61 %).

ν/cm^{-1} 3079 (ν(HC=CH$_2$)), 2979 (ν(HC=CH$_2$)), 2926 (m, ν_{as}(CH$_2$)), 2869 (m, ν_s(CH$_2$)), 1736 (m, ν(C=C), 1604 (s, (C=C)), 1506, 1457, 1423 ((m, δ_{as}(CH$_2$)), 1379, 1293, 1243, 1013 (s, γ(CH$_2$)), 1171, 1056 (s, ν(C-O)), 927 (m, γ(HC=CH$_2$)), 832, 703, 685 (neat).

Reaction of (24) with 3,5-dihydroxybenzylalcohol

Compound **(24)** (0.072g, 0.25 mmol) was dissolved in acetone (15 ml). K_2CO_3 (0.06 g, 0.40 mmol), 18-crown-6 (0.02 g, 0.06 mmol) and 3,5-dihydroxybenzylalcohol (0.02 g, 0.15 mmol) were added and the mixture was refluxed for 72 hours. The mixture was allowed to cool to room temperature and then filtered. The solvent was removed from the filtrate on a rotary evaporator to give a pale orange oil. The oil was pre-absorbed onto silica and was transferred to a silica gel column (20cm in length). The column was eluted with 50 % CH_2Cl_2 in hexane then 5 % THF in CH_2Cl_2. The second fraction was collected and the solvents were removed from the filtrate on a rotary evaporator to give the product **(26)** as a yellow oil, (0.06 g, 73 %). (Found: C, 68.63; H, 6.83. $C_{33}H_{36}O_7$ (544.65) requires C, 72.78; H, 6.66)%;

ν/cm^{-1} 3412 (OH), 3082 (ν(HC=CH$_2$)), 2977 (ν(HC=CH$_2$)), 2935 (m, ν_{as}(CH$_2$)), 2873 (m, ν_s(CH$_2$)), 1720 (m, ν(C=C), 1597 (s, (C=C), 1453, 1423 ((m, δ_{as}(CH$_2$)), 1379, 1320, 1295, 996 (s, γ(CH$_2$)), 1164, 1054 (s, ν(C-O)), 928 (m, γ(HC=CH$_2$)), 835, 770, 686 (neat).

Reaction of (26) with CBr_4/PPh_3

Compound **(26)** (0.17 g, 0.3 mmol) was dissolved in THF (2 ml). CBr_4 (0.10 g, 0.30 mmol) followed by PPh_3 (0.08 g, 0.97 mmol) was added and the orange mixture stirred for 40 minutes at room temperature. A second batch of CBr_4 (0.10 g, 0.30 mmol) and PPh_3 (0.08 g, 0.30 mmol) were added and the mixture stirred for another 20 minutes during which time a beige precipitate formed. The reaction mixture was stirred for a further 1 hour. After a total reaction time of 2 hours, the mixture was poured into distilled water (20 ml) and the organic products were separated by extraction into CH_2Cl_2 (3x10 ml). The organic layer was collected and dried over $MgSO_4$ and the mixture was filtered. The solvent was removed on a rotary evaporator. The residual yellow oil was pre-absorbed onto silica and transferred to a silica-gel column, (20cm in length). The column was eluted with 50 % CH_2Cl_2 in hexane and then 100 % CH_2Cl_2. The second fraction was collected and the solvents removed from the eluent using a rotary evaporator to give a yellow sticky oil as product **(27)**, (0.09 g, 51 %). (Found: C, 68.45; H, 6.84. $C_{33}H_{35}BrO_6$ (607.54) requires C, 65.24; H, 5.81)%;

ν/cm^{-1} 3080 (ν(HC=CH$_2$)), 2957 (ν(HC=CH$_2$)), 2926 (m, ν_{as}(CH$_2$)), 2867 (m, ν_s(CH$_2$)), 1723 (m, ν(C=C), 1596 (s, (C=C)), 1453, 1423 ((m, δ_{as}(CH$_2$)), 1378, 1318, 1294, 995 (s, γ(CH$_2$)), 1163, 1049 (s, ν(C-O)), 927 (m, γ(HC=CH$_2$)), 834, 742, 669 (neat).

Reaction of (27) with core

Compound **(27)** (0.30 g, 0.49 mmol) was dissolved in dry acetone (15 ml). K_2CO_3 (0.09 g, 0.06 mmol), 18-crown-6 (0.02 g, 0.08 mmol) and 1,1,1-tris(4-hydroxyphenol)ethane (0.05 g, 0.16 mmol) were added. The yellow suspension was refluxed for 72 hours. The orange suspension was allowed to cool to room temperature then filtered. The filtrate was concentrated on a rotary evaporator to give an orange oil. The oil was pre-absorbed onto silica and was transferred to a silica gel column (20 cm in length). The column was eluted with initially with 50 % CH_2Cl_2 in hexane, 100 % CH_2Cl_2 and finally 5 % THF in CH_2Cl_2. Three fractions were collected, the first two fractions were characterised by TLC to be unreacted 1,1,1-tris(4-hydroxyphenol)ethane and compound **(27)** respectively. The solvents of the third fraction were removed using a rotary evaporator to give a yellow sticky oil as product **(28)**, (0.16 g, 53 %). (Found: C, 68.35; H, 7.23. $C_{119}H_{108}O_{21}$ (1886.26) requires C, 75.80; H, 6.26)%;

ν/cm^{-1} 3082 (ν(HC=CH$_2$)), 2977 (ν(HC=CH$_2$)), 2940 (m, ν_{as}(CH$_2$)), 2873 (m, ν_s(CH$_2$)), 1720 (m, ν(C=C), 1597 (s, (C=C)), 1454, 1423 ((m, δ_{as}(CH$_2$)), 1380, 1320, 1296, , 995 (s, γ(CH$_2$)), 1165, 1056 (s, ν(C-O)), 930 (m, γ(HC=CH$_2$)), 836, 740, 703, 691 (neat).

2.6 REFERENCES

1 a) J.-P. Majoral and A.-M. Caminade, *Chem. Rev.*, **1999**, *99*, 845.

b) D. A. Tomalia, *Adv. Mater.*, **1994**, *6*, 529.

c) J. M. J. Fréchet, *Science*, **1994**, *263*, 1710.

2 a) B. Romagnoli and W. Hayes, *J. Mater. Chem.*, **2002**, *12*, 767.

b) D. Astruc and F. Chardac, *Chem. Rev.*, **2001**, *101*, 2991.

c) J.L. Fillaut, J Linares, D. Astruc, *Angew. Chem. Int. Ed. Engl.*, **1994**, *30*, 2460.

d) A. M. Herring, B. D. Steffey, A. Miedaner, S. A. Wander, D. L. DuBois, *Inorg. Chem.* **1995**, *34*, 1100.

e) J. W. J. Knapen, A. W. van der Made, J. C. de Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove, G. van Koten, *Nature*, **1994**, *372*, 659.

3 N. J. Turro, J. K. Barton, D. A. Tomalia, *Acc. Chem. Res.*, **1991**, *24*, 332.

4 a) J. H. Cameron, A. Facher, G. Latterman, S. Diele, *Adv. Mater.*, **1997**, *9*, 398.

b) D. M. Junge and D. V. McGrath, *J. Chem. Soc. Chem. Commun.*, **1997**, 857.

c) S. Seroni, G. Denti, S. Campagna, A. Juris, M. Ciano, V. Balzani, *Angew. Chem. Int. Ed. Engl.*, **1992**, *31*, 1493.

5 A. Miedenaar, C. J. Curtis, R. M. Barkley, D. L. DuBois, *Inorg. Chem.*, **1994**, *33*, 5482.

6 E Cloutet, J - L Fillaunt, D. Astruc, Y. Gnanou, *Macromolecules*, **1999**, *32*, 1043.

7 N. Tomioka, D. Takasu, T. Takahashi, T. Aida, *Angew. Chem. Int. Ed.*, **1998**, 37, 1531.

8 M. Bardaji, M. Kustos, A - M Caminade, J - P Majoral, B. Chaudret, *Organometallics*, **1997**, *16*, 403.

9 a) E Cloutet, J.-L. Fillaut, Y. Gnanou, D. Astruc, *J. Chem. Soc. Chem. Commun.*, **1994**, 2433.

b) E. Cloutet, J.-L. Fillaut, Y. Gnanou, D. Astruc, *J. Chem. Soc. Chem. Commun.*, **1996**, 2047.

c) E. Cloutet, Y. Gnanou, J.-L. Fillaut, D. Astruc, *J. Chem. Soc. Chem. Commun.*, **1996**, 1565.

d) V. Marvaud and D. Astruc, *J. Chem. Soc. Chem. Commun.*, **1997**, 773.

10 D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Polym. J.*, **1985**, *17*, 117.

11 G. R. Newkome, Z. Yao, G. R. Baker, V. K. Gupta, *J. Org. Chem.*, **1985**, *50*, 2004.

12 a) C. J. Hawker and J.M.J. Fréchet, *J. Chem. Soc. Chem. Commun.*, **1990**, 1010.

b) Craig J. Hawker and J.M.J. Fréchet, *J. Am. Chem. Soc.*, **1990**, *112*, 7638.

13 F. Moulines and D. Astruc, *Angew. Chem. Int. Ed. Engl.*, **1988**, *27*, 1347.

14 F. Moulines, B. Gloaguen, D. Astruc, *Angew. Chem. Int. Ed. Engl.*, **1992**, *31*, 458.

15 F. Moulines, L. Djakovitch, R. Boese, B. Gloaguen, W. Thiel, J.-L. Fillaut, M.-H. Delville, D. Astruc, *Angew. Chem. Int. Ed. Engl.*, **1993**, *32*, 1075.

16 H - W Marx, F. Moulines, T. Wagner, D. Astruc, *Angew. Chem. Int. Ed. Engl.*, **1996**, *35*, 1701.

17 J. Guittard, J.–C. Blais, D. Astruc, *Pure & Appl. Chem.*, **1998**, *70*, 809.

18 V. Sartor, L. Djakovitch, J-L Fillaut, F. Moulines, F. Neveu, V. Marvaud, J. Guittard, J.-C. Blais, D. Astruc, *J. Am. Chem. Soc.*, **1999**, *121*, 2929.

19 M. A. Scmidt, H. G. Alt, W. J. Milius, *Organomet. Chem.*, **1997**, *541*, 3.

20 A. W. van der Made and P. W. N. M. van Leeuwen, *J. Chem. Soc. Chem. Commun.*, **1992**, 1400.

21 a) G. E. Oosterom, R. J. van Haaren, J. N. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Chem. Commun.*, **1999**, 1119.

b) G. E. Oosterom, J. N. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Angew. Chem. Int. Ed.*, **2001**, *40*, 128.

22 L.-L. Zhou and J. Roovers, *Macromolecules*, **1993**, *26*, 963.

23 D. Seyfreth and D. Y. Son, *Organometallics*, **1994**, *13*, 2682.

24 K. Lorenz, R. Mulhaupt, H. Frey, *Macromolecules*, **1995**, *28*, 6657.

25 X. Zhang, K. J. Haxton, L. Ropartz, D. J. Cole-Hamilton, R. E. Morris, *J. Chem Soc., Dalton Trans.*, **2001**, 3261.

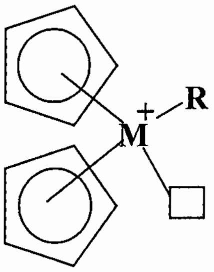
CHAPTER 3

METALLATION OF ALLYLARYL-ETHER DENDRIMERS AND RELATED MODEL COMPOUNDS

3.1. INTRODUCTION

3.1.1. SUPPORTED METALLOCENE CATALYSTS

Group IV metallocene catalysts exhibit excellent activities and stereospecifities for the polymerisation of olefins. In these systems a cationic metallocene containing one alkyl or hydride ligand and a vacant co-ordination site is reported to be the active catalyst (Figure 3.1.). Numerous examples of cationic group IV metallocenes for the polymerisation of alkenes are available.[1]



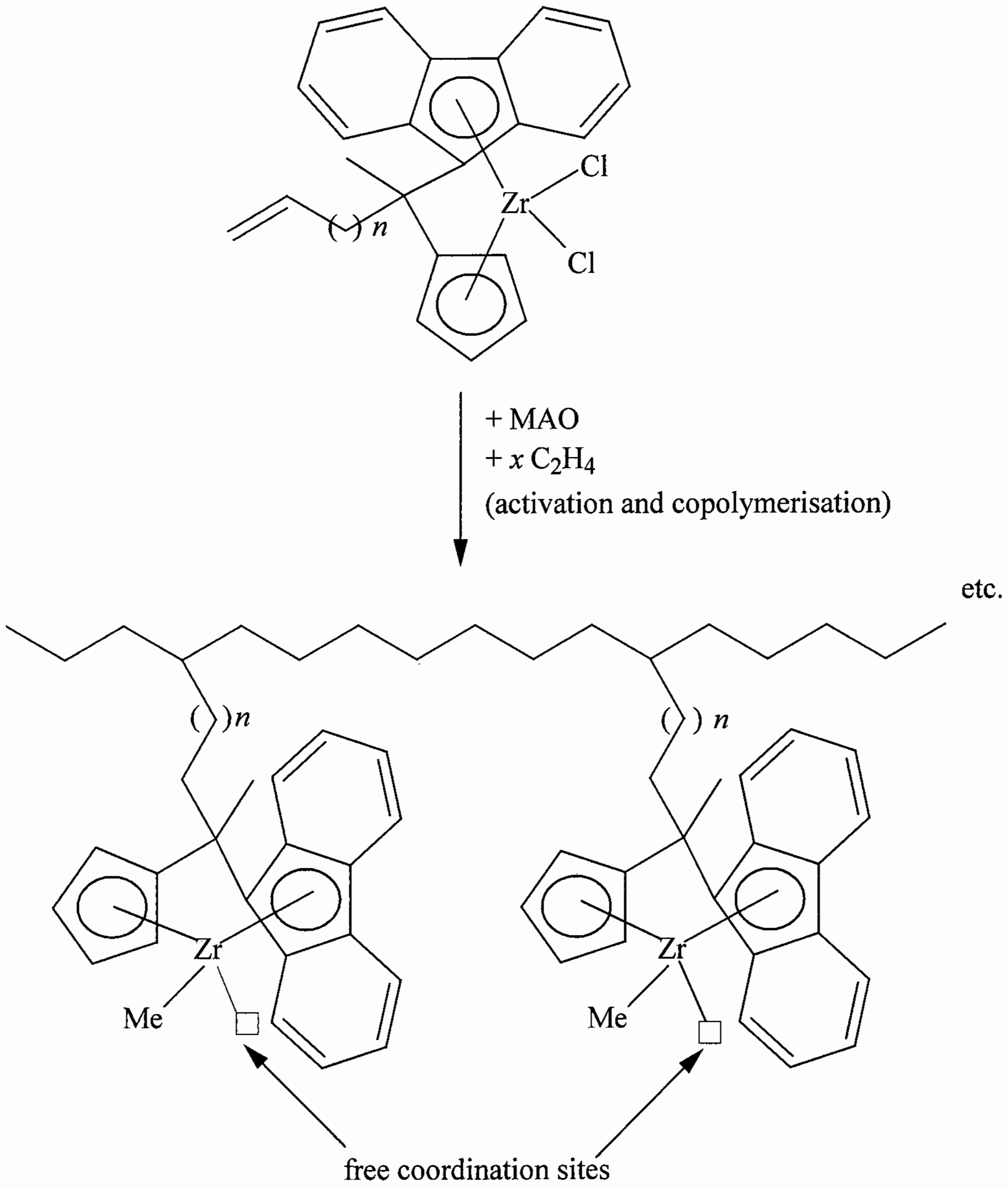
R= CH_3, H, polymer, X^- counterion

M = Ti, Zr, Hf

☐ = vacant co-ordination site

Figure 3.1. Active, cationic metallocene catalyst for the polymerisation of olefins.

Many commercial polymerisation processes require metallocene catalysts to be supported. This modification is needed to avoid reactor fouling with finely dispersed polymer particles, to prevent excessive swelling of polymers, and to produce polymer particles of a desired regular morphology. As described in Chapter 1, several techniques have been developed to synthesize supported metallocene catalysts. One approach is the use of cross-linked polystyrene as support material.[2, 3, 4] Another method involves the fixation of the catalyst on the surface of an inorganic support such as silica, alumina or magnesium dichloride, by either an absorption process or via chemical bonding.[5, 6] Recently Alt *et al* reported the self-immobilization of metallocene catalysts into the growing polymer chain for example polyethylene.[7] The proposed mechanism for the self-immobilization is presented in Scheme 3.1.



Scheme 3.1. **Proposed mechanism for the "self-immobilization" of a homogeneous *ansa*-metallocene complex into a growing polymer chain to form a heterogeneous catalyst.**

3.1.2. DENDRIMERS AS CATALYSTS SUPPORTS

One of the most promising developments related to dendrimer research is the preparation of novel and efficient catalytically active hyperbranched metal-containing macromolecules. The application of soluble metallo-polymers in the field of catalysis[8] has been thoroughly explored. This can be attributed to the numerous advantages related to anchoring catalytic species to polymeric supports – especially if the macromolecular support is soluble in the reaction medium[9].

In comparison to their mononuclear homogeneous counterparts, these macromolecular support systems have been found to be more stable and less corrosive or toxic.

Dendrimers possess unique structural and chemical properties that render them as attractive alternatives in the development of new materials, which combine the main advantages of both homogeneous and heterogeneous catalysts.[10] Some of these properties are:

i) excellent solubility in common organic solvents (advantage of homogeneous catalysts);
ii) unlike linear polymers they maintain a stable three-dimensional shape with minimally-entangled structure therefore the catalytic sites are easily accessible to the substrates leading to high catalytic activity (advantage of homogeneous catalysts);
iii) ease of removal from the reaction media by membrane and ulta-filtration techniques as a direct result of their large size when compared to products (advantage of heterogeneous catalysts).

Catalytic sites can be incorporated within the dendritic structure in several ways:

i) at the central core or focal point of the dentritic wedges;
ii) at branching points;
iii) at the peripheral surface of dendrimers.

In this chapter we investigate the use of dendrimers as support material for metallocene catalyst precursors. The catalyst is incorporated at the peripheral surface of the dendrimer.

3.1.3. PERIPHERALLY FUNCTIONALISED DENDRITIC CATALYSTS

The first example of a dendrimer employed as a catalyst support was reported by Van Koten *et al* in 1994.[11] They describe the preparation of 0th and 1st generation polysilane dendrimers functionalised with diaminoarylnickel(II) complexes at their peripheral surfaces (Figure 3.2.). The homogeneous catalysts were used in Kharasch-type additions of polyhalogenoalkanes to olefins. In comparison to the monomeric counterpart, a reduction of 20 – 30 % in the catalytic activity was observed when the dendritic catalysts were employed. However, the potential application of physical separation methods (i.e. filtration) was described for these hyperbranched systems. Numerous dendritic catalysts have since been reported in literature.[12] Amoungst these is the report by Moss *et al* of a hexabranch ruthenium dendrimer supported on silica (Figure 3.3.).[13]

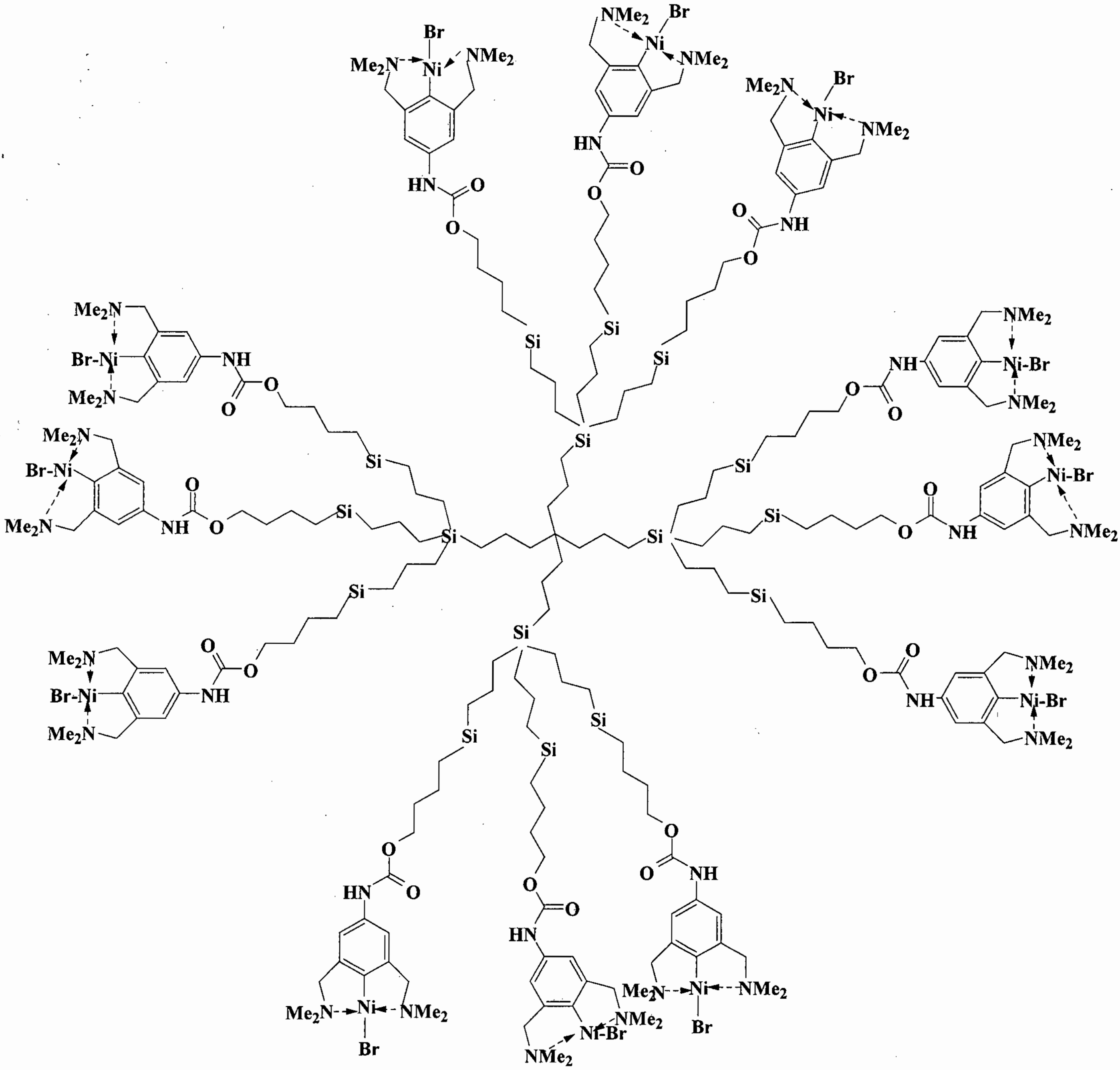


Figure 3.2. **Van Koten's polysilane dendritic catalyst utilised in the Kharasch-type addition of polyhalogenoalkanes to olefin substrates.**

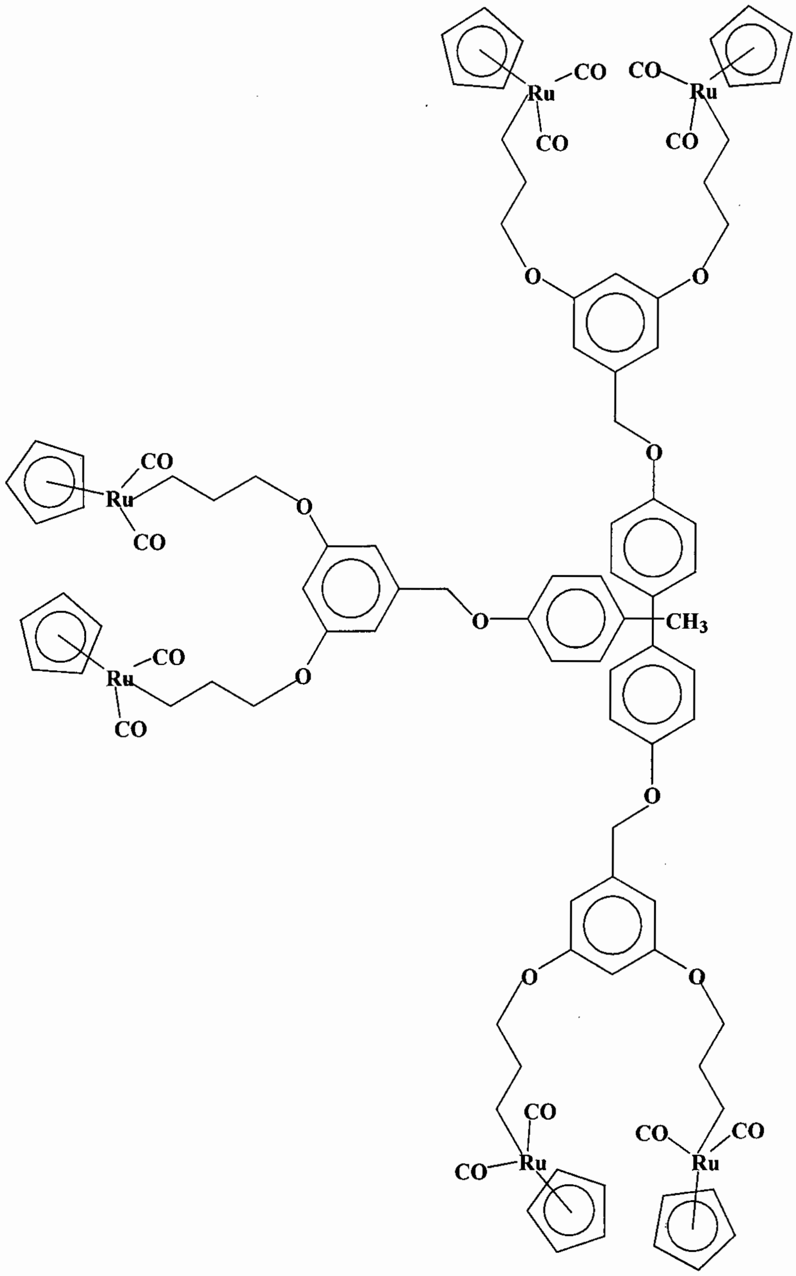


Figure 3.3. **Moss' hexabranch ruthenium dendrimer, whose silica-supported version was examined as a catalyst of the Fischer-Tropsch synthesis.**

The termini of the dendritic branches are 18-electron [RuCp(CO)$_2$alkyl] groups. Under Fischer-Tropsch conditions this dendrimer is metastable. Further studies on this dendritic catalyst in the CO hydrogenation showed that a single ruthenium site is not sufficient for the Fischer-Tropsch synthesis.

A metallocene catalyst can be attached to a dendrimer in various ways (Figure 3.4.):

i) σ-bond, the zirconocene is bound to the dendrimer via a M-C σ-bond;

ii) π-bond, the zirconocene is bound via the Cp spectator ligand of the metal to the dendrimer;

iii) *ansa*-bound, the bond between the dendrimer and the bridge between the two Cp rings of the metal.

iv) a fourth possibility, a bond between the dendrimer and the zirconocene via a η^3-allyl group, however such a species is not useful as the η^3-allyl group would deactivate the zirconocene for polymerisation reactions.

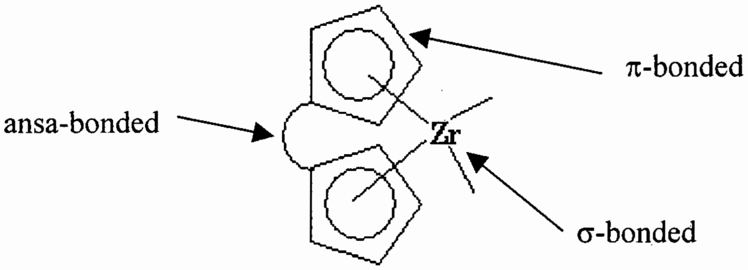
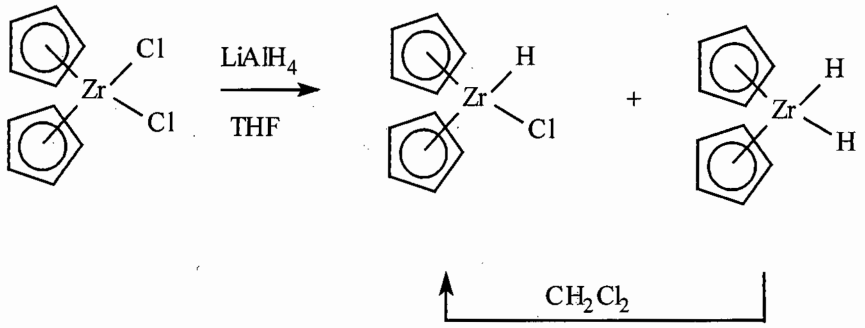


Figure 3.4. Examples of linkage between zirconocene catalyst and dendrimer.

In this study the attachment of zirconocene on the periphery of a dendrimer via M-C σ-bonds is investigated and reported.

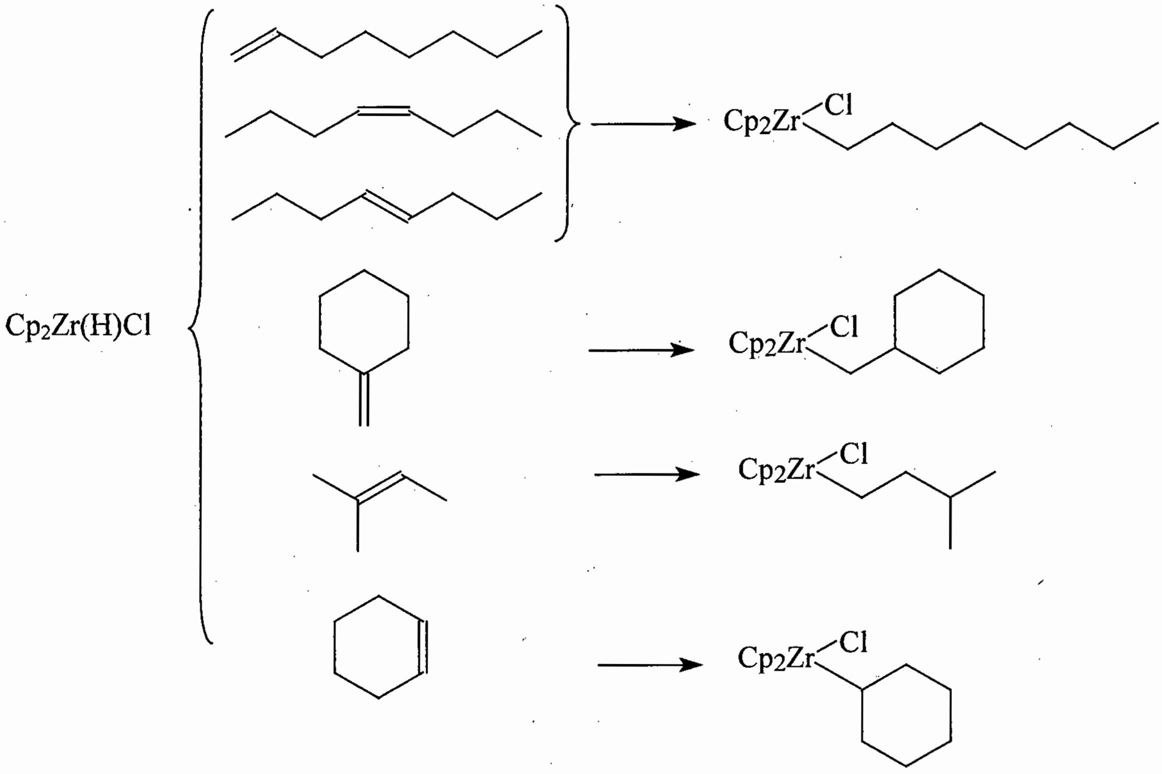
3.1.4. HYDROZIRCONATION OF ALKENES

The metallation of dendrimers with alkenyl termini was achieved by reaction with $Cp_2Zr(H)Cl$, resulting in hydrozirconation of the alkene moiety to form the corresponding zirconiumalkyl products. Dendrimers with 6 and 12 peripheral alkenyl functionalities have been employed in this study. In addition to the dendritic zirconium compounds, model compounds were also prepared for comparative studies. $Cp_2Zr(H)Cl$, combines with a wide variety of activated or non-activated alkenes under mild conditions. The utility of $Cp_2Zr(H)Cl$ for hydrozirconation was discovered by Schwartz *et al.*[14] Many subsequent applications of this useful reagent have been documented.[15] $Cp_2Zr(H)Cl$ was first prepared by Wailes *et al*[16] by reaction of Cp_2ZrCl_2 with $LiAl(OtBu)_3H$ or $LiAlH_4$. Another method utilizes sodium bis(2-methoxy)aluminium hydride (RED-Al) as reducing agent.[17] Later Buchwald *et al* developed an experimentally simple procedure for the preparation of the Schwartz reagent.[18] They reported the reduction of Cp_2ZrCl_2 to a mixture of $Cp_2Zr(H)Cl$ and Cp_2ZrH_2 using a solution of $LiAlH_4$ in ether. Washing the mixture with a minimum amount of CH_2Cl_2, converts the Cp_2ZrH_2 into the desired $Cp_2Zr(H)Cl$ as presented in Scheme 3.2.



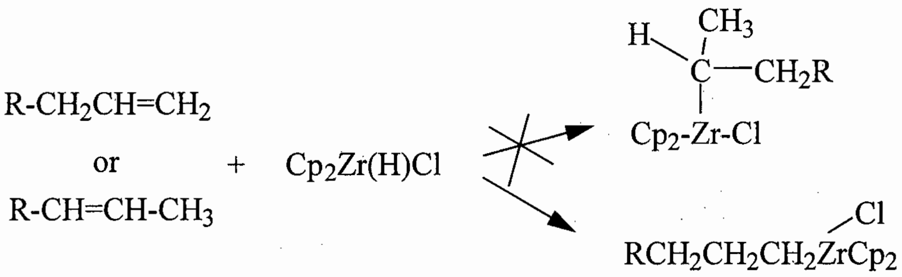
Scheme 3.2. Preparation of $Cp_2Zr(H)Cl$, Schwartz's reagent.

During the hydrozirconation process the double bond of an alkene becomes saturated by the insertion of an unsaturated hydrocarbon into the Zr-H bond. Some examples of this are illustrated in Scheme 3.3.[14]



Scheme 3.3. Examples of hydrozirconation reactions of alkenes with $Cp_2Zr(H)Cl$.[14]

With terminal or internal alkenes, the zirconium favours the terminal position for both electronic and steric reasons.



The large size of the Cp_2ZrCl- group ensures that it will become attached to the least hindered position of an alkene. This is achieved by either regiospecific addition of Zr-H to a terminal olefin or addition to an internal olefin, followed by migration past primary or secondary carbons to the least hindered terminus of the alkyl chain.[6]

The zirconium alkyl products are thermally stable. They may however decompose by β -hydrogen transfer. This is because the preferred decomposition pathway for the metal alkyl compounds is β-elimination, which is favoured by an electronic transfer from the metal d-orbitals into the anti-bonding σ^* orbitals of the β C-H bond. The zirconium alkyl is extremely sensitive to i) water or other protic reagents; ii) other electrophiles such as $PbCl_2$, Br_2 or I_2;

e.g.

$$\begin{tikzcd}
4\,ZrMe_2(C_5H_5)_2 + 2\,PbCl_2 \arrow[r, "fast"] & 4\,ZrClMe(C_5H_5)_2 + Pb + PbMe_4 \arrow[d, "slow"', "2\,PbCl_2"] \\
& 4\,ZrCl_2(Cp)_2 + Pb + PbMe_4
\end{tikzcd}$$

iii) or to multiply bonded reagents such as NO or SO_2.[6]

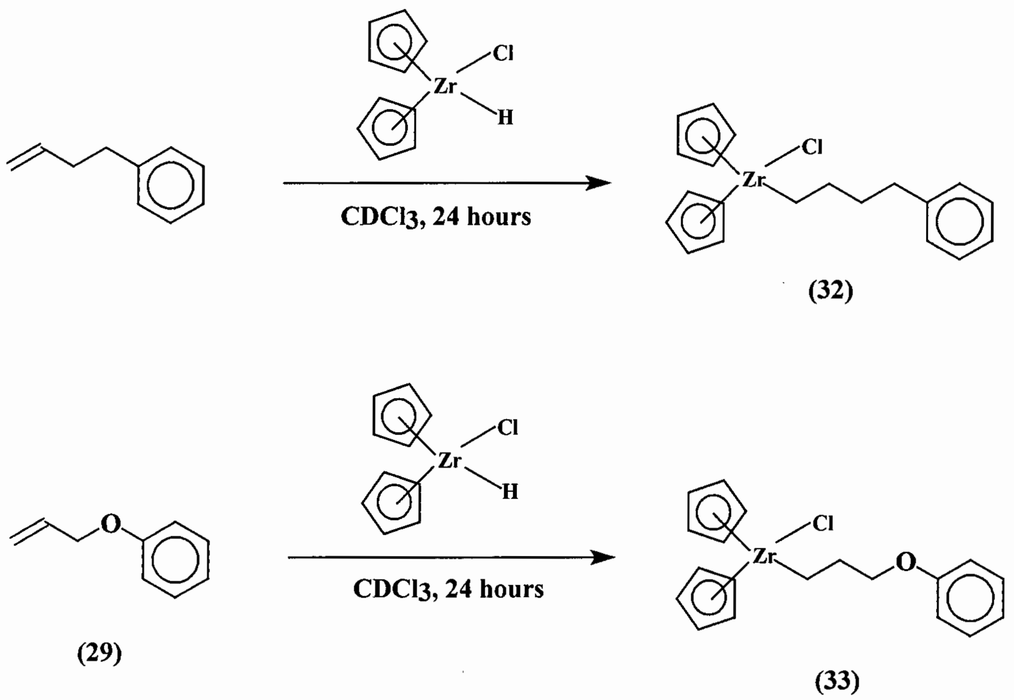
Zirconium alkyls are susceptible to hydrolysis yielding alkanes and are protonated rapidly by dilute aqueous acid. Due to their ready reaction with a range of electrophiles these organometallic reagents are useful as synthetic intermediates.

3.2. HYDROZIRCONATION OF MODEL COMPOUNDS AND ALLYLARYL-ETHER DENDRIMERS

In chapter 2, we reported the synthesis of the first and second generation dendrimers containing allyl functionalities on the periphery. In this chapter, we report the metallation of these dendrimers. Since the products are air and moisture sensitive, all operations and experiments were performed in a glovebox kept under an atmosphere of nitrogen. The metallation of the dendrimers was achieved by reacting the alkenes with $Cp_2Zr(H)Cl$ (Scheme 3.6. and Scheme 3.7.). This results in the hydrozirconation of the terminal double bonds to form the corresponding zirconium alkyl products. This leads to the formation of an organometallic dendrimer containing Zr-C σ-bonds on the periphery of the molecule. The products were characterised largely by NMR spectroscopy. A dinuclear zirconium complex **(34)** was also prepared by reaction of compound **(30)** with $Cp_2Zr(H)Cl$ (Scheme 3.5.), as well as a tetranuclear complex **(35)** by reaction of 1,2,4,5-tetrakis(butenyl)benzene **(31)** with $Cp_2Zr(H)Cl$ (Scheme 3.5.). The starting materials, compounds **(30)** and **(31)** were prepared by using the procedures described in the experimental Section 3.5. In addition to the multinuclear complexes above, model mononuclear zirconium complexes, **(32)** and **(33)** have also been prepared (Scheme 3.4.). These have a structure related to that of the multinuclear catalyst precursors. The new zirconium alkyl complexes prepared are highly oxygen and moisture sensitive, readily soluble in common organic solvents, thermally stable and can be stored under an inert atmosphere for extended periods. Complexes **(32)** and **(35)** are yellow crystalline solids, while complexes **(33)**, **(34)**, **(35)**, **(36)** and **(37)** are yellow oils.

Synthesis of mononuclear complexes, (32) and (33).

The model compounds, $Cp_2Zr\{(CH_2)_4Ph\}(Cl)$ **(32)** and $Cp_2Zr\{(CH_2)_3OPh\}(Cl)$ **(33)** were prepared by reaction of 4-phenyl-1-butene and compound **(29)** with 1 molar equivalent of $Cp_2Zr(H)Cl$ respectively (Scheme 3.4.). After addition of the hydride to the colourless alkene solutions, the hydride mixture was initially cloudy but went to a clear yellow colour after less than 1 minute of reaction time. The ^1H NMR spectra of both solutions after 24 hours showed that all the alkene was hydrozirconated. Compound **(32)** gave a triplet at δ 0.96 ppm and **(33)** gave a triplet at δ 1.04 ppm for $ZrC\underline{H}_2$. The dueterated solvents were removed to give complex **(32)** as a yellow crystalline solid and complex **(33)** as a yellow oil.

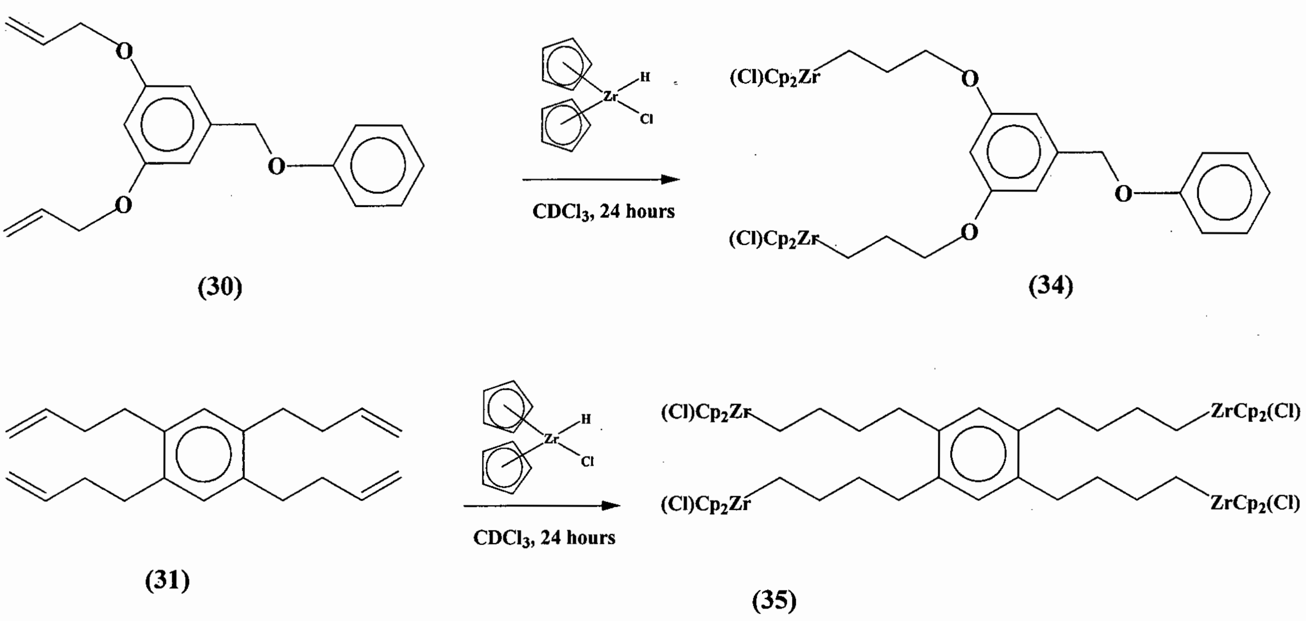


Scheme 3.4. Reaction of 4-phenyl-1-butene and compound (29) with $Cp_2Zr(H)Cl$.

The model compound 4-phenyl-1-butene was reacted with $Cp_2Zr(H)Cl$ in a number of different solvents including $CDCl_3$, C_6D_6, THF and toluene. The hydrozirconation reaction in THF and toluene goes to completion in approximately 30 - 60 minutes, while the reaction in $CDCl_3$ and C_6D_6 is complete in 24 hours, as judged by NMR experiments. The rate of hydrozirconation in these solvents are toluene > THF > C_6D_6 > $CDCl_3$. The reactive monomer $Cp_2Zr(H)Cl$ is more soluble in toluene and THF and this results in a faster hydrozirconation reaction in these solvents.

Synthesis of binuclear (34) and tetranuclear (35) complexes.

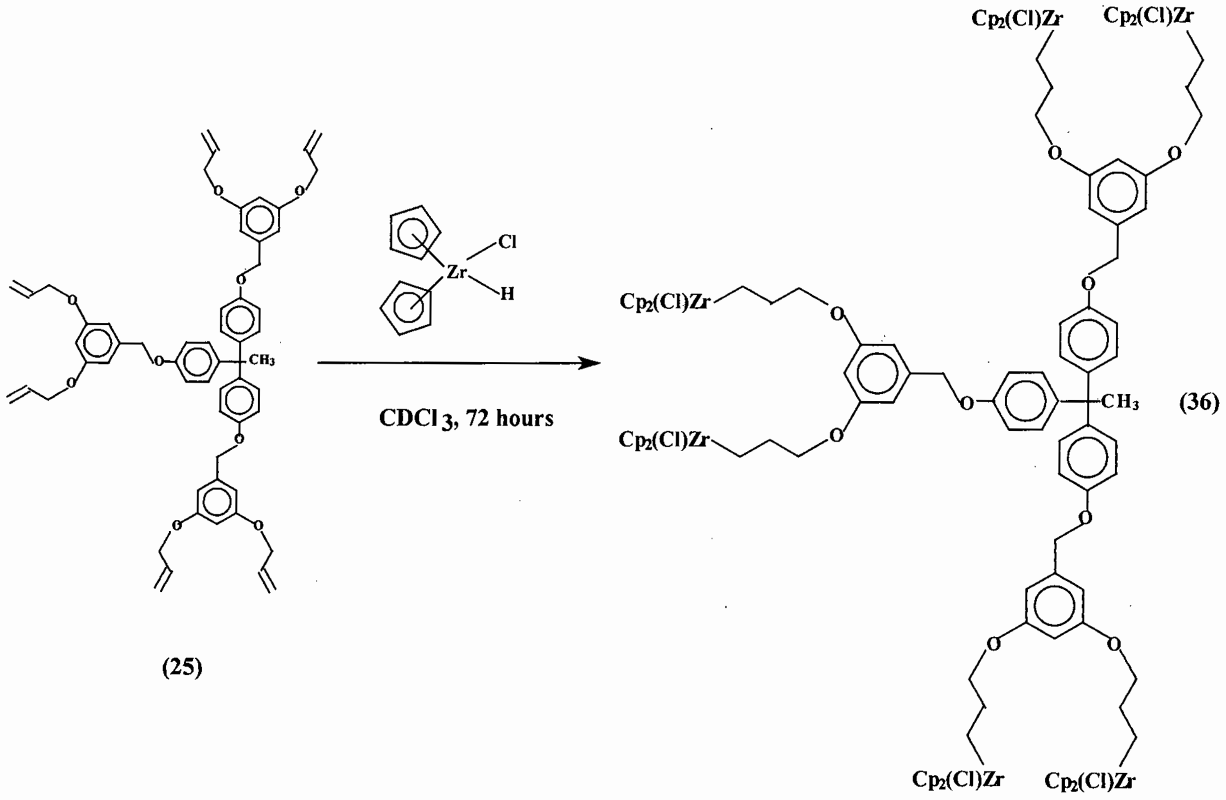
To a clear yellow solution of compound **(30)** in $CDCl_3$ was added 2 molar equivalents of $Cp_2Zr(H)Cl$ (Scheme 3.5.). The reaction mixture went from cloudy to a clear yellow colour within approximately 1 minute of addition of the hydride. The reaction mixture was transferred to an NMR tube and monitored by ^1H NMR spectroscopy. After 24 hours all the alkene was consumed and a new triplet at δ 0.96 ppm was observed. This peak was assigned to $ZrC\underline{H_2}$ and confirmed that the desired product **(34)** was formed. The dueterated solvent was removed to give a yellow oil as complex **(34)**. Similarly, compound **(31)** was treated with 4 molar equivalents of $Cp_2Zr(H)Cl$ in $CDCl_3$ (Scheme 3.5.). After 24 hours of reaction in an NMR tube, all the alkene was consumed and a triplet at δ 0.99 ppm was observed for $ZrC\underline{H_2}$. The deuterated solvent was removed to give a yellow crystalline solid as complex **(35)**.



Scheme 3.5. Reaction of compounds (30) and (31) with $Cp_2Zr(H)Cl$.

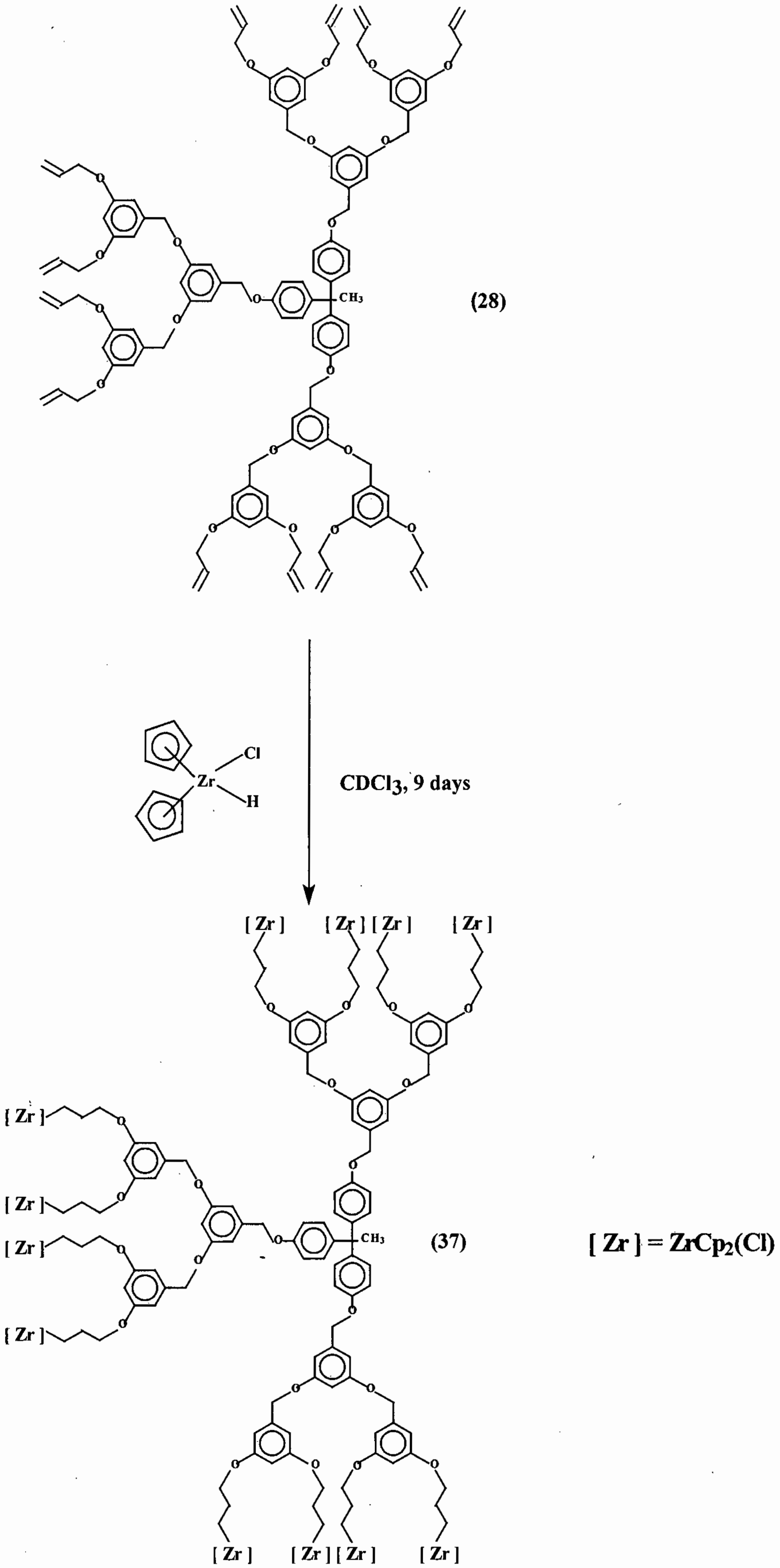
Synthesis of the complexes (36) and (37).

A clear yellow solution of dendrimer **(25)** in $CDCl_3$ was treated with 6 molar equivalents of $Cp_2Zr(H)Cl$ for 72 hours at room temperature (Scheme 3.6.). Upon addition of $Cp_2Zr(H)Cl$ to the solution of **(25)** in $CDCl_3$, the mixture turned from cloudy to a clear yellow colour after stirring the mixture for approximately 5 minutes. After 24 hours, the ^1H NMR spectrum of the solution showed the presence of vinyl protons in the region δ 5.22 - 6.18 ppm. The reaction solution was then allowed to stand in an NMR tube for 72 hours. The NMR spectrum was again recorded on the sample to confirm that all the allyl groups were consumed. The solvent was removed to give the product **(36)** as a yellow oil.



Scheme 3.6. Reaction of dendrimer (25) with $Cp_2Zr(H)Cl$.

A clear yellow solution of dendrimer **(28)** was treated in a similar way with $Cp_2Zr(H)Cl$ in $CDCl_3$ at room temperature (Scheme 3.7.) in an NMR tube. The cloudy suspension went to a clear yellow colour after approximately 5 minutes. After 72 hours, the ^1H NMR spectrum indicated new multiplet at δ 0.92 - 0.97 ppm for $Zr\text{-}CH_2$. The ^1H NMR spectrum also showed allyl protons, which indicated that not all the allyl groups were hydrozirconated. The reaction was continued for 9 days, with daily monitoring of the reaction by ^1H NMR to see if vinyl protons were still present. After day 3, a second batch of $Cp_2Zr(H)Cl$ was added, but the reaction still did not go to completion. The extended reaction time of the hydrozirconation process of up to 9 days resulted in competitive decomposition of the zirconiumalkyl complex in the solvent to other zirconocene species, including Cp_2ZrCl_2. The decomposition of the desired product was apparent in the ^1H NMR due to the disappearance of the $ZrCH_2$ peak at δ 0.92 - 0.97 ppm and the formation of several cyclopentadienyl (Cp) peaks.



Scheme 3.7. Proposed reaction of dendrimer (28) with $Cp_2Zr(H)Cl$.

In conclusion, the hydrozirconation of the 12 allyl dendrimer results in partial hydrozirconation of the allyl groups, yielding a product which contain less than 12 Zr centres. TLC was performed on a sample kept in the glovebox, and compared to R_f values of the starting material, compound **(28)**. Results showed that the sample kept under nitrogen only gave one spot on the TLC plate, which could suggest that only one compound is present.

As mentioned earlier, all the zirconium alkyl complexes **(32)** – **(37)** prepared are highly unstable in air and moisture. Due to their unstable nature, complete characterisation of these products were difficult and therefore only the ^{1}H NMR and ^{13}C NMR spectra are reported in the next Section 3.3.

3.3. CHARACTERISATION OF METALLATED DENDRIMERS

The NMR data of the hydrozirconated alkenes **(32)** to **(37)** are presented in Tables 3.1. and 3.2. ^{1}H NMR and ^{13}C NMR spectroscopy were performed in $CDCl_3$ and/ or C_6D_6.

3.3.1. ^{1}H NMR SPECTRA

The signal for $ZrCH_2$ as observed in $CDCl_3$ appears in the region of δ 0.90 – 1.18 ppm. This particular signal is important, since it confirms the incorporation of the metallocene within the dendrimer. Figure 3.5 shows the ^{1}H NMR spectrum of the hydrozirconated model compound **(32)** as observed in C_6D_6 in the region of δ 0 – 10 ppm. The resonances for the alkene functional group of the starting material, 4-phenyl-1-butene is not observed, indicating that all the alkene is hydrozirconated. A new signal at δ 0.96 ppm and δ 1.07 ppm is observed in $CDCl_3$ and C_6D_6 respectively due to $ZrCH_2$.

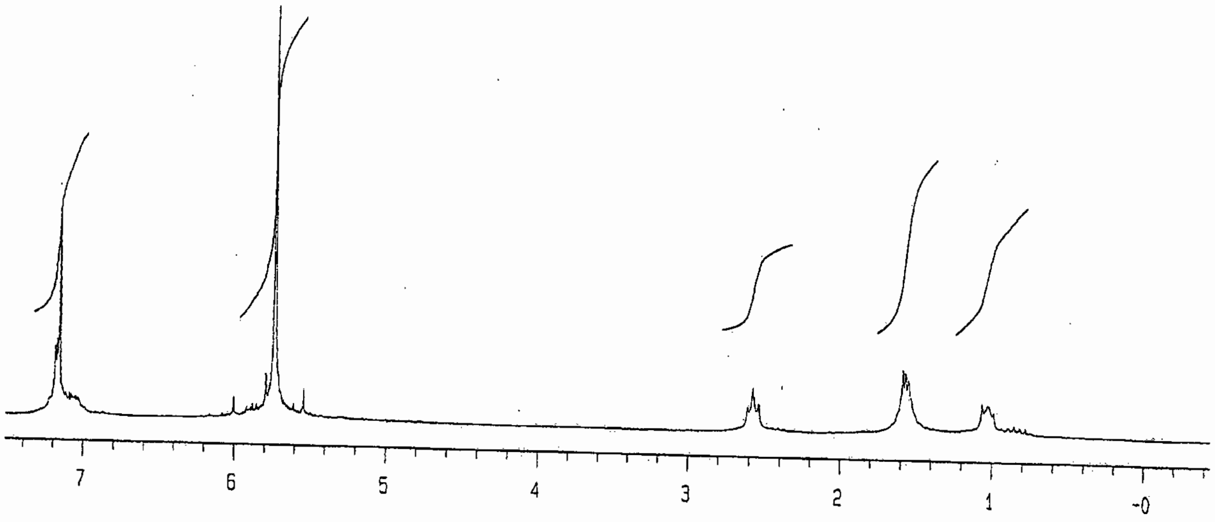
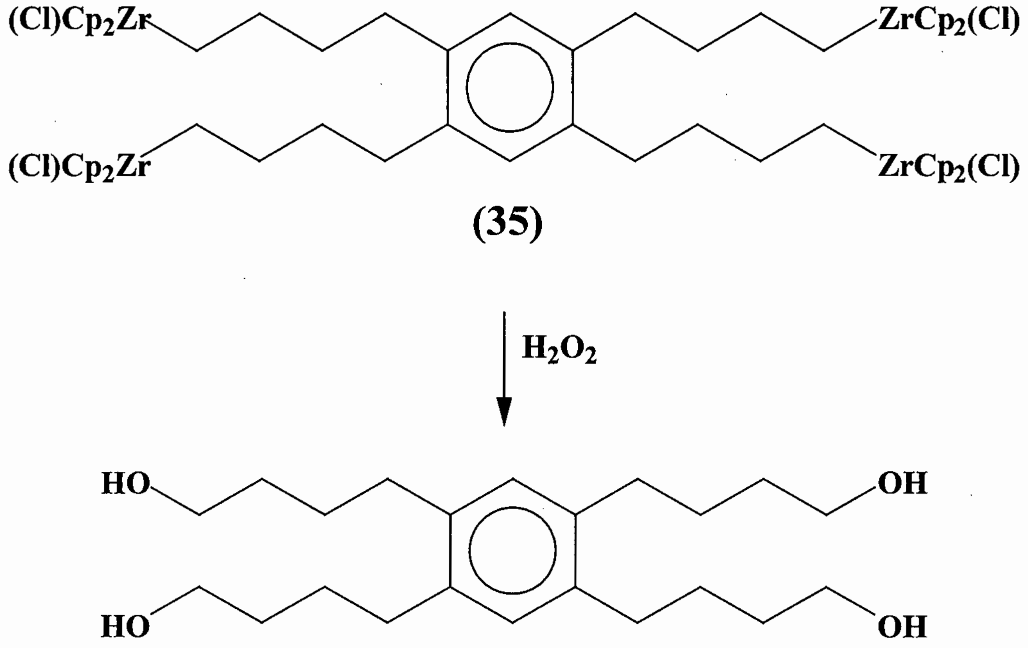


Figure 3.5. ^{1}H NMR spectrum of compound (32) in the region of δ 0 – 7 ppm in C_6D_6.

In order to gain additional information about the product of the hydrozirconation reaction, derivativisation of product **(35)** was performed. The hydrozirconation product of **(31)** was reacted with H_2O_2: after the appropriate work-up the organic product appeared to be 1,2,4,5-tetrakis(butanol)benzene; as was concluded from the ^{1}H NMR spectrum. The triplet at δ 0.99 ppm for $ZrCH_2$ was no longer present. A triplet for the newly formed CH_2OH is observed at δ 3.99 ppm.



Scheme 3.8. Reaction of compounds (35) with H_2O_2.

Table 3.1. **^{1}H NMR data of hydrozirconated alkenes**

COMPOUND NO.	CHEMICAL SHIFT^a (δppm) (CDCl$_3$)	CHEMICAL SHIFT^a (δppm) (C$_6$D$_6$)	ASSIGNMENT
(32)	m, 7.17 - 7.36, 5H	m, 7.16 – 7.20, 5H	Ar$\underline{H}$
	s, 6.32, 10H	s, 5.73, 10H	Cp
	m, 2.57 - 2.64, 2H	t, 2.58, $^3J_{H-H}$ = 7.6Hz, 2H	C$\underline{H}_2$-Ar
	m, 1.55 - 1.67, 2H	m, 1.54 - 1.57, 4H	C$\underline{H}_2$CH$_2$Ar
	m, 1.3 - 1.44, 2H		C$\underline{H}_2$CH$_2$-Zr
	t , 0.96, $^3J_{H-H}$ = 8.0Hz, 2H	t, 1.07 , $^3J_{H-H}$ = 8.2 Hz, 2H	C$\underline{H}_2$-Zr
(33)	m, 7.22 - 7.26, 2H	m, 7.02 - 7.15, 5H	Ar$\underline{H}$
	m, 6.88 – 6.99, 3H		Ar$\underline{H}$
	s, 6.31, 10H	s, 5.72, 10H	Cp
	t, 3.92, $^3J_{H-H}$ =7.1Hz, 2H	t, 3.66, $^3J_{H-H}$ = 4.0Hz, 2H	C$\underline{H}_2$-OAr
	m, 1.81„ 2H	m, 1.90 – 2.02, 2H	C$\underline{H}_2$CH$_2$-OAr
	t, 1.04, $^3J_{H-H}$ = 8.2Hz, 2H	m, 0.97 - 1.12, 2H	C$\underline{H}_2$-Zr
(34)	m, 6.59 – 6.62, 2H		ArH
	m, 6.95 – 6.99, 3H		Ar$\underline{H}$
	m, 7.25 – 7.37, 3H		Ar$\underline{H}$
	s, 6.37, 20H		Cp
	t, 3.71, $^3J_{H-H}$ = 6.0Hz, 4H		C$\underline{H}_2$-OAr
	m, 2.00, 4H		C$\underline{H}_2$CH$_2$-OAr
	t, 0.96, $^3J_{H-H}$ = 8.0Hz, 4H		C$\underline{H}_2$-Zr
	s, 2H, 4.99		ArC$\underline{H}_2$-O

Table 1. continued.

(35)	s, 6.9, 2H		Ar$\underline{H}$
	s, 5.96, 10H		Cp
	t, 2.50, $J_{H\text{-}H}$ = 3.0Hz, 2H		$C\underline{H}_2$-Ar
	m, 1.55 - 1.65, 2H		$C\underline{H}_2CH_2Ar$
	m, 1.41 –1.46, 2H		$C\underline{H}_2CH_2$-Zr
	t, 0.99, $J_{H\text{-}H}$ = 8.4Hz, 2H		$C\underline{H}_2$-Zr
(36)	br m, 6.80 – 7.19, 21H	br m, 6.90 – 7.15, 21H	Ar$\underline{H}$
	s, 6.31, 60H	s, 5.73, 60H	Cp
	t, 3.72, $J_{H\text{-}H}$ = 6.0Hz, 12H	m, 3.81, 12H	$C\underline{H}_2$-OAr
	m, 2.01 – 2.08, 12H	m, 1.99 – 2.04, 12H	$C\underline{H}_2CH_2$-OAr
	t, 0.95, $J_{H\text{-}H}$ = 8.8Hz, 12H	m, 0.09 – 1.01, 12H	$C\underline{H}_2$-Zr
	s, 4.99, 6H	s, 4.98, 6H	ArC$\underline{H}_2$-O
	s, 1.28, 3H	s, 1.25, 3H	$C\underline{H}_3$
(37)	br m, 6.75 – 7.15, 39H		Ar$\underline{H}$
	s, 6.29, 120H		Cp
	m, 3.69 – 3.78, 24H		$C\underline{H}_2$-OAr
	m, 2.05 – 2.17, 24H		$C\underline{H}_2CH_2$-OAr
	m, 0.92 – 0.97, 24H		$C\underline{H}_2$-Zr
	s, 4.99, 16H		ArC$\underline{H}_2$-O
	s, 4.53, 6H		ArC$\underline{H}_2$-core

[a] br = broad; s = singlet; d = doublet; t = triplet; m = multiplet

3.3.2. ^{13}C NMR SPECTRA

The ^{13}C NMR spectra gave further information of the incorporation of the metallocene within the dendrimer. Complete assignments of the signals in the ^{13}C NMR spectra of compounds **(32)** – **(36)** were possible. These provided further support for the assignments made in the ^{1}H NMR spectra. Resonances for the $ZrCH_2$ carbons are observed in the region of δ 50 - 70 ppm. Spectral data are presented in Table 3.3.

Table 3.3. **^{13}C NMR data of hydrozirconated alkenes**

COMPOUND NO.	CHEMICAL SHIFT (δppm) (CDCl$_3$)	ASSIGNMENT
(32)	136.42	Ar$\underline{C}$
	121.82, 121.75	Ar$\underline{C}$
	115.47	Cp
	26.78	$\underline{C}H_2$-Ar
	28.81	$\underline{C}H_2CH_2Ar$
	30.99	$\underline{C}H_2CH_2$-Zr
	47.60	$\underline{C}H_2$-Zr
(33)	118.47	Ar$\underline{C}$
	127.38, 127.41	Ar$\underline{C}$
	114.00	Cp
	8.54	$\underline{C}H_2$-OAr
	20.63	$\underline{C}H_2CH_2$-OAr
	67.43	$\underline{C}H_2$-Zr

(34)	160.02	Ar$\underline{C}$
	129.43, 121.09	Ar$\underline{C}$
	114.05	Cp
	10.01	$\underline{C}H_2$-OAr
	22.43	$\underline{C}H_2CH_2$-OAr
	69.80	$\underline{C}H_2$-Zr
(35)	129.82, 137,67	Ar$\underline{C}$
	115.96	Cp
	31.92	$C\underline{H_2}$-Ar
	34.26	$C\underline{H_2}CH_2Ar$
	37.52	$C\underline{H_2}CH_2$-Zr
	56.20	$C\underline{H_2}$-Zr
(36)	159.95, 139.85 129.63, 112.75	Ar$\underline{C^{core}}$
	133.16, 117.72 106.22, 99.32	Ar$\underline{C}$
	115.97	Cp
	69.15	$C\underline{H_2}$-OAr $C\underline{H_2}CH_2$-OAr
	68.92	$\underline{C}H_2$-Zr
	70.01	Ar$C\underline{H_2}$-O

3.4. CONCLUSION

The hydrozirconation of the model compound 4-phenyl-1-butene and compounds **(30)** - **(32)** were successful as judged by ^{1}H NMR and ^{13}C NMR spectra. Hydrozirconation of dendrimer **(25)** gave an organometallic complex containing 6 zirconium centres on the periphery. The hydrozirconation of dendrimer **(28)** only resulted in partial metallation of the peripheral alkene groups. The zirconium alkyl complexes prepared were investigated for their catalytic activity towards ethylene polymerisation. The results obtained for these new species are compared against that for standard precursors such as Cp_2ZrCl_2 and $Cp_2Zr(H)Cl$. These results are discussed in Chapter 4.

3.5. EXPERIMENTAL

General Experimental Procedure

All operations involving the handling of solids were carried out in a Unilab glovebox from M. Braun. All reactions were carried out using standard Schlenk techniques under an atmosphere of nitrogen. Infrared spectra were recorded on a Paragon 1000 Fourier Transform Infrared Spectrophotometer as neat thin films between NaCl disks. ^{1}H NMR and ^{13}C NMR spectra were recorded as solutions in $CDCl_3$ or C_6D_6 on a Varian GEMINI 2000 spectrometer with tetramethylsilane as reference standard. The ^{1}H NMR spectra were recorded at 200-MHz and ^{13}C NMR at 50.3-MHz. Mass spectra were recorded on a FINNIGAN MAT GCQ GC/MS. Microanalysis data were obtained from the University of Western Cape Microanalytical Laboratory and University of Cape Town Microanalytical Laboratory. TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica for flash chromatography was Merck Kieselgel 60 (230 – 400 mesh). Acetone, THF, hexane and dichloromethane were purchased from Merck. Acetone was dried over drierite. THF was dried by refluxing over sodium wire and distilled from Na-benzophenone under nitrogen. K_2CO_3 was dried at 90^0C under high vacuum for 6 hours before use. Deuterated solvents $CDCl_3$ and C_6D_6 were extensively dried prior to use. $CDCl_3$ was dried over $CaCl_2$ and distilled prior to use. C_6D_6 was dried over sodium wire and distilled prior to use.

Reaction of phenol with allylbromide to prepare (29)

Phenol (3.00 g, 32.00 mmol); allylbromide (3.85 g, 32.00 mmol); 18-crown-6 (1.68 g, 6.40 mmol) and K_2CO_3 (11.00 g, 79.00 mmol) were added to a 2-necked round bottom flask. Acetone (100 ml) was added and the solution was refluxed for 72 hours. The orange mixture was filtered and the solvent removed on a rotary evaporator to give an orange oil. The oil was re-dissolved in a minimum of hexane/ CH_2Cl_2. The solution was transferred to a silica gel column. The column was eluted with hexane. The second colourless band was collected. The solvent was removed to give a colourless oil as pure product **(29)**, (2.51 g, 59 %).

δ_H($CDCl_3$, 200 MHz): 6.89 – 6.96 (m, 3H, Ar$\underline{H}$); 7.24 – 7.34 (m, 2H, Ar$\underline{H}$); 6.98 - 6.19 (m, 1H, C$\underline{H}$=); 5.24 –5.46 (m, 2H, C$\underline{H_2}$=); 4.53 – 4.56 (m, 2H, C$\underline{H_2}$O). $\delta_{C\{H\}}$($CDCl_3$ 50.3 MHz): 158.26, 133.38, 129.41, 129.39, 120.82 (Ar$\underline{C}$); 117.54, 114.75 ($\underline{C}$=$\underline{C}$); 68.73 ($\underline{C}H_2$-). *m/z* (GC/MS) 134 (M^+). (Found: C, 79.89; H, 7.12. $C_9H_{10}O$ (134.18) requires C, 80.56; H, 7.51)%.

Reaction of (24) with phenol to prepare (30)

To a 2-necked round bottom flask was added compound **(24)** (0.33 g, 1.16 mmol); phenol (0.11 g, 1.16 mmol); K_2CO_3 (0.40 g, 2.91 mmol) and 18-crown-6 (0.62 g, 0.23 mmol). Acetone (40ml) was added to form a yellow suspension and this was refluxed for 72 hours. The orange/brown mixture was filtered and the solvent was removed from the filtrate to give an orange oil. The oil was re-dissolved in a minimum of CH_2Cl_2 and transferred to a silica gel column. The column was washed with 20% CH_2Cl_2 in hexane. The first colourless band was collected as pure product **(30)**, (0.22 g, 65 %).

ν/cm^{-1} 3074 (ν(HC=CH_2)), 3042 (ν(HC=CH_2)), 2926 (m, ν_{as}(CH_2)) 2870 (m, ν_s(CH_2)), 1735 (m, ν(C=C), 1597 (s, (C=C), 1495, 1471 ((m, δ_{as}(CH_2)) 1382, 1294, 1032 (s, γ(CH_2)), 1238, 1167 (s, ν(C-O), 927 (m, γ(HC=CH_2)), 832, 754, 691 (neat);

δ_H($CDCl_3$, 200 MHz): 7.22 – 7.34 (m, 2H, Ar$\underline{H}$); 6.92 – 7.01 (m, 3H, Ar$\underline{H}$); 6.61 – 6.12 (m, 2H, Ar$\underline{H}$); 6.43 – 6.46 (m, 1H, Ar$\underline{H}$); 5.97 – 6.18 (m, 2H, C$\underline{H}$=); 5.24 – 5.46 (m, 4H, C$\underline{H_2}$=); 5.0 (s, 2H, ArC$\underline{H_2}$O); 4.51 – 4.53 (m, 4H, ArOC$\underline{H_2}$). $\delta_{C\{H\}}$($CDCl_3$ 50.3 MHz): 159.94, 158.69, 139.47, 133.13, 129.44, 120.96 (Ar$\underline{C}$); 117.72, 114.88 ($\underline{C}$=$\underline{C}$); 106.26 (Ar$\underline{C}H_2$); 69.83, 68.90 ($\underline{C}H_2$). *m/z* (GC/MS) 296 (M^+). (Found: C, 76.43; H, 6.23. $C_{12}H_{14}O_2$ (190) requires C, 77.00; H, 6.80)%.

Reaction of allylmagnesiumbromide with tetrakis-(bromomethyl)benzene to prepare (31)

To a 2-necked round bottom flask was added terakis-(bromomethyl)benzene (1.11 g, 2.46 mmol) and dry ether (20 ml). To the white suspension was added slowly over 5 minutes, allylmagnesiumbromide 1M in ether solution, (10 ml, 10.0 mmol). The solution went to a clear yellow colour upon addition of the Grignard reagent. The solution was refluxed for 4 hours and then stirred at room temperature for 20 hours. To the solution, now lime green in colour was added aq. NH_4Cl (1M, 20 ml) until bubbling ceased. The ether layer was separated from the aqueous layer using a separating funnel. The aqueous layer was washed with ether (2x10 ml). The ether extracts were combined and dried over $MgSO_4$ then filtered. The solvent was evaporated on a rotary evaporator to give a neon green oil as pure product **(31)**, (0.70 g, 96 %).

ν/cm^{-1} 3076 ($\nu(HC{=}CH_2)$), 3000 ($\nu(HC{=}CH_2)$), 2930 (m, $\nu_{as}(CH_2)$) 2865 (m, $\nu_s(CH_2)$), 1640 (s, (C=C), 1503, 1440 ((m, $\delta_{as}(CH_2)$) 995 (s, $\gamma(CH_2)$), 910 (m, $\gamma(HC{=}CH_2)$), 756 (neat); δ_H($CDCl_3$, 200 MHz): 6.99 (s, 2H, Ar$\underline{H}$); 5.82 – 5.99 (m, 4H, C$\underline{H}$=); 4.99 – 5.15 (m, 8H, C$\underline{H_2}$=); 2.66 – 2.78 (m, 8H, C$\underline{H_2}$$CH_2$Ar); 2.30 – 2.46 (m, 8H, C$\underline{H_2}$Ar). $\delta_{C\{H\}}$($CDCl_3$ 50.3 MHz): 138.39, 137.05, 129.94 (Ar$\underline{C}$); 116.78, 114.70 ($\underline{C}{=}\underline{C}$); 35.35, 31.75 ($\underline{C}H_2$). *m/z* (GC/MS) 294 ($M^+$). (Found: C, 89.62; H, 10.49. $C_{22}H_{30}$ (294.48) requires C, 89.73; H, 10.27)%.

Reaction of 4-phenyl-1-butene with $Cp_2Zr(H)Cl$

$Cp_2Zr(H)Cl$ (0.06 g, 0.25 mmol) was weighed into a small Schlenk tube. Dry solvent, C_6D_6 or $CDCl_3$ (0.5 ml) was added. To the resulting suspension 4-phenyl-1-butene (0.03 g, 0.25mmol) was added. The solution turned to an orange colour upon addition of the alkene. The solution was allowed to stir for 1 hour then transferred to an NMR tube for analysis of complex **(32)**. After 24 hours the ^1H NMR spectrum was consistent with the formation of complex **(32)**.

Reaction of (29) with $Cp_2Zr(H)Cl$

$Cp_2Zr(H)Cl$ (0.01 g, 0.04 mmol) was weighed into a small Schlenk tube. Dry C_6D_6 or $CDCl_3$ (0.5 ml) was added. To the suspension was added the model compound **(26)** (0.05 g, 0.04 mmol). The mixture was stirred for 5 minutes until all the solids dissolved. The yellow/orange solution was then transferred to an NMR tube. The reaction were monitored by ^1H NMR for the formation of complex **(33)**. After 24 hours the ^1H NMR spectrum was consistent with the formation of complex **(33)**.

Reaction of (30) with $Cp_2Zr(H)Cl$

$Cp_2Zr(H)Cl$ (013 g, 0.05 mmol) was added into a Schlenk tube. Dry $CDCl_3$ (0.5 ml) was added. To the suspension was added the model compound **(30)** (0.01 g, 0.02 mmol). The mixture was stirred for 2 minutes until all the solids dissolved. The yellow/orange solution was then transferred to an NMR tube. The reaction was monitored by ^1H NMR and after 24 hours the ^1H NMR spectrum was consistent with the formation of complex **(34)**.

Reaction of (31) with $Cp_2Zr(H)Cl$

$Cp_2Zr(H)Cl$ (0.25 g, 0.09 mmol) was weighed into a small Schlenk tube. $CDCl_3$ (0.5 ml) was added. To the suspension compound **(31)** (0.06 mg, 0.22 mmol) was added. The solution turned to an orange colour upon addition of the alkene. The solution was allowed to stir for 1 hour then transferred to a NMR tube. After 24 hours the ^1H NMR spectrum was consistent with the formation of complex **(35)**.

Reaction of (25) with $Cp_2Zr(H)Cl$

$Cp_2Zr(H)Cl$ (0.01 g, 0.038 mmol) was added weighed into a Schlenk tube. Dry C_6D_6 or $CDCl_3$ (0.5ml) was added. To the suspension was added the dendrimer **(25)** (0.06 g, 0.006 mmol). The mixture was stirred for 2 minutes until all the solids dissolved. The yellow/orange solution was then transferred to an NMR tube. The reaction was monitored by ^1H NMR for the formation of complex **(36)**. After 72 hours the ^1H NMR spectrum was consistent with the formation of complex **(36)**.

Reaction of (28) with $Cp_2Zr(H)Cl$

$Cp_2Zr(H)Cl$ (13 mg, 0.048 mmol) was transferred into a Schlenk tube. Dry $CDCl_3$ (0.5 ml) was added. To the suspension was added the model compound **(28)** (0.07 g, 0.004 mmol). The mixture was stirred for 2 minutes until all the solids dissolved. The yellow/orange solution was then transferred to an NMR tube. The reaction was monitored by ^1H NMR for 9 days for the formation of complex **(37)**.

3.6 REFERENCES

1 a) W. Kaminsky, M. Arndt, *Adv. Polym. Sci.*, **1997**, *127*, 143.

b) A. L. McKnight and R. M. Waymouth, *Chem. Rev.*, **1998**, *98*, 2587.

c) R. F. Jordan, *J. Mol. Catal.*, **1998**, *128*, 1.

d) W. Kaminsky, *Metalorganic Catalysts for Synthesis of Polymerisations Recent Results by Ziegler-Natta and Metallocene investigations, Springer-Verlag, Berlin*, **1999**, 1.

e) T. J. Marks and J. C. Stevens, *Topics in Catalysis*, **1999**, *7*, 1.

f) J. A. Gladys, *Chem. Rev.*, **2000**, *100*, 1391.

g) G. W. Coates, *J. Chem. Soc., Dalton Trans.*, **2002**, 467.

2 R. H. Grubbs, C. Gibbons, L. C. Kroll, W. D. Bonds, Jr and C. H. Brubaker, *J. Am Chem. Soc.*, **1973**, *95*, 2373.

3 L. Sun, C. C. Hsu, D. W. Bacon, *J. Polym. Sci. Part A*, **1994**, *32*, 2127.

4 S. B. Roscoe, J. M. Frechet, J. F. Walzer, A. J. Dias, *Science*, **1998**, *280*, 270.

5 R. Jackson, J. Ruddlesden, D. J. Thompson, R. Whelan, *J. Organomet. Chem.*, **1977**, *125*, 57.

6 W. Kaminsky, *Macromol. Chem. Phys.*, **1996**, *197*, 3907.

7 a) B. Peifer, W. Milius, H. G. Alt, *J. Organomet. Chem.*, **1998**, *553*, 205.

b) H. G. Alt, M. Jung, G. Kher, *J. Organomet. Chem.*, **1998**, *562*, 153.

c) H. G. Alt, and M. Jung, *J. Organomet. Chem.*, **1998**, *562*, 229.

d) H. G. Alt and M. Jung, *J. Organomet. Chem.*, **1998**, *568*, 87.

8 F. Kodor, S. G. A. Kolmschot, R. A. Sheldon, *Enantiomer*, **1999**, *4*, 497.

9 D. J. Graven and K. D. Janda, *Chem. Rev.*, **1997**, *97*, 489.

10 a) G. E. Oosterom, S. Steffens, N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Topics in Catalysis*, **2002**, *19*, 61.

b) J. N. H. Reek, D. de Groot, G. E. Oosterom, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Rev. Molec. Biotech.*, **2002**, *90*, 159.

11 J. W. J. Kaapen, A. W. van der Made, J. C. Wilde, P. W. N. M. van Leeuwen, P. Wijkens, D. M. Grove and G. Van Koten, *Nature*, **1994**, *372*, 659.

12 a) D. Astruc and F. Chardac, *Chem. Rev.*, **2001**, *101*, 2991.

b) B. Romagnoli and W. Hayes, *J. Mater. Chem.*, **2002**, *12*, 769.

13 M. Claeys, M. Hearshaw, J. R. Moss, E. van Steen, *Stud. Surf. Sci. Catal.*, **2000**, *130B*, 1157.

14 a) J.Schwartz and D. W. Hart, *J. Am. Chem. Soc.*, **1974**, *96*, 8115.

b) J. Schwartz and J. A. Labinger, *Angew. Chem. Int. Ed. Engl.*, **1976**, 15, 333.

c) D. W. Hart and T. F. Blackburn, J. Schwartz, *J. Am. Chem. Soc.*, **1975**, 97, 680.

d) C. A. Bertelo and J. Schwartz, *J. Am. Chem. Soc.*, **1976**, 98, 262.

15 a) H. Takahashi, *Synthesis,* **1988**, 1.

b) J. A. Labinger, *Comprehensive Organic Synthesis*, B. M. Trost, I Fleming, Eds., Pergomen Press: Oxford, **1991**, 451.

c) P. Wipf and W. Xu, *J. Org. Chem.*, **1993**, *58*, 825.

d) P. Wipf, H. Takahashi, H. Jahn, P. D. G. Coish, *Pure & Appl Chem*, **1997**, *69*, 639.

e) P. Wipf, H Takahashi, N. Zhuang, *N. Pure. Appl. Chem.*, **1998**, *70*, 1077.

f) P. J. Chirik, M. W. Day, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.*, **1999**, *121*, 10308.

16 a) P. C. Wailes and H. J. Weigold, *Organomet. Chem.*, **1970**, 24, 405.

b) P. C. Wailes and H. J. Weigold, *Inorg. Syn.*, **1979**, *xix*, 223.

17 D. B. Carr and J. Schwartz, *J. Am. Chem. Soc.*, **1979**, *101*, 3521.

18 S. L. Buchwald, S. J. LaMaire, R. B. Nielsen, B. T. Watson, S. M. King, *Tetr. Lett.*, **1987**, *28*, 3895.

CHAPTER 4

ATTEMPTED ACTIVATION OF METALLATED MODEL COMPLEXES USING SILVER SALTS (AgX, WHERE X = OSO_2CF_3, ClO_4 or BPh_4), METHYL ALUMINOXANE (MAO) OR $B(C_6F_5)_3$ AND SUBSEQUENT POLYMERIZATION OF ETHYLENE

4.1. INTRODUCTION

In recent years there has been an increase in exploration and commercialization of new alkene polymerisation catalysts based on single-site and metallocene coordination catalysts[1]. The vast number of specifically designed transition metal complexes (catalyst precursors) and main-group organometallic compounds (co-catalysts) allows unprecedented control over polymer stereochemistry, molecular weight and co-monomer- incorporation.

Co-catalysts, often in the form of main group organometallic compounds in traditional two-component Ziegler-Natta catalytic systems, have played an important role in the development of new polymerisation catalyst systems. The discovery of new and more effective co-catalysts has contributed significantly to the fundamental understanding, as well as to technology developments in this field. The importance of the co-catalyst in metal-catalysed polymerisation processes can be defined as follows:[2]

i) To form active catalysts, catalyst precursors must be transformed into active species by an effective and appropriate activating agent;

ii) A successful activation process requires many co-catalyst features for constant kinetic and thermodynamic considerations of the co-catalyst/ precursor reaction;

iii) The co-catalyst, which becomes an anion after the activation process, is the vital part of a catalytically active cation-anion ion pair.

The above features may significantly influence polymerisation characteristics and polymer properties. Some examples of co-catalysts for the activation of catalyst precursors for the polymerization of olefins are discussed below.

4.1.1 MAO AS ACTIVATING AGENT

Aluminium alkyls, including trialkylaluminiums and alkylaluminium chlorides, are important in classical heterogeneous Ziegler-Natta coordination polymerisation catalysis.[3] A wide variety of homogeneous Ziegler-Natta catalysts based on aluminium alkyls as co-catalysts for alkene polymerisation have also been reported.[4]

By addition of water to the halogen-free, polymerisation-inactive catalyst system, $Cp_2ZrMe_2/AlMe_3$, Sinn and Kaminsky observed a high activity for ethylene polymerisation.[5] This led to the discovery of the highly efficient activator, oligomeric methylaluminoxane (MAO).[6] This discovery which, was a result of research efforts seeking more effective co-catalysts, rejuvenated Ziegler-Natta catalysis. This led to major advances in controlling polymer stereochemistry and architecture and began the metallocene and single-site polymerisation catalysis era.[7] As outlined in chapter 1, the MAO co-catalyst is believed to alkylate the metallocene; scavenge for impurities; stabilise the cationic centre in an ion-pair interaction and possibly prevent bimetallic deactivation processes from occurring.

Despite its unique effectiveness as a co-catalyst the exact composition of MAO still remains unclear.[8] Depending on the nature of the hydrated salt (the H_2O source) used for the MAO synthesis and the exact MAO synthetic conditions, MAO-activated metallocenes may exhibit widely differing activities in alkene polymerisation.

4.1.2 SILVER SALTS

Another useful reagent for the activation of zirconocene species is AgX (where X= OSO_2CF_3, ClO_4 and BPh_4).[9] Jordan *et al* reported the synthesis and structure of $[Cp_2Zr(CH_3)(THF)][BPh_4]$ formed by reaction of $Ag[BPh_4]$ and $Cp_2Zr(CH_3)_2$. The activated complex polymerizes ethylene in CH_2Cl_2 solution and alkylates polar substrates, including ketones and nitriles.[10]

Activation with AgX can be used for selective activation of zirconocene alkylchlorides leading to the abstraction of chloride with Ag^+. The chloride is displaced with the weakly co-ordinating $[B(C_6F_5)_4]^-$. The reaction with $Ag[B(C_6H_5)_4]$ was reported to be successful only in strongly co-ordinating acetonitrile. This gives rise to problems because the $[Cp_2ZrR(CH_3CN)_n]^+$ complexes that are initially formed can undergo rapid CH_3CN insertion, or may be resistant to subsequent ligand exchange.[11]

4.1.3 PERFLUOROARYL BORANES

A cheaper and more selective alternative to MAO activation is the use of the so-called perfluoroaryl boranes. In the early 1990s Marks[12] and Ewen[2] independently discovered that, in combination with group 4 metallocene alkyls, strongly Lewis acidic tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, promotes highly efficient alkene polymerisation. Over the past few years the research groups of Marks and Piers have developed a number of new and effective perfluoroarylborane activators as well as bi-functional boranes.[13]

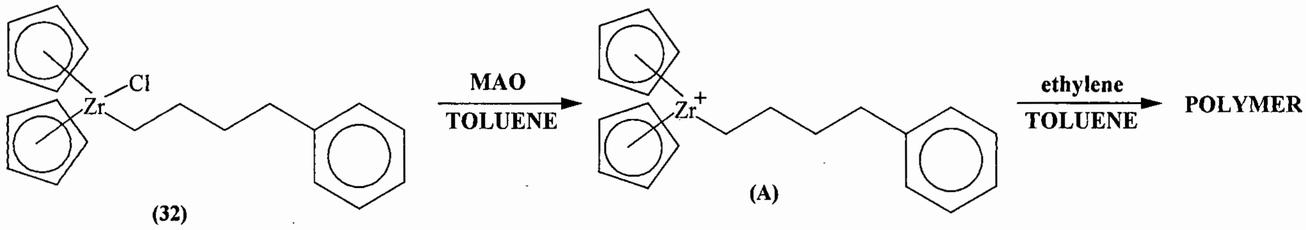
With specially designed boron compounds it is possible to stabilise the activated metallocenium cation, after it has been generated by methyl abstraction. One equivalent of activator is needed thus the amounts of perflouroaryl borane required are far less than the amounts of MAO employed for activation. The boron compounds are not pyrophoric and are easy to deal with on a large scale.

4.2 RESULTS AND DISCUSSION

The new multinuclear species together with analogous mononuclear model complexes were activated using a number of different activating agents including, methylaluminoxane (MAO), AgX (where X= OSO_2CF_3, ClO_4 and BPh_4) and $B(C_6F_5)_3$. The activated complexes were assessed for their polymerisation ability using ethylene as feedstock.

4.2.1 ACTIVATION OF CATALYST PRECURSORS WITH MAO AND POLYMERISATION OF ETHYLENE.

Complexes **(32)** – **(37)** were investigated for their polymerisation ability towards ethylene using methylaluminoxane (MAO) as co-catalyst. The proposed mechanism of activation is described in Scheme 4.1. It is believed that MAO alkylates the metallocene and then abstracts the methyl group to generate the catalytically active species **(A)**. The activity of the new catalysts derived from **(32)** – **(36)** is compared with conventional systems such as Cp_2ZrCl_2 and $Cp_2Zr(H)Cl$.



Scheme 4.1 Proposed activation of catalyst precursor with MAO.

To determine a standard polymerisation protocol, several polymerisation reactions were investigated using the model complex **(32)** as catalyst precursor. In this way the best conditions to be used for polymerisation experiments were found. The reproducibility of the polymerisation experiments was also checked. Certain parameters were kept constant i.e. pressure, temperature, nature and volume of the solvent and reaction time, however the [Zr]:[Al] ratio was changed. Table 4.1 gives details of the polymerisation experiments performed.

Table 4.1. Polymerisation results for standard catalysts and for the model complex (32) at varying [Zr]:[Al] ratios.

PRECURSOR	[Zr]:[Al]	POLYMER YIELD (g)	TON*
Cp_2ZrCl_2	1:1300	2.6	$4.56x10^4$
$Cp_2Zr(H)Cl$	1:1300	3.0	$5.26x10^4$
32	1:1300	1.5	$2.63x10^4$
32	1:656	5.5	$9.45x10^4$
32	1:500	5.0	$8.77x10^4$
32	1:400	0.8	$1.40x10^4$
32	1: 350	0.0	0.0

T = 23 – 25 °C; Zr = 40μmol; toluene = 30 ml; time = 1.5 hours

**TON (turn over number) defined as (g of polymer) (mol of Zr)$^{-1}$ (hour)$^{-1}$*

The conditions used were according to literature[14] with some modifications. The conditions were kept constant for each polymerisation experiment for comparative studies. The temperature was kept constant by immersing the reaction vessel in an ice/ water bath. Rigorous removal of oxygen, water and other contaminants from the reactor, solvent and monomer is essential for activation and polymerisation experiments.

A solution of catalyst precursor, **(32)** (40μmol), in toluene (30ml) was activated with 10% MAO in toluene. Upon addition of the MAO, a white cloud formed above the solution and the solution went from a very pale yellow colour to dark yellow. This indicated that a cationic zirconocene had formed. Ethylene was bubbled through the solution whilst stirring vigorously. After approximately 20 seconds, large amounts of white polymer started to precipitate from the solution. Ethylene was continued to bubble through the solution for 15 minutes, and the solution was stirred for 30 minutes. This cycle of bubbling of ethylene for 15 minutes and stirring for 30 minutes was continued for a total reaction time of 1.5 hours. The reaction was quenched by addition of ethanol. The polymer was collected on a Buchner funnel and washed with ethanol and distilled water. The polymers were further purified by washing with 1M HCl followed by distilled water then ethanol and finally dried in the oven at 60-70 °C for 3 days. The final polymer product was isolated as insoluble white granules.

The [Zr]:[Al] ratio significantly influences the activity of the catalyst system. The results show that a high MAO concentration, relative to the catalyst concentration is required for the catalyst to be activated for ethylene polymerisation. Initially a [Zr]:[Al] ratio of 1:1300 was used for polymerisation experiments. For complex **(32)**, reducing the amount of MAO was found to increase the activity. However a [Zr]:[Al] ratio lower than 1:500 show loss in activity. This could be due to impurities that remain in the system after activation with MAO. At a [Zr]:[Al] ratio of 350:1, complex **(32)** remained inactive, (see Table 4.1).

From the polymerisation experiments with the model complex **(32)**, a ratio of [Zr]:[Al] of 1:656 was found to give the highest turnover number, (TON). The polymerisation ability of complexes **(33)** – **(36)** was investigated using the same conditions as for the model system. The results obtained are compared against that for the standard precursor, Cp_2ZrCl_2, (see Table 4.2). The precursor used has a strong impact on the polymerisation behavior as determined from the activity, (TON). The tetranuclear complex **(35)** has a higher polymerisation activity than the model mononuclear complex **(32)**. The reason for this behavior may be due to the increased number of zirconium centres on complex **(35)** as potential polymerisation sites. A similar result is also observed for complex **(36)**, which has a high activity compared to complexes **(33)** and **(34)**. The order of activity is **(35)** > **(32)** > **(36)** > **(34)** > **(33)**. Complexes **(36)**, **(34)** and **(33)** show lower activity compared to **(35)** and **(32)**, this could be due to the oxygen atoms contained within the structure of the former complexes. Oxygen can have a destabilising effect on the zirconium complexes due the complexes' high oxophilicity resulting in the formation of $[(C_5H_5)_2ZrCl]_2O$.[15]

Table 4.2. Polymerisation results for complexes (32) – (36) using MAO as activator.

CATALYST PRECURSOR	**POLYMER YIELD (g)**	**POLYMER M.P. ^0C**	**TON***
Cp_2ZrCl_2 (standard)	3.9	120.50	$7.01x10^4$
(32)	5.5	131.50	$9.45x10^4$
(33)	3	120.38	$5.26\ x10^4$
(34)	4	121.94	$7.01x10^4$
(35)	7.3	132.10	$12.28x10^4$
(36)	4.5	124.42	$7.89x10^4$

T = 23 – 25 °C; Zr = 40μmol; [Zr]:[Al] = 1:656; toluene = 30 ml; time = 1.5 hours

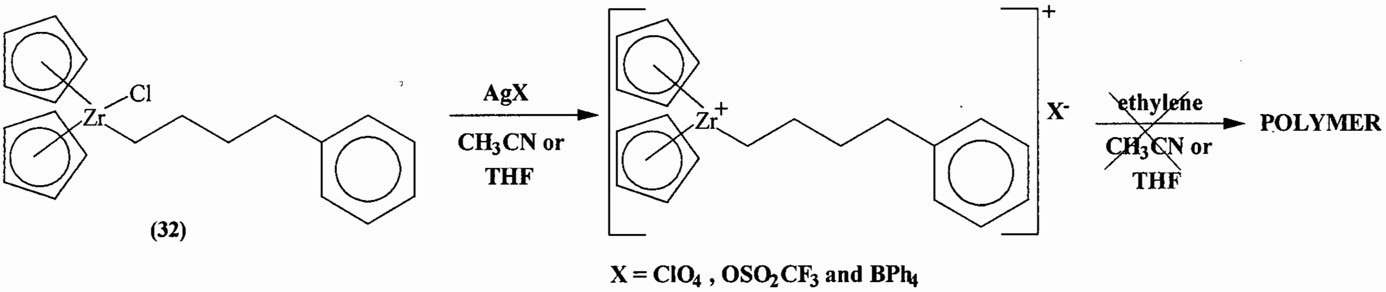
**TON (turn over number) defined as (g of polymer) (mol of Zr)$^{-1}$ (hour)$^{-1}$*

Table 4.2 gives the melting points of polymers synthesised with complexes **(32)** to **(36)** as well as with the model system Cp_2ZrCl_2. The melting points of the polyethylenes were in the range 120.38 ^0C - 132.10 ^0C. The melting point of the polymers differs for all catalysts, which indicates that each catalyst yields a polymer with slightly different properties. The texture of the polymers as determined by electron microscopy, differs for all of the catalysts. (see Appendix A) The catalyst prepared from the model complex **(32)** for example yields a powdery polymer with a melting point of 131.50 ^{0}C, while the tetra-zirconium precursor **(35)** yields a more granular polymer with a melting point of 132.10 ^{0}C. The texture of the polymer is also determined by the reaction conditions. Continuous bubbling leads to a hard, granular polymer, whereas bubbling with intervals of stirring leads to a softer, more powdery polymer.

4.2.2 ACTIVATION OF CATALYST PRECURSORS WITH SILVER SALTS AgX, WHERE X = OSO_2CF_3, ClO_4 and BPh_4 AND ATTEMPTED POLYMERISATION OF ETHYLENE.

Jordan and co-workers reported that cationic $Cp_2Zr(IV)$ alkyl complexes are highly reactive as a result of the high electrophilicity at the metal center. They reported the preparation of the cationic complexes $Cp_2Zr(R)(L)_n^+$ (L = THF, CH_3CN; R = CH_3) via X^- or R^- abstraction from Zr(IV) by Ag^+.

omplexes **(32)** and **(35)** were reacted with the silver salts AgX, (X = OSO_2CF_3, ClO_4 and BPh_4) to induce chloride abstraction from the zirconium center. (Scheme 4.2.) The unstable products were immediately tested for their polymerisation activity towards ethylene. The results for **(32)** are presented in Table 4.3.



Scheme 4.2. Proposed activation of catalyst precursor with silver salts.

THF and CH_3CN were used as solvents for the attempted preparation of the active cationic complexes and *in situ* polymerisation of ethylene. The results showed however that polymerisation did not occur. In the case of CH_3CN, a solvent adduct, $[Cp_2Zr(CH_3CN)_2]^{2+}$ was formed, as suggested by the ^1H NMR spectrum. (Table 4.3) This indicated that abstraction of both the Cl^- and R^- groups were taking place. Only the complex formed using $AgOSO_2CF_3$

showed some activity. Here, an oligomeric product was formed. Changing the solvent for the activation step to THF does not seem to have any effect on this particular step. After the attempted polymerisation of ethylene in THF, $[Cp_2Zr(THF)_2]^{2+}$ was formed, as was observed by the ^1H NMR spectrum . Similar to the reactions in CH_3CN, using THF as solvent, only the complex formed from $AgOSO_2CF_3$ gives an oligomeric product. Washing the activated complex $[Cp_2Zr(CH_3CN)_2]^{2+}$ with THF, leads to displacement of CH_3CN from $[Cp_2Zr(CH_3CN)_2]^{2+}$ to form $[Cp_2Zr(THF)_2]^{2+}$.

Table 4.3. Attempted polymerisation results for mononuclear complex (32) using silver salts as activator.

ACTIVATING SALT	**SOLVENT**	**RESULTS**	**CHARACTERISATION ^1H NMR δ($CDCl_3$)**
$AgClO_4$	THF	white solid, $[(C_5H_5)_2ZrCl]_2O$	6.30 ZrCp
$AgClO_4$	CH_3CN	white solid, $[(C_5H_5)_2ZrCl]_2O$	6.30 ZrCp
$Ag(OSO_4CF_3)$	THF	brown tar, oligomeric product $(CH_2)_nCH_3$ and uncharacterised ZrCp by-products.	0.94 (t, CH_3); 1.58 (s, CH_2); 6.30 – 6.50 ZrCp
$Ag(OSO_4CF_3)$	CH_3CN	Brown sticky solid, oligomeric product $(CH_2)_nCH_3$ and uncharacterised ZrCp by-product.	0.93 (t, CH_3); 1.59 (s, CH_2); 6.5 ZrCp
$AgBPh_4$	THF	Yellow solid, $[Cp_2Zr(THF)_2]^{2+}$	7.23-6.7 (m, 20H, $[C_6H_5]_4$); 6.49 (s, 10H, Cp); 3.74 (m, 4H, $O(CH_2CH_2)_2$); 1.85 (m, 4H, $O(CH_2CH_2)_2$)
$AgBPh_4$	CH_3CN	Yellow solid, $[Cp_2Zr(CH_3CN)_2]^{2+}$	7.50-6.7 (m, 20H, $[C_6H_5]_4$); 6.49 (s, 10H, Cp); 1.94 (m, 6H, $(CH_3CN)_2$)

4.2.3 ATTEMPTED ACTIVATION OF CATALYST PRECURSOR WITH $B(C_6F_5)_3$.

Earlier the attempted activation of the model mononuclear complex **(32)** by abstraction of the chloride ion with a number of different silver salts viz.($AgOSO_4CF_3$, $AgClO_4$ and $AgBPh_4$) was described. The activated complexes were immediately reacted with ethylene to see if any oligomerisation or polymerisation would occur. However analysis of the products after reaction with ethylene indicated that amongst other products, $[Cp_2Zr(THF)_2]^{2+}$ or $[Cp_2Zr(CH_3CN)_2]^{2+}$ were formed. It would therefore appear that both the chloride ion and the alkyl groups are abstracted. One other possible route to activate the mononuclear complex is the methylation of the complex with MeLi or MeMgI, followed by methyl abstraction with $B(C_6F_5)_3$.[2, 12]

Marks and co-workers have shown that zirconium dialkyls are activated by these perflouroarylboranes to form highly active “cationic-like” metallocene polymerisation catalysts.[2, 12] The cationic species $[Cp_2ZrR]^+$ can be isolated as the salt $[Cp_2ZrR]^+[B(C_6F_5)_3]^-$.

The reaction of the model complex **(32)** with MeMgI in C_6D_6 gave the desired product after 7 minutes of reaction time, as suggested by ^1H NMR. It appeared that the desired zirconocene dialkyl complex was very unstable. After 10 minutes, the ^1H NMR spectrum of the reaction mixture of MeMgI and complex **(32)** showed decomposition products. This observation is consistent with the reported instability of the alkene insertion product of zirconocene dihydride[16] and with the decomposition of the Cp_2ZrCl_2/BuLi system (Negishi system)[17] to give ‘zirconocene’ (Cp_2Zr).

After reacting the mononuclear complex **(32)** with an equimolar amount of MeMgI in C_6D_6 for 7 minutes, the product was immediately reacted with $B(C_6F_5)_3$. This reaction yielded a mixture of products. Several Cp peaks were observed in the ^1H NMR spectrum as well as multiple alkyl resonances. The desired cationic product could not be identified. Polymerisation of ethylene with the products from the reaction of $Cp_2Zr(Me)[(CH_2)_4Ph]$ with $B(C_6F_5)_3$ was not pursued.

4.3 CHARACTERISATION OF POLYETHYLENE SAMPLES

The polymers prepared from the catalyst precursors, **(32)** – **(36)**, and MAO were isolated as insoluble white granules. All polymers prepared were purified by washing with 1M HCl (40ml) followed by distilled water (20ml) then ethanol (40ml) and finally dried in the oven at 60-70 ^{0}C for 3days.

Due to their insolubility in most common solvents, characterisation was difficult. The techniques used to characterise the solid samples include FTIR, DSC, GPC, SEM and EDS.

4.3.1 GEL PERMEATION CHROMATOGRAPHY OF POLYETHYLENE SAMPLES

GPC results show that the polyethylene samples have comparable molecular weights. The GPC curves for both polyethylene samples are very similar. (see Appendix B) The polydispersity of the polymer prepared from the tetranuclear complex **(35)** is lower than that for the mononuclear model complex **(32)**.

Table 4.4. Analytical data of polyethylene samples.

CATALYST PRECURSOR	**M. P. (^{0}C)**	**Mn** $(x10^3)$	**Mw** $(x10^3)$	**POLYDISPERSITY INDEX$^\#$**
(32)	131.50	4.36	11.1	2.54
(35)	132.10	5.56	11.8	2.13

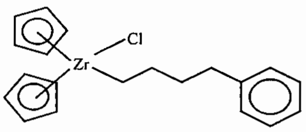
$^\#$ Mw/Mn

4.3.2 INFRARED SPECTRA OF POLYETHYLENE SAMPLES

IR spectra of the polyethylene samples suggested that linear polyethylenes were formed. The IR spectra of the acid washed polymers were compared with the IR spectra of the polymers before washing with acid. The IR spectra of the unwashed polymers give peaks corresponding to aluminium oxide residues, whereas these peaks are minor in the acid washed polymers.

EDS of the unwashed polymers gives high percentages of aluminium in the sample. (see Appendix C) After washing with dilute HCl however these aluminium percentages dropped significantly but are not totally diminished. In addition, trace amounts of chloride is detected, after HCl washing.

Table 4.5. IR Spectra of polymers prepared from different catalyst precursors.

CATALYST PRECURSOR	**FREQUENCY* (DRIFTS in KBr matrix) (cm^{-1})**	**ASSIGNMENT**
Cp_2ZrCl_2	2954, 2916, 2849 (s) 1472 (s) 729 (m)	C-H stretch C-C stretch C-H bend
(32) 	2917 - 2848 (s) 1654 - 1522 (w) 1473 (s) 730 (m)	C-H stretch C=C stretch C-C stretch C-H bend

(35)	2917, 2850 (s) 1664 - 1555 (w) 1473 (s) 730 (m)	C-H stretch C=C stretch C-C stretch C-H bend

*s = strong, m = medium, w = weak

4.3.3 ^{1}H NMR AND ^{13}C NMR SPECTRA OF POLYETHYLENE SAMPLES

^{1}H NMR and ^{13}C NMR spectra of the polyethylene samples is consistent with NMR data reported in literature for polyethylene.[18] Chain branching was not detected in the NMR spectra and the polymer appeared to be high-density polyethylene.

Table 4.7. **^{1}H NMR and ^{13}C NMR data for polymers prepared from complexes (32) and (35).**

CATALYST PRECURSOR	^{1}H NMR AT 90 ^{0}C (ppm)	^{13}C NMR AT 90 ^{0}C (ppm)
(32)	**a = 1.36, b = 1.34 c = 0.94**	**d = 28.38**
(35)	**a = 1.34, b=1.32 c = 0.92**	**d = 28.36**

NMR spectra were run in mixtures of 1,2-dichlorobenzene and DMSO-d_6.

a, b, c – chemical shifts (ppm) of the CH_2 groups (a and b) and CH_3 terminal groups (c) in ^{1}H NMR.
d – chemical shift of CH_2 groups in ^{13}C NMR.

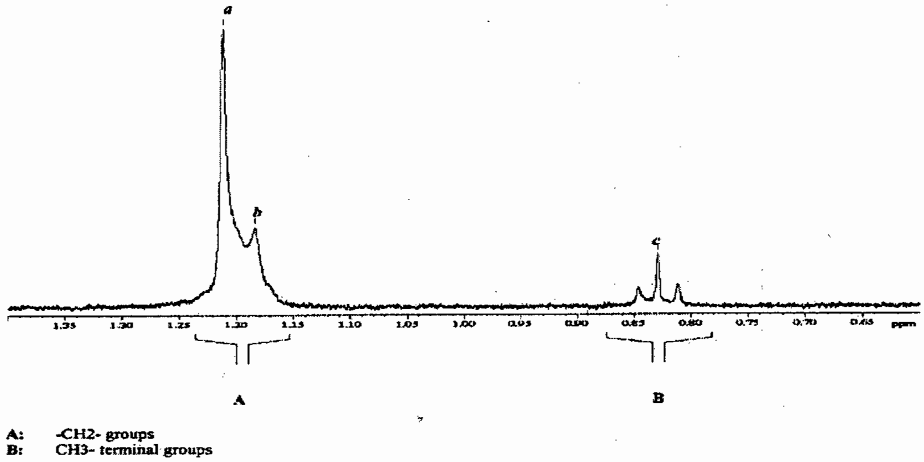


Figure 4.1. **^{1}H NMR spectrum of a polyethylene sample prepared from complex (32).**

4.4 CONCLUSION

Polymerisation of ethylene using complexes **(32)** – **(36)**, as well as Cp_2ZrCl_2, together with MAO as activating agent was performed. High concentrations of MAO are needed to activate the catalyst precursors. The polyethylene formed from the various catalyst precursors appeared to be slightly different. The melting points of the polyethylene samples are similar. The textures as determined from scanning electron microscopy as well as the polydispersity of the polyethylene samples are slightly different.

Attempted activation of the model mononuclear complex **(32)**, with the activating agents $AgOSO_2CF_3$, $AgClO_4$, $AgBPh_4$ and $B(C_6F_5)_3$, and subsequent polymerisation of ethylene with the products were unsuccessful.

4.5 EXPERIMENTAL

General experimental procedures

All operations involving handling of solids were carried out in a Unilab glovebox from M. Braun. All reactions were carried out using standard Schlenk techniques under an atmosphere of nitrogen. Infrared spectra were recorded on a Paragon 1000 Fourier Transform Infrared Spectrophotometer as Drifts in KBr matrix. ^1H NMR and ^{13}C NMR spectra were recorded at the National NMR Laboratory, Institute of Organic Chemistry, Romania Academy, Romania. The NMR spectra were obtained as solutions in 1,2-dichlorobenzene and DMSO-d_6 on a Bruker Advance DRX40 400 spectrometer with DMSO-d_6 as reference standard. Scanning electron micrographs were performed at the SEM Laboratory, University of Western Cape. SEM analysis was done at magnification of 200 and 1000. EDS was done at 25kV. DSC data were performed on a Perkin Elmer PC 7 system at the University of Cape Town, Crystallography Department. Approximately 4 mg samples were heated at a scanning rate of 10 °C/min from 40 – 250 °C. Mn and Mw distributions of polymers were measured at Optokem, using a Waters-Millipore 150C High Temperature GPC instrument with a light scattering/ RI data collector. The samples were made up as approximately 3 mg/ml solutions in 1,2,4-trichlorobenzene. The sample mixture was measured at 145 °C with a flow rate of 1 ml/min. The GPC was equipped with 2 linear Water Styragel HT columns. 10% MAO in toluene solution, $AgOSO_2CF_3$, $AgClO_4$ and $B(C_6F_5)_3$ were purchased from Aldrich. THF, CH_3CN and toluene were purchased from Merck. THF and toluene were rigorously dried by refluxing over sodium wire and distilled from Na-benzophenone under nitrogen. CH_3CN was dried over P_2O_5 and distilled prior to use. $CDCl_3$ and C_6D_6 were extensively dried prior to use. $CDCl_3$ was dried over $CaCl_2$ and distilled prior to use. C_6D_6 was dried over sodium wire and distilled prior to use.

General method for polymerisation experiments with MAO as activator

(40 μmol) of complex **(32)** – **(36)** in dry toluene (1ml) was prepared in a Schlenk tube kept in a glovebox. Toluene (15ml) followed by MAO (10% in toluene) (656 equivalent) was added and the yellow solution was stirred for 10 minutes. A white cloud formed above the solution. The Schlenk tube containing the activated catalyst was removed from the glovebox and attached to a nitogen line. The reaction vessel was immersed in an ice/ water bath. Polymerisation reactions were highly exothermic. Ice was added to maintain the temperature at 23 – 25°C. Ethylene was bubbled trough the solution whilst stirring vigorously. After approximately 20 seconds, large amounts of polymer started to precipitate from the solution. Ethylene was bubbled through the solution for 15min then stirred for 30min under an atmosphere of ethylene. This cycle of bubbling ethylene for 15 minutes and stirring for 30 minutes was repeated. After a total reaction time of 1.5 hours, ethanol (15ml) was added and more white polymer formed. The polymer was collected on a Buchner funnel and washed with 1M HCl (40ml) followed by distilled water (20ml) then ethanol (40ml). The resulting white granules were finally dried in the oven at 60-70 ^{0}C for 3days.

Preparation of $Ag[B(C_6H_5)_4]$[19]

$Ag[B(C_6H_5)_4]$ was prepared by mixing aqueous solutions of equimolar amounts of $AgNO_3$ and $Na[B(C_6H_5)_4]$. The desired product immediately precipitated as a white solid and was isolated through filtration through a D-frit. The solid was washed with distilled water (3x10ml) followed by a minimum amount of ethanol. Drying under vacuum for several hours gave the desired product $Ag[B(C_6H_5)_4]$. This reagent is light sensitive and slowly decomposes even when kept in the dark.

Reaction of (32) with $Ag[B(C_6H_5)_4]$ followed by ethylene

$Ag[B(C_6H_5)_4]$ (0.20g, 1.5mmol) was added to a solution of complex **(32)** (0.58 g, 1.5 mmol) in THF or CH_3CN (10 ml) kept at 0 °C. The reaction mixture was stirred for 1 hour at 0 °C. A grey precipitate formed. The mixture was then allowed to warm to room temperature and stirred for a further 2 hours. The mixture was filtered through a D-frit and the solvent was removed. The resulting white solid was re-dissolved in toluene (15 ml) and ethylene was bubbled through the solution for 30 minutes. The mixture was filtered and the filtrate was concentrated to a yellow solid. The product was analysed by ^{1}H NMR.

Reaction of (32) with AgX (where X = OSO_2CF_3*,* ClO_4*) followed by ethylene*

AgX (1.5 mmol) was added to a solution of **(32)** (1.5 mmol) in THF or CH_3CN (10 ml) kept at 0 °C. A darkening of the solution was observed and a brown precipitate formed. The mixture was stirred at room temperature for 1 hour. The resulting mixture was filtered through a pad of celite. The filtrate was collected into a Schlenk tube, kept under an atmosphere of nitrogen. Ethylene was bubbled through the yellow solution for 30 minutes. The solution turned a dark green colour but no precipitate formed. The solution was stirred under an atmosphere of ethylene for 1 hour. The solvent was removed to give a white solid for the $AgClO_4$ activated complex and a brown sticky solid for the $AgOSO_2CF_3$ activated complex. The products from the $AgOSO_2CF_3$ activated catalyst were shown to be oligomers by ^{1}H NMR.

Preparation of $[ZrCp(Me\{(CH_2)_4Ph\}]$

To a suspension of $[Cp_2Zr(H)Cl]_n$ (0.03g, 0.12mmol) in dry C_6D_6 (0.5 ml) was added 4-phenyl-1-butene (0.02g, 0.12mmol) and the solution was stirred for 24 hours. The ^{1}H NMR spectrum was recorded of the yellow solution at this time which confirmed the formation of the desired monoalkyl complex, $[Cp_2Zr(Cl)][(CH_2)_4Ph]$. Solid MeMgI (0.02g, 0.12mmol) was added and the yellow solution went immediately to a red colour. The reaction was monitored by ^{1}H NMR spectroscopy. After 7 minutes the ^{1}H NMR spectrum showed that the desired methylated complex, $[Cp_2Zr(Me)\{(CH_2)_4Ph\}]$ had formed.

δ_H($CDCl_3$, 200 MHz): 5.67 (s, 10H, Cp); 7.12 – 7.16 (m, 5H, Ar$\underline{H}$); 2.85 – 2.92 (m, 2H, $C\underline{H_2}Ph$); 2.52 –2.61 (m, 2H, $C\underline{H_2}$); 2.15 – 2.19 (m, 2H, $C\underline{H_2}$); 0.09 (s, 2H, $ZrC\underline{H_2}$); -0.17 (s, 3H, $C\underline{H_3}$). $\delta_{C\{H\}}$($CDCl_3$ 50.3 MHz): 136.42, 121.82, 121.75 (Ar$\underline{C}$); 105.47 (Cp); 26.78, 28.81, 30.99 ($\underline{C}H_2$); 47.60 ($Zr\underline{C}H_2$); 28.30 (CH_3).

Reaction of [ZrCp(Me){$(CH_2)_4$Ph}] with $B(C_6F_5)_3$

$B(C_6F_5)_3$ (0.06g, 0.12mmol) was added to a solution of $Cp_2Zr(Me)[(CH_2)_4Ph]$ in C_6D_6 (0.5ml). The reaction was monitored by ^1H NMR spectroscopy and showed several Cp peaks as well as multiple alkyl resonances. The desired cationic product could not be identified.

4.6 REFERENCES

1 a) G. W. Coates, *J. Chem. Soc., Dalton Trans.*, **2002**, 467 and references therein.

b) G. W. Coates, *Chem. Rev.*, **2000**, *100*, 1223.

c) G. G. Hlatky, *Chem. Rev.*, **2000**, *100*, 1347.

d) T. J. Marks and J. C. E.. Stevens, *Topic. In Catalysis.*, Baltzer: Amsterdam, **1999**, *7*, 1.

e) W. Kaminsky, *Ed. Metalorg. Catal. For Synth. And Polym.: Recent results in Ziegler-Natta and Metallocene Investigations*; Springer-Verlang Berlin, **1999**.

f) G. J. P. Britovsek, V. C. Gibson, D. . Wass, *Angew. Chem., Int. Ed. Engl.*, **1999**, *38*, 428.

g) P. C. Mohring and N. J. Coville, *J. Organomet. Chem.*, **1994**, *479*, 1.

2 E. Y.-X. Chen and T. J. Marks, *Chem. Rev.*, **2000**, *100*, 1391.

3 a) J. Boor, *Jr. Ziegler-Natta Catalysis and Polymerizations*, Academic Press: New York, **1979**.

b) J. C. W. Chien, *Ed. Coordination Polymeriszation*, Academic Press: New York, **1975**.

4 a) See reference 1a) and cited references therein.

b) H. Licht, H. G. Alt and M. M. Karim, *J. Organomet. Chem.*, **2000**, *599*, 261.

5 A. A. Cordes. G. Herwig, W. M. A. Kaminsky, R. Mottweiler, J. Pein, H. Sinn, H. J. Vollmer, *Angew, Chem., Int. Ed. Engl.*, **1976**, *15*, 630.

6 a) H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, **1980**, *18*, 99.

b) H. Sinn, W. Kaminsky, H.-J. Vollmer, R. Woldt, *Angew. Chem., Int. Ed. Engl.*, **1980**, *19*, 390.

7 a) U. Stehling, J. Diebold, R. Kirsten, W. Roll, H.-H. Britzinger, *Organometallics*, **1994**, *13*, 964.

b) J. A. Ewan, R. L. Jones, A. Razavi, J. D. J. Ferrare, *J. Am. Chem. Soc.*, **1988**, *110*, 6255.

c) G. W. Coates and R. M. Waymouth, *Science*, **1995**, *267*, 217.

8 H. Sinn, W. Kaminsky, H. Hoker, *Eds. Aluminoxanes*, Macromoleclar Symposia 97, Huthig & Wepf: Helderberg, Gemany, **1995**.

9 a) U. Thewalt and H. P. Klein, *J. Organomet. Chem.*, **1980**, *194*, 297.

b) U. Thewalt and W. Lasser, *J. Organomet. Chem.*, **1984**, *276*, 341.

10 a) R. F. Jordan, W. E. Dasher, S. F. Echols, *J. Am. Chem. Soc.*, **1986**, *108*, 1718.

b) R. F. Jordan, C. S. Bajgur, R. Willett, B. J. Scott, *J. Am. Chem. Soc.*, **1986**, *108*, 7410.

11 a) R. F. Jordan, *Adv. Organomet. Chem.*, **1985**, *294*, 321.

b) D. M. Roddick, R. H. Heyn, T. D. Tilley, *Organometallics*, **1989**, *8*, 324.

c) B. D. Martin, S. A. Matchett, J. R. Norton, O. P. Anderson, *J. Am. Chem. Soc.*, **1985**, *107*, 7952.

d) A. R. Siedle, R. A. Newmark, W. B. Gleason, W. M. Lamanna, *Organometallics*, **1990**, *9*, 1290.

12 a) X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.*, **1994**, *116*, 10015.

b) X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.*, **1991**, *113*, 3623.

13 a) W. E. Piers and T. Chivers, *Chem. Soc. Rev.*, **1997**, *26*, 345.

b) L. Li and T. Marks, *J. Organometallics.*, **1998**, *17*, 3996.

14 H. Hagihara, T. Shiono, T. Ikeda, *Macromolecules*, **1997**, *30*, 4783.

15 A. F. Reid, J. S. Shannon, J. M. Swan, P. C. Wailes, *Aust. J. Chem*, **1965**, *18*, 173.

16 P. C. Wayles, H. Weigold, A. P Bell, *J. Organomet. Chem.*, **1972**, *43*, C32.

17 E. –I. Negishi and T. Takahashi, *Acc. Chem. Res.*, **1994**, *27*, 124 and references therein.

18 a) J. H. Z. dos Santos, T. Uozumi, T. Teranishi, T. Sano, K. Soga, *Polymer*, **2001**, *42*, 4517 and references therein.

b) E. Kolodka, W.-J. Wang, P. A. Charpentier, S. Zhu, A. E. Hamielec, *Polymer*, **2000**, *41*, 3985.

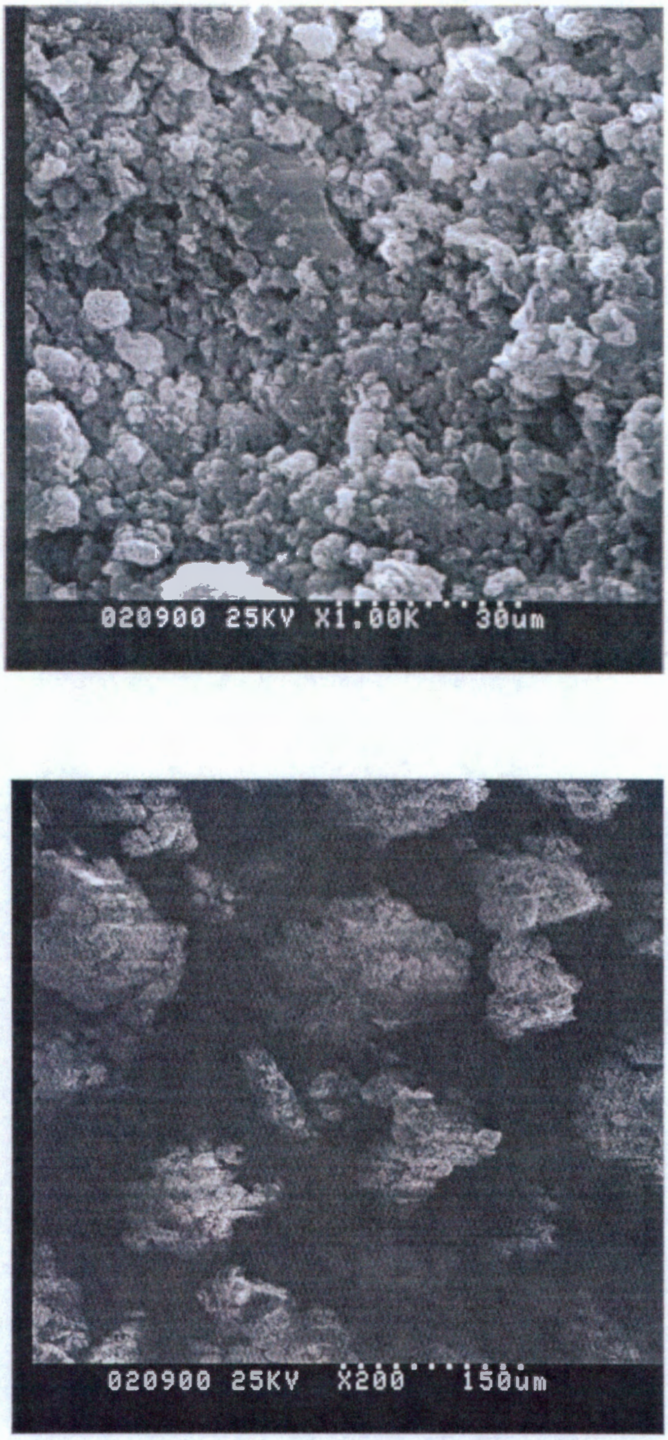
c) J. A. Smith, K. R. Brzezinska, D. J. Valenti, K. B. Wagener, *Macromolecules*, **2000**, *33*, 3781.

d) E. H. Licht, H. G. Alt, M. M. Karim, *J. Organomet. Chem*, **2000**, *599*, 275.

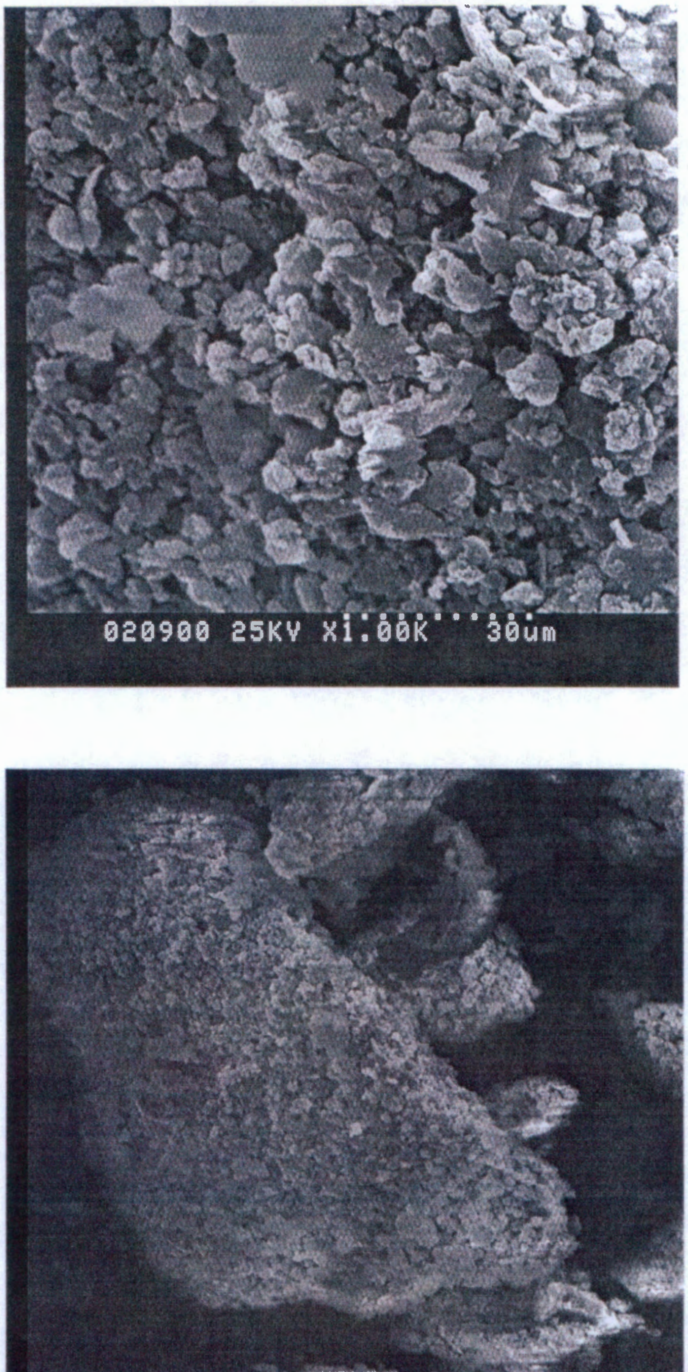
e) H. G. Alt and M. Jung, *J. Organomet. Chem.*, **1998**, *568*, 87.

19 R. F. Jordan and S. F. Echols, *Inorg. Chem.*, **1987**, *26*, 385.

APPENDIX A SCANNING ELECTRON MICROGRAPHS

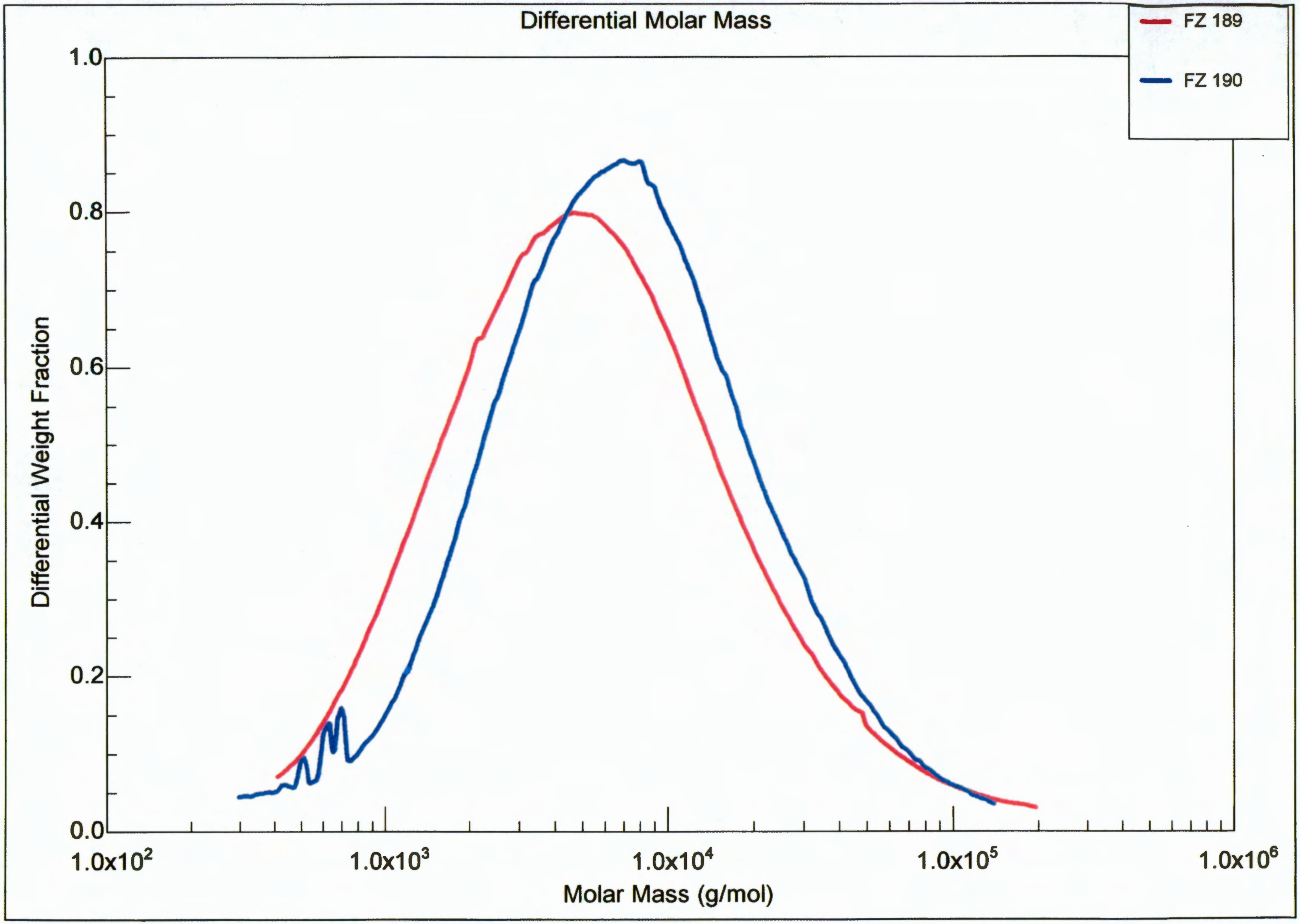


APPENDIX A: **SEM of polyethylene samples prepared from (32).**



APPENDIX A: SEM of polyethylene samples prepared from (35).

APPENDIX B GEL PERMEATION CHROMATOGRAPHY CURVES



APPENDIX B GPC curves of polyethylene samples prepared from (32) — and (35) —

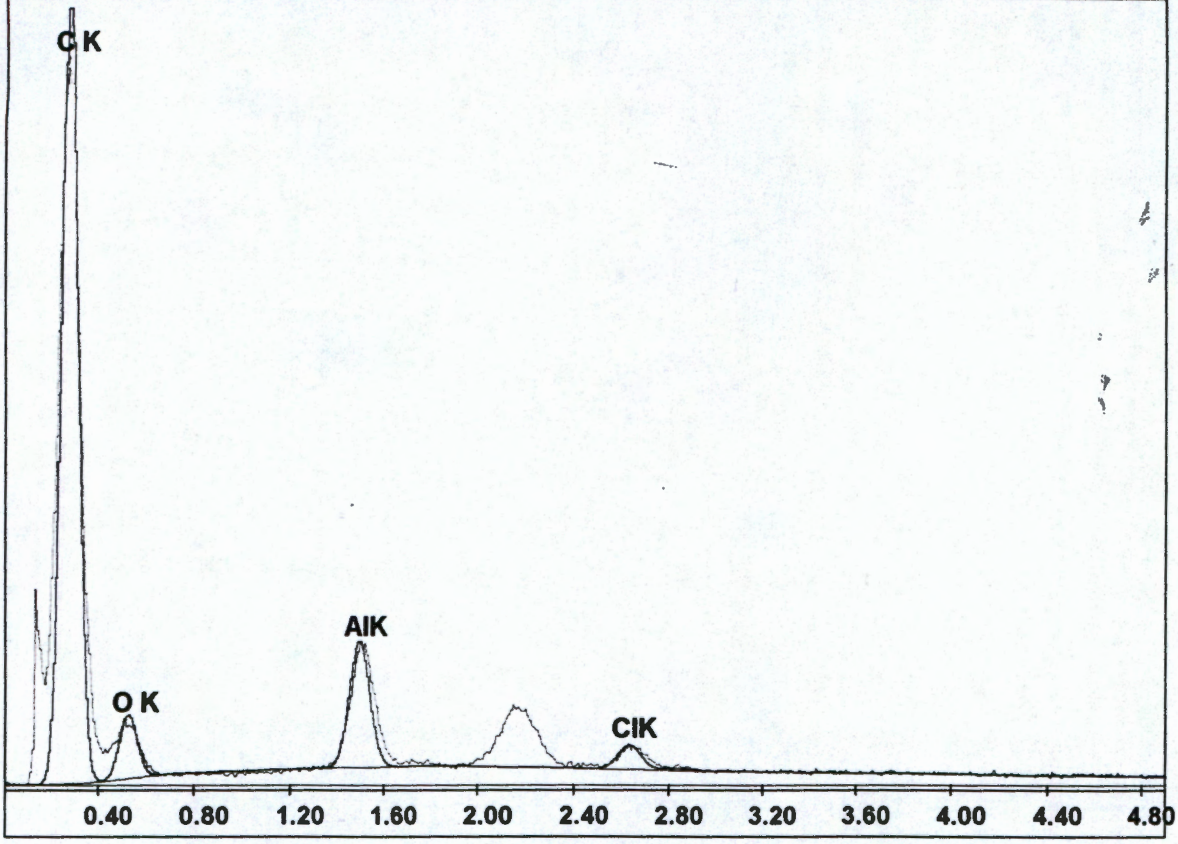
APPENDIX C ELECTRON DIFFERENTIAL SCANNING

D:\DX4\EDS\USR\FAZLIN\FZ140B.spc-/-peakgen.spc

A : Fz140 **B : ClK**

kV:15.0 **Tilt:0.0** **Take-off:34.7** **Det Type:SUTW+** **Res:145** **Tc:40**

FS : 7903 **Lsec : 100** **20-Sep-99** **11:27:30**



EDAX ZAF Quantification (Standardless)
Element Normalized

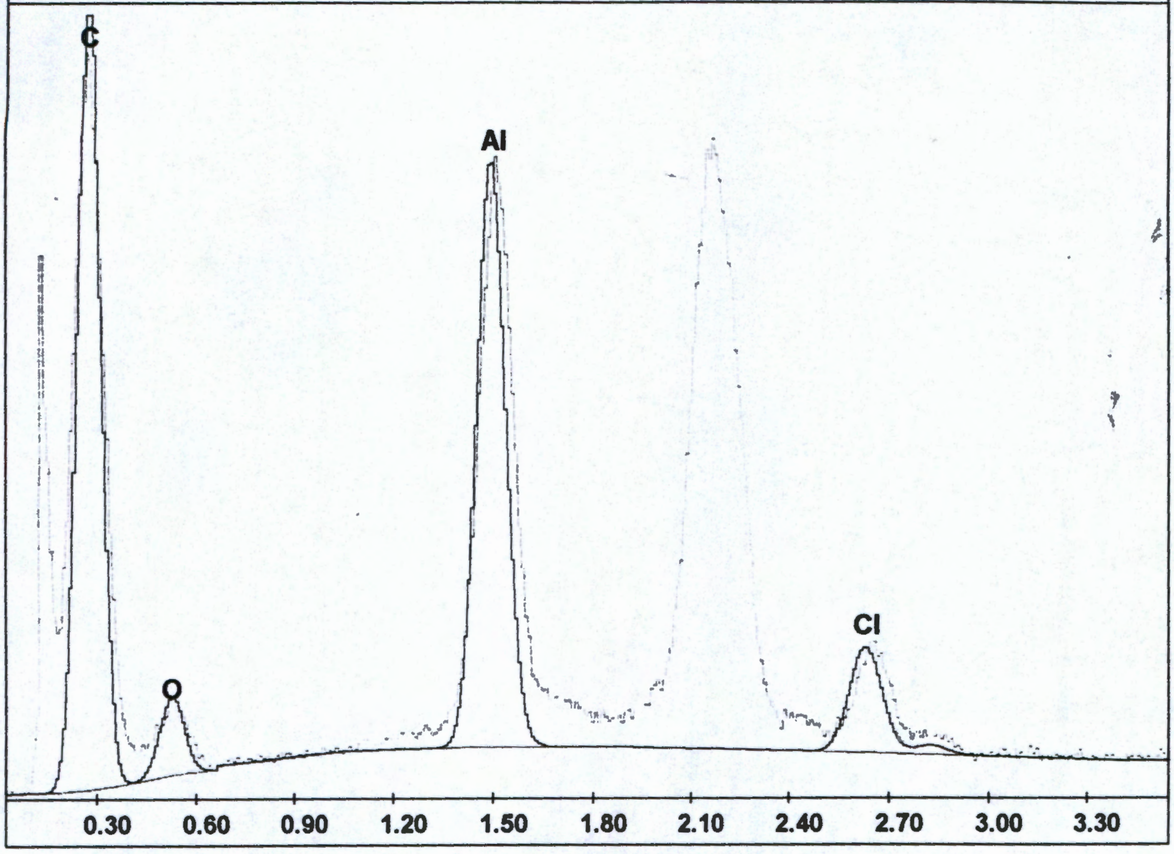
```
Element    Wt %     At %   K-Ratio      Z        A        F
   C K    75.68    83.29   0.3609   1.0115   0.4714   1.0001
   O K    15.00    12.39   0.0317   0.9925   0.2130   1.0001
   AlK     7.18     3.52   0.0580   0.9170   0.8801   1.0004
   ClK     2.13     0.80   0.0189   0.8891   0.9948   1.0000
  Total  100.00   100.00

Element   Net Inte.      Bkgd Inte.      Inte. Error        P/B
  C K      569.60           1.21             0.42         470.74
  O K       48.96           6.57             1.52           7.45
  AlK      103.93          17.90             1.06           5.81
  ClK       22.97          18.67             2.81           1.23
```

CORE OF POLYMER

D:\DX4\EDS\USR\FAZLIN\FZ141.spc

Label:Fz141

kV:25.0	Tilt:0.0	Take-off:34.7	Det Type:SUTW+	Res:145	Tc:40
FS : 2697	Lsec : 100			20-Sep-99	13:08:27



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt %	At %	K-Ratio	Z	A	F
C K	72.33	81.80	0.2284	1.0137	0.3114	1.0001
O K	13.23	11.23	0.0183	0.9983	0.1386	1.0002
AlK	11.94	6.01	0.0841	0.9332	0.7545	1.0007
ClK	2.51	0.96	0.0214	0.9018	0.9474	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	192.04	1.41	0.72	136.20
O K	20.28	6.38	2.55	3.18
AlK	163.96	15.88	0.82	10.32
ClK	34.59	16.62	2.07	2.08