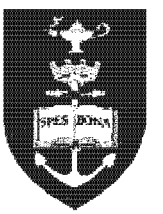
THE SYNTHESIS AND CHEMISTRY OF NEW CARBOSILANE DENDRIMERS AND THEIR USE IN POLYMERISATION CATALYSIS

Reinout Meijboom



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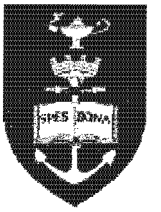
Reinout Meijboom



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

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Abbreviations

Bu	=	butyl
Cp	=	cyclopentadienyl
Cp*	=	pentamethylcyclopentadienyl
EI	=	electron impact
Et	=	ethyl
FAB	=	fast atom bombardment
Fp	=	$CpFe(CO)_2$
G	=	generation
HSQC	=	Heteronuclear Single Quantum Coherence
IR	=	infrared
MAO	=	methylalumoxane
M^+	=	molecular ion
Me	=	methyl
m/z	=	mass to charge ration
n	=	normal
NMR	=	nuclear magnetic resonance
Ph	=	phenyl
Pr	=	propyl
R	=	alkyl
Rp	=	$CpRu(CO)_2$
tert	=	tertiary
THF	=	tetrahydrofuran
TMS	=	tetramethylsilane

IR spectroscopy

ν	=	stretch vibration
δ	=	bend or deformation vibration
γ	=	out-of-plane deformation vibration
as	=	antisymmetric
s	=	symmetric
s	=	strong intensity
m	=	medium intensity
w	=	weak intensity

NMR spectroscopy

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

Note on nomenclature

In written formulae, the metal is mentioned first and then the ligands in order of electron demand. This convention has been used in the synopsis but in the main text metallocenes have been written in the form Cp_2ML_2 (Cp = η^5-cyclopentadienyl, M = Ti, Zr, Hf; L = ligand). This notation indicates that the η^5-Cp-ligands are non-reactive and the complete Cp_2M is treated as a unit. This description is in agreement with most of the literature published in this area.

Most compounds have been numbered using the following general formula:

$Gn_1(f)n_2$ e.g. $G1(allyl)_4$

G: This character represents the word 'generation'.

n_1: The 'generation' number, the number of layers in the dendrimer. The zeroth generation being the monomeric model compound.

F: The functional group on the surface of the dendrimer. In this example an allyl group.

n_2: The number of functional groups in the molecule.

I find a text more accessible if the compound numbers are systematic, because it gives a direct description of the compound rather than an abstract number. Therefore it is clearer as to which compound is mentioned in the text.

Not all compounds could be fitted into the above-mentioned system. Normal (roman) numbering has been applied to the compounds that are not dendrimer related.

Abstract

The immobilisation of homogeneous catalysts is an area of research that attracts a great deal of attention. The immobilisation of catalysts on organic polymers and on inorganic materials such as silica is a well-known strategy. Recently, dendrimers have also been used as support materials. In this thesis, an investigation towards the immobilisation of homogeneous polymerisation catalysts on dendrimers is described.

Chapter 1 gives an overview of the immobilisation of homogeneous catalysts, with the emphasis on their immobilisation on dendrimers. This is followed by a description of the use of Group 4 metallocene compounds as catalysts in homogeneous alkene polymerisation reactions. Here, special attention is given to the immobilisation of the metallocene catalysts. These two areas have both been studied extensively and this chapter gives an introduction; it is not intended to be comprehensive.

The synthesis of the carbosilane dendrimers used in this work is described in Chapter 2. The first step was to hydrosilylate tetraallylsilane ($G1(allyl)_4$) with trichlorosilane. This was followed by reacting the product with allyl Grignard reagent. Dendrimers with a three-carbon spacer and an allyl functionality on the surface, e.g. $Si[CH_2CH_2CH_2Si(CH_2CH{=}CH_2)_3]_4$, ($G2(allyl)_{12}$) were isolated in high yields. The dendrimers, $G1(allyl)_4$ and $G2(allyl)_{12}$, were reacted with various silanes such as chlorodimethylsilane and (chloromethyl)dimethylsilane to give the corresponding halide-terminated dendrimers. Additional functionalisation of the halide with various nucleophiles, such as $[CpFe(CO)_2]^-$ and $[CpRu(CO)_2]^-$, is also described.

In Chapter 3, the synthesis and characterisation of lithiated dendrimers is described. These dendrimers have a $SiCH_2Li$ functionality on the surface and are the first lithiated dendrimers to be prepared that are not stabilised by a π-electron system. The lithiated dendrimers were synthesised by cleaving the C-S bond in a dendrimer functionalised with a $-SiMe_2CH_2SPh$ group. The bond cleavage reaction was performed in THF with a mixture of naphthalene and lithium. These *in situ* generated lithiated dendrimers were then reacted with a number of silyl and stannyl chlorides. The main products of these reactions were dendrimers with a tributyltin functionality on the surface ($-SiMe_2CH_2SnBu_3$). These were used to generate the lithiated dendrimers through lithium-tin exchange reactions resulting in the isolation and spectroscopic characterisation of dendrimers with four or twelve lithium atoms on the surface.

Chapter 4 reports on the synthesis of various mononuclear zirconocene compounds of the type $Cp_2ZrL_1L_2$ ($Cp = \eta^5\text{-}C_5H_5$; L_1, L_2 = halide, hydride, alkyl). In order to attach a zirconocene moiety to the surface of the dendrimer, an investigation into the type of ligand system required (L_1 L2), was necessary. The focus of this investigation was thus on the attachment of the zirconocene moiety to the dendrimer through the ligand system, and the subsequent activation of the attached zirconocene group for alkene polymerisation reactions.

Zirconocenes of the type $Cp_2ZrMe(CH_2SiMe_2R)$ (R = alkyl) were stable and readily synthesised. The methyl group could be selectively abstracted using $B(C_6F_5)_3$ to give zirconocene cations of the type $[Cp_2Zr(CH_2SiMe_2R)]^+$.

The synthesis of dendritic zirconocene compounds is described in Chapter 5. Successful hydrozirconation reactions of the allyl-terminated dendrimers gave compounds with four, $Si(CH_2CH_2CH_2ZrCp_2Cl)_4$, or twelve zirconocene units on the surface. Reaction of the lithiated dendrimers with chloromethylzirconocene also afforded zirconated dendrimers, though these could not be completely purified.

The hydrozirconated dendrimers were used as a precatalyst, along with methylalumoxane (MAO), in catalytic alkene polymerisation reactions. The allyl-terminated dendrimers, described in Chapter 2, were used as monomers in catalytic alkene polymerisation reactions. A description of these reactions is found in Chapter 6.

Conclusions and a final overview are given in Chapter 7, followed by the experimental details in Chapter 8.

Contents

Chapter 1

Introduction to immobilised homogeneous catalysts and homogeneous Group 4 metallocene catalysts

1.1 General Introduction

Most organic chemicals produced in bulk quantities are oxygenated compounds (alcohols, ketones and carboxylic acids) or unsaturated hydrocarbons (ethene, propene and butadiene). The latter compounds can be polymerised to higher hydrocarbons such as polyethene, polypropene and the various rubbers. Many of these bulk chemicals are used as starting materials for the syntheses of other compounds. The feedstock for these chemicals was, in the early 20th century, mainly coal or coal tar products. As the oil and natural gas industries developed, a shift towards ethene, obtained by cracking, and other alkenes, occurred for providing the major sources for organic synthesis.

At present, the lighter alkenes are used in bulk processes such as polymerisation, oligomerisation, Wacker oxidation and epoxidation to make polymers (plastics), acetaldehyde and glycols.[1] The higher alkenes are important intermediates for the production of (biodegradable) detergents, lubricants and plasticiser alcohols.[1] In addition, alkenes serve as precursors for the preparation of a broad range of pharmaceuticals.

In most conversions starting from methane or petroleum fractions, transition metals or their compounds are used as catalysts.* In most processes, the transition metals are supported on metal-oxide, carbon or various inorganic supports, to give heterogeneous catalysts. The processes in which the catalyst remains in the same phase as the feedstock, mainly in solution or liquid phase chemistry, are called homogeneous catalytic processes.

The term 'catalyst' requires some care in defining. In heterogeneous reactions, where, for example, a liquid hydrocarbon is cracked over a solid which does not undergo any change, there may be some justification for using the term, in so far that it denotes a substance added to accelerate the reaction. Homogeneous reactions, however, are often complex and proceed through multiple reaction steps linked in a closed cycle. This 'catalytic' cycle often describes a number of different organometallic species, all of which are essential to the catalytic cycle. Obviously, the concept of *one* 'catalytic' species that does not undergo any change is strictly

* Catalyst: Substance which alters the velocity of a chemical reaction and may be recovered essentially unaltered in form and amount at the end of the reaction (Dictionary of Chemistry, McGraw-Hill, New York, 1997).

speaking incorrect for these reactions, as it is difficult to identify one species as *the* catalyst in the reaction. We do, however, speak of catalytic reactions and often identify the species that will initiate the catalytic cycle as the catalyst — thus, the use of the term catalyst can refer to the catalyst precursor as well.

The principles of homogeneous catalysis are mainly based on co-ordinative unsaturation, oxidative-addition and insertion reactions, as well as attacks by electrophiles and nucleophiles on co-ordinated ligands. Many of these principles may also have applicability in heterogeneous catalysis.

1.2 Homogeneous versus heterogeneous catalysts

Heterogeneous catalysis makes up the majority of the catalytic synthetic processes used in industry. From an academic point of view, the major disadvantage of heterogeneous catalysis is the problem of analysing the catalytically active species and the multiple (molecularly different) catalytic sites. These multiple catalytically active sites can result in multiple products; or, in the case of polymerisations, in a broad molecular weight distribution. A detailed mechanistic description of heterogeneous catalysis is therefore a difficult task. These reactions are often modelled through comparison with soluble metal complexes. In homogeneous catalysis, all pre-catalytic species are identical, resulting in identical catalytic transitions, and therefore a detailed description of the mechanism might be obtained. This generally results in a precisely described product. In alkene polymerisation catalysis, homogeneous catalysts result in a narrow molecular weight distribution. Other advantages of homogeneous catalysts are faster kinetics, stereo-selectivity, good accessibility of catalytic sites, the possibility of gaining a good understanding of the catalytic process, and the possibility of 'tailoring' a catalyst to a process or product.

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

Table 1.1: Characteristics of homogeneous and heterogeneous catalysts

With all these advantages of homogeneous catalysis, why are most industrial processes heterogeneous? The most important reasons, besides the (generally) lower costs, are the easy

separation of the heterogeneous catalysts from the product stream by filtration processes, and their higher thermal stability. The characteristics of homogeneous and heterogeneous catalysts are summarised in *Table 1.1*.

1.3 Immobilisation of homogeneous catalysts

One of the methods for overcoming the technical problems associated with homogeneous catalysts, yet retaining their advantages, is to support the well-defined, homogeneous catalyst (or precursor) on surfaces, polymers or on a different phase. Alternatively, the organometallic species can be supported inside the cavity of a zeolite ("ship in a bottle").[2] In this way, the catalyst remains the original homogeneous species — but it can be isolated with the zeolite by filtration after reaction, or it can be used in a continuous process.

Well-defined organometallic species can be supported on an inorganic surface. The surface can act as a ligand or it can be functionalised with a ligand prior to immobilisation. When the surface is functionalised with a ligand, a spacer can be used to take the organometallic species away from the surface and into the solution, thus reducing diffusion limitations. An ideal surface-anchored metal catalyst must combine high catalytic activity and selectivity with a long lifetime and negligible deactivation by poisons or leaching. A thermally stable and mechanically durable support contributes significantly to these properties. Inorganic oxide surfaces such as silica, glass and single crystal silicon are some examples of such supports, and have been widely used.[3]

The first step in the immobilisation of transition metal complexes on inorganic supports involves the construction of tethered monolayers of donor ligands such as amines or phosphines on the support. In the traditional synthetic routes to such thin films, the weakly acidic surface of silica and the silane condensation reactions of donor molecules containing terminal trialkoxy groups are used (*Figure 1.1*).

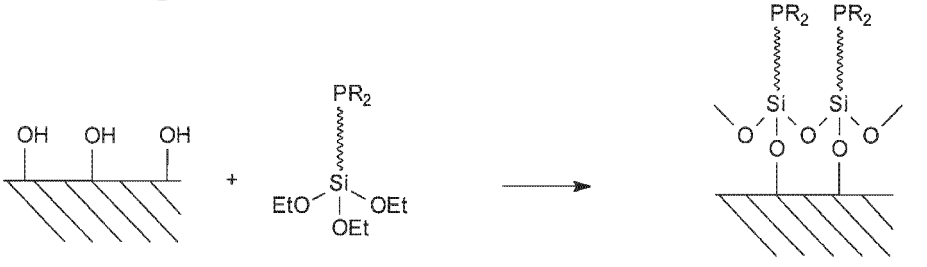


Figure 1.1: Condensation of a trialkoxysilane to a surface

It is therefore possible to synthesise terminal donor ligands anchored to an inorganic surface. The donor ligands can then be used to produce densely packed monolayers of a variety of transition

metals that are practically hanging off the surface and are effectively dissolved in the reaction medium.

Organometallic species can also be supported on poly-siloxanes through sol-gel procedures.[4] By using this method, a support can be generated which represents an intermediate between inorganic (silica, alumina, etc.) and organic supports (polymers). An example of this procedure is the use of [ω-(tetramethylcyclopentadienyl)alkyl]methylethoxy silanes as co-monomers in the sol-gel procedure.[4] This gave a polymeric gel, which was crushed and sieved after drying. Once isolated, the tetramethylcyclopentadienyl moiety could be deprotonated by using an excess of butyllithium, followed by reaction with the appropriate metal-halide; in this case $CpTiCl_3$.[4] In this example, the catalytically active titanocene was immobilised *via* a sol-gel procedure. It is probable that, with the right choice of metal, the procedure of sol-gel formation, followed by attachment of the metal, could be reversed. Thus it can be speculated that it might be possible to attach the metal to the ligand first, resulting in the formation of a well-defined organometallic species, followed by immobilisation in the sol-gel process.

Polymer-bound catalysts might also be useful in addressing problems pertaining to the separation of homogeneous catalysts. For example, low molecular weight polyethene (± 2500 ethene units) has been functionalised at the chain end in order to form a polymeric ligand. The resulting catalysts are soluble in boiling toluene (110 °C) but are insoluble at room temperature. This offers the advantage of switching from a soluble catalyst during process conditions to an insoluble catalyst after termination of the reaction.

Dendrimers are macromolecules with a well-defined globular shape. Dendrimers (from the Greek δενδρον, dendron = tree, and polymers) are molecules with a regular, snowflake-like, highly branched structure. Since Vögtle and co-workers synthesised the first examples of such highly branched structures in 1978,[5] much research has been devoted to the synthesis and application of dendritic molecules.[6] A description of the synthesis and a short introduction to dendrimers is given in Chapter 2; in the present chapter we limit the discussion to dendrimers in catalysis. Dendrimers have molecular weights that can be as high as 700 000 Dalton and radii that can vary between 10 and 500 Ångstrom. Dendrimers have a very regular and controllable pattern of branching, and are mono-dispersed; so all molecules have exactly the same molecular weight and structural dimensions. Van Koten and co-workers utilised the unique, well-defined structure of the dendrimer to immobilise a catalyst for the first time in 1994.[7] The catalytically active dendrimer that Van Koten and co-workers described, is a well-characterised, soluble poly-carbosilane dendrimer with diamino arylnickel(II) complexes on the surface (*Figure 1.2*). The

diamino arylnickel complexes have been shown to catalyse the Kharasch addition of CCl_4 to alkenes in a rate comparable to the monometallic complexes.

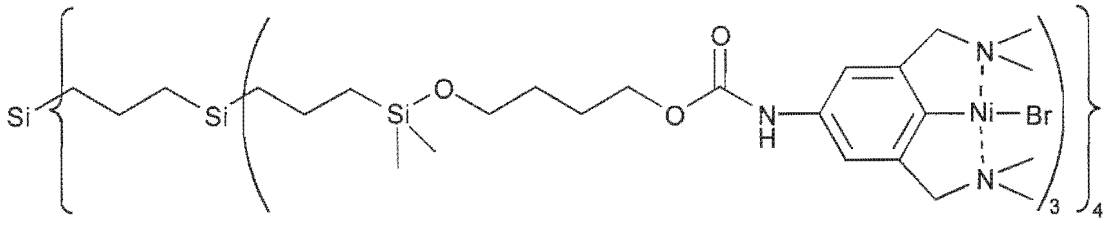


Figure 1.2: Van Koten's dendritic diamino arylnickel functionalised dendrimer[7]

Van Koten and co-workers showed that dendritic catalysts exhibit the advantageous properties of homogeneous catalysts, but can be recovered after the reaction. The large size and relative rigidity of the dendrimers allow them to be removed from solvent streams by nano-filtration methods.[8] Van Koten and co-workers also showed that many modifications are possible to dendrimer-based organometallic catalysts, and that the catalytic centre is independent of the dendrimer on which it is immobilised.[9] For example, a dendrimer containing the same catalytic moiety (based on the 'pincer' ligand, see *Figure 1.2*) was immobilised on an amino acid based dendrimer. It appeared that the catalytic activity per catalytic site was comparable to the activity found per catalytic site on the carbosilane dendrimers. Therefore, it can be concluded that the activity of a catalytic site on a dendrimer is independent of the nature of the dendrimer (provided the catalytic moiety is *not* reactive towards possible functionalities in the dendrimer).

Polymeric catalysts which consist of conventional homogeneous catalytic species anchored to a polymer carrier, have the advantage that they are generally less corrosive, more stable, more active and more selective than their mononuclear counterparts. Depending on whether the polymeric carrier is linear or cross-linked, the polymeric catalyst may be soluble or insoluble. The latter has the advantage that it can be easily separated by filtration from the product reaction mixture, but the disadvantage is that reactions taking place on the interior surface of a porous catalyst particle encounter resistance to mass transport through the pores.

Despite the obvious advantage of retaining the characteristics of a homogeneous catalyst, yet offering the possibility of separation by (up to now expensive)* filtration methods, only a few research groups have paid attention to dendrimers as potential catalyst carriers. Most of the catalytically active systems reported to date have been investigated or devised by a handful of

* Nano-filtration using membranes is expensive. It is, however, probable that these costs will decrease upon finding large-scale industrial applications of the aforementioned methods.

research groups[10] (Astruc, Van Koten, Van Leeuwen, Reetz, Cuadrado, Majoral and Moss). Most of these groups have concentrated on similar routes for immobilising the catalyst: immobilisation of a donor ligand (P, N or O based) on the surface of a dendrimer followed by co-ordination of the metal and testing for catalytic activity. The majority of the dendrimers reported are based on the poly-carbosilane dendrimers that Van Koten and co-workers used. A limited number of examples may be found in the literature of dendrimers with the catalytically active centre at the core of the dendrimer.[11] Some examples of dendrimers with catalytically active transition metal containing groups on the surface are given below.

Van Koten's group, in collaboration with the groups of Vogt, Kragl and Keim, reported the synthesis and use of carbosilane dendrimers as a core on which to immobilise ω-diphenyl-phosphanylcarboxylic acid ester functionalities.[8] These acid ester functionalities were then used as hemilabile ligands to immobilise palladium species. The resulting palladium-containing dendrimer (see *Figure 1.3*) was used as a catalyst in the hydrovinylation of styrene. The catalytic reaction was carried out continuously in a pressure membrane reactor (using nanofiltration membranes), to give chiral 3-phenylbut-1-ene.

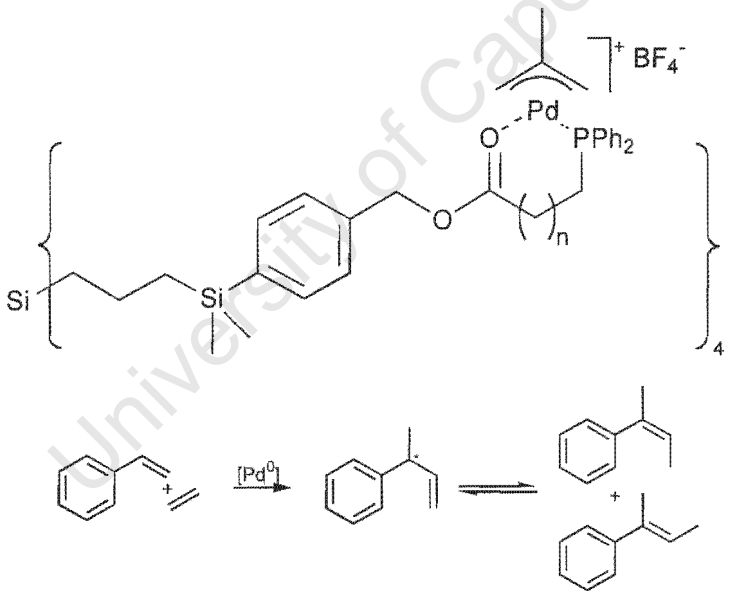


Figure 1.3: The palladium containing dendrimer and the reaction it catalyses[8]

Van Leeuwen's group, at the University of Amsterdam, showed recently that carbosilane dendrimers can be functionalised with diphenylphosphine groups, resulting in dendrimers functionalised with one or two phosphines per branch.[12] These dendrimers were shown to react with $[(\eta^3\text{-}C_3H_5)PdCl]_2$ to give Pd(allyl)-terminated dendrimers. These palladium-containing dendrimers were active in the allylic alkylation reaction of allyl trifluoroacetate and sodium diethyl

methylmalonate, yielding allylmethylmalonate. The authors showed that catalytic activity was retained in the system — comparable to the monomeric system for batch reactions, for dendrimers containing 4 and 12 palladium groups. These dendritic catalysts were shown to work in continuous-flow reactors as well — however, lower turnover numbers were reported, indicating that in the membrane reactor technology other problems, not related to the dendrimer, were present.

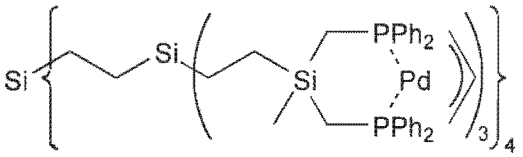


Figure 1.4: Van Leeuwen's palladium(allyl) terminated dendrimer[12]

Reetz and co-workers were able to illustrate the same principle by performing Heck reactions, using a platinum catalyst immobilised on a DAB (diaminobutane) based dendrimer.[13] The DAB dendrimers were the first dendrimers that were commercially available.* Reetz and co-workers functionalised the DAB dendrimers with diphenylphosphine groups, followed by co-ordination of platinum to the phosphine groups.[13] The authors reported that separation was readily accomplished by precipitation. Quantitative recovery of the dendrimer was achieved, and the recycled dendritic species was catalytically as active as the original dendrimer. Higher rates of reaction were achieved in this system than with the 'monomeric' parent compound, something which was not observed in the other systems mentioned above.

Dendrimers with the catalytically active moiety at the core have been investigated by various groups, in order to create artificial enzyme mimics (dendrizymes). Some examples of dendrizymes have been published by Brunner.[11] He designed chelating phosphines, well-known from enantioselective transition metal catalysis, containing dendritic wedges as alkyl groups on the phosphine. He called these ligands expanded phosphines. These expanded phosphines should have a P-P skeleton (for example $R_2PCH_2CH_2PR_2$) which ensures a chelating effect on the metal. By using chiral dendrons for group R, it is possible to create a phosphine that is completely enveloped in a local 'dendritic' environment. Successive co-ordination of these phosphines to rhodium, for example, affords hydrogenation catalysts (*Figure 1.5*) with behaviour strongly dependent on the substitution pattern of the dendrons. These dendrimers were shown to be active in the stereoselective hydrogenation of acetamidocinnamic acid.

* Produced by DSM, available from Aldrich

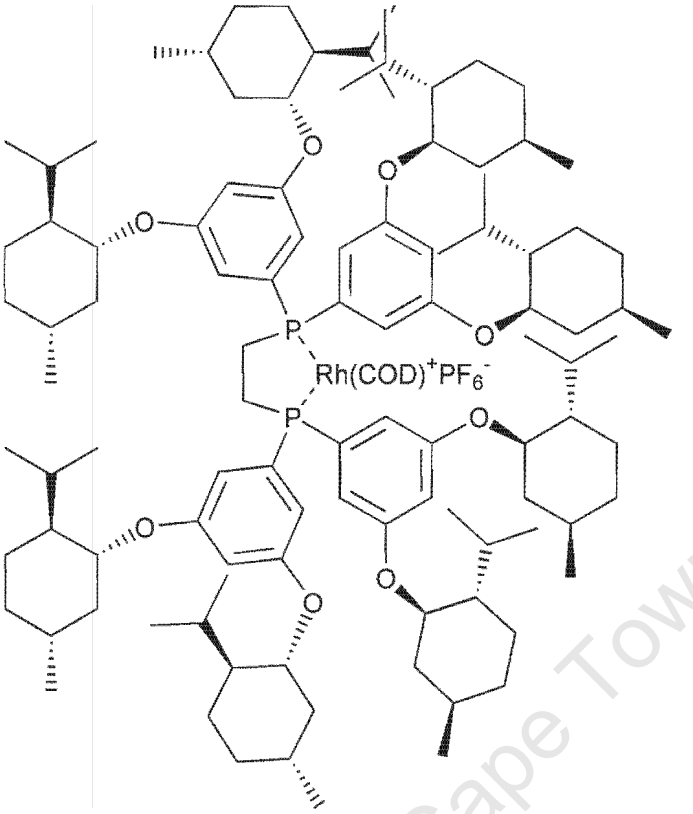


Figure 1.5: Rhodium containing dendrizyme for catalytic hydrogenations[11]

A variety of high-valent metalloporphyrins have been employed as catalysts for the oxidation of organic substrates.[14] The shape-selectivity of the metalloporphyrin catalyst has been shown to be strongly influenced by the extent of the steric crowding present at the faces of the porphyrin.[14] A wide range of sterically hindered metalloporphyrins has been employed for regio- or shape-selective alkene epoxidation or alkane hydroxylation reactions.[14] In order to generate a very sterically hindered system, Moore, Suslick *et al.* have functionalised a porphyrin core by attaching polyester dendritic wedges to it.[15] Thus a sterically hindered, highly soluble manganese porphyrin system was synthesised. The system appeared to be highly selective for the epoxidation of the 1-alkene functionality in nonconjugated dienes, as compared to the unsubstituted manganese porphyrin complex.

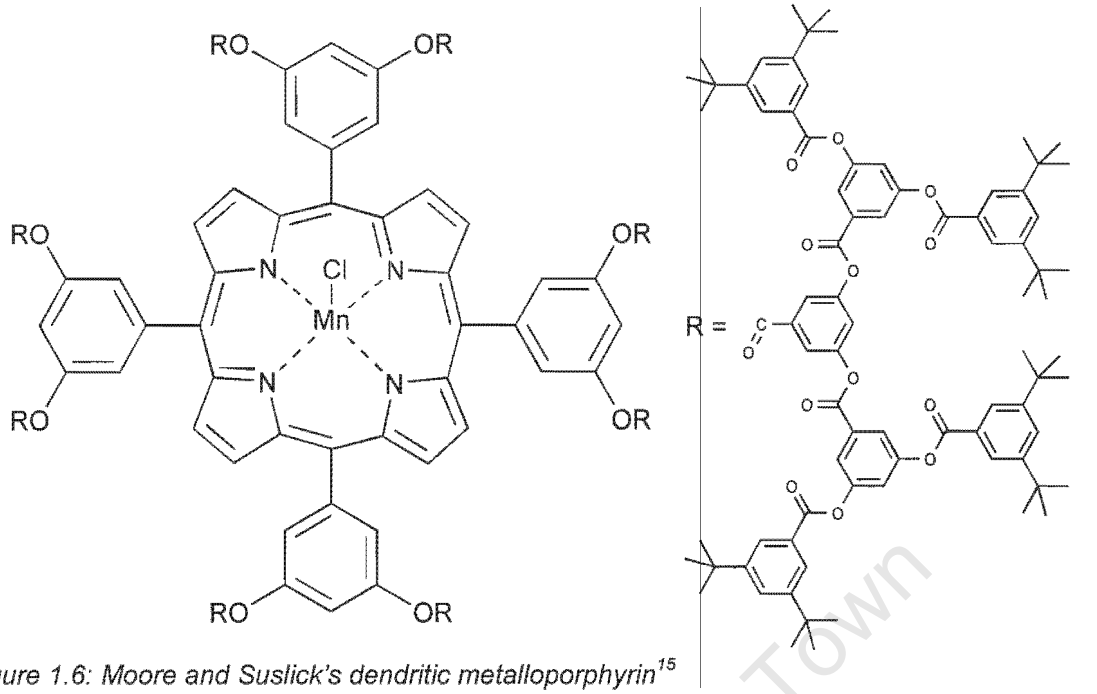


Figure 1.6: Moore and Suslick's dendritic metalloporphyrin[15]

1.4 Zirconocenes as homogeneous alkene polymerisation catalysts

Over the last four and a half decades, catalytic polymerisation of 1-alkenes has developed from Ziegler's small-scale laboratory experiments to gigantic industrial applications (53.6 million metric tonnes in 1995).[16] At present, a wide range of polymers with a broad variation of chemical and mechanical properties is produced in bulk amounts from very simple 1-alkenes such as ethene and propene. These poly-1-alkenes are used on a large scale for packaging, car bumpers and dashboards, fibres, films, etc.

Up to 1980, heterogeneous catalysts, and particularly titanium compounds, were exclusively used for the preparation of polyethene under low pressure. Generally, multiple catalytic sites are simultaneously active in heterogeneous systems. All of these sites have individual characteristics, resulting in polymer mixtures with broad molecular weight distributions. The major breakthrough was made by Sinn and Kaminsky,[17] who discovered that zirconocene dichloride, Cp_2ZrCl_2 (Cp = η^5-C_5H_5), and other Group 4 metallocene dichlorides, can be activated for catalytic polymerisation of 1-alkenes by adding MAO (methylaluminium oxane).[17] It was found that the catalytic activity of the metal, as well as the average molecular weight of the polymers, increased dramatically. The catalysts are soluble in the reaction mixture and form, at least at the beginning of the process, a homogeneous system.

Owing to their homogeneous nature, every catalyst molecule has an active site at an identical position within the molecule. Due to the availability of every metal atom for catalytic reaction, the

metallocene catalysts can be many times as active as their heterogeneous counterparts. Variation of the aromatic spectator ligands, the possibility of introducing a bridge, the nature of the metal and the method of activating the complex, provide a large number of parameters to control the polymerisation reaction (*Figure 1.7*). These possibilities of varying the catalytically active complex are reflected in the stereospecificity, chain branching, chain length, specificity towards monomers and the generation of block copolymers. In other words, Group 4 metallocene based catalysts can produce tailored polyalkenes for almost every possible purpose.

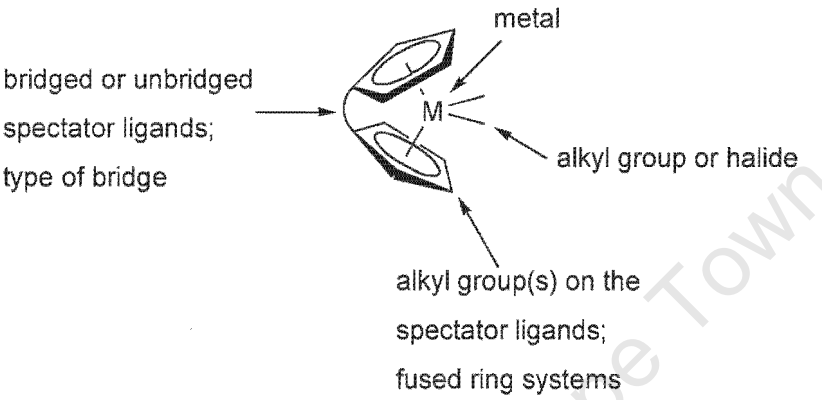


Figure 1.7: Metallocene with the various groups that can be varied

The most common starting material for these catalytic studies is the zirconocene dichloride complex, Cp_2ZrCl_2, or derivatives thereof. These compounds are air stable. They are, however, very sensitive to moisture due to the high oxophilicity of zirconium. In general, the hafnium compounds are slightly more stable than the zirconium compounds. Depending on the nature of the aromatic spectator ligand, several methods for the preparation of bridged (*Figure 1.10*), unbridged (*Figures 1.8 and 1.9*) or half-sandwich metallocenes are available.

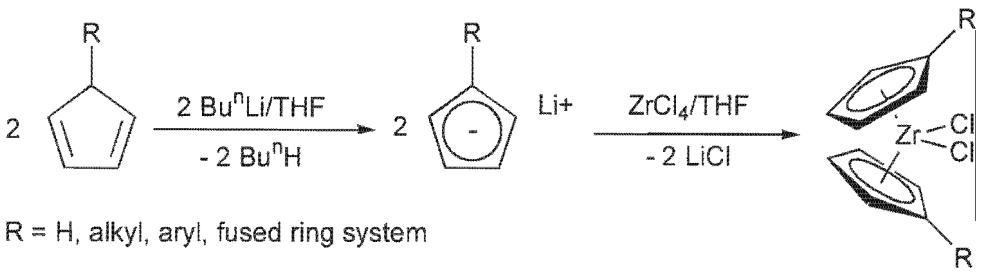


Figure 1.8: Preparation of unbridged metallocene complexes

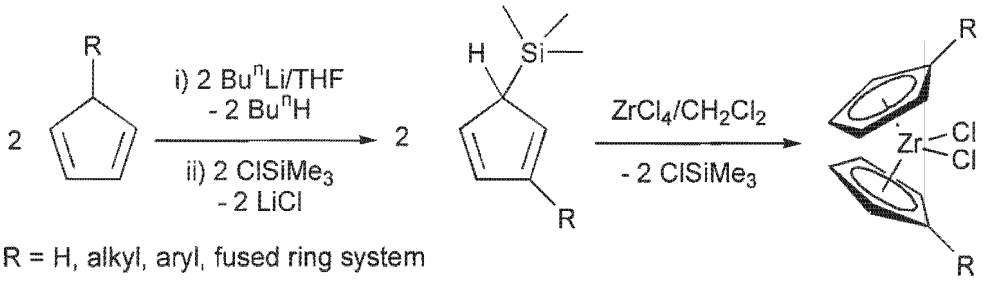


Figure 1.9: Preparation of unbridged metallocene complexes via $SiMe_3$ elimination[18]

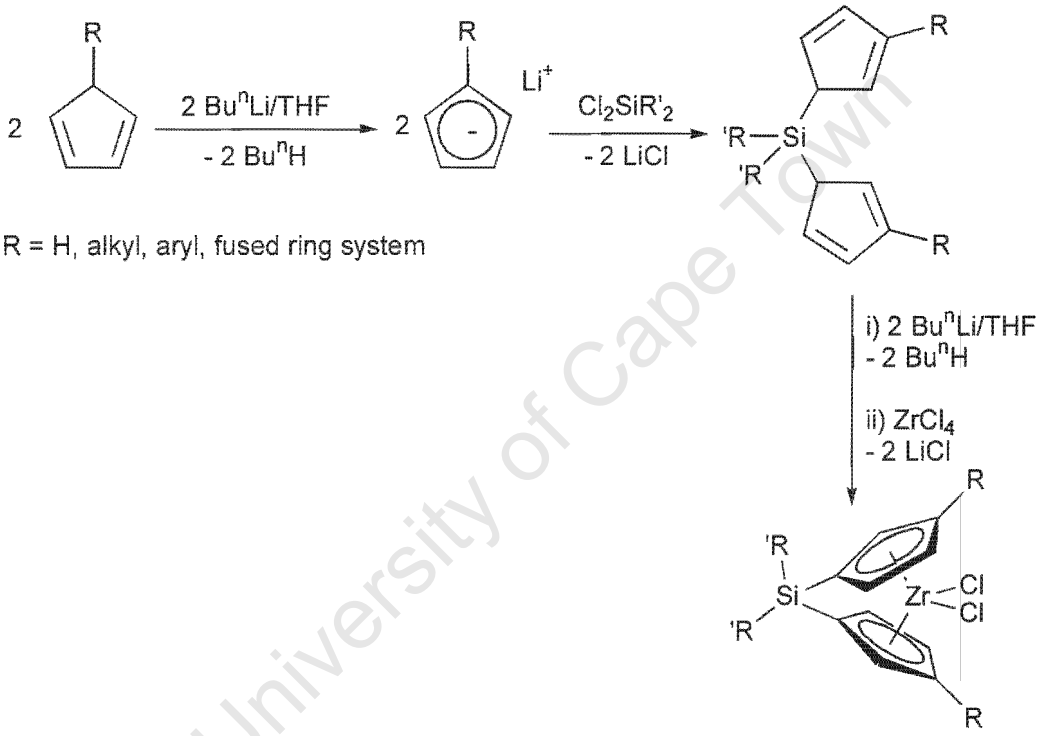


Figure 1.10: Preparation of ansa*-metallocene complexes*

In order to obtain active catalysts, it is necessary to activate the metallocene dichloride. The activation of metallocenes is most commonly performed using MAO (methylaluminium oxane). The reaction of this agent with the metallocene dichloride creates a cationic metallocene mono-methyl complex that is purported to be the actual catalyst. Despite numerous studies and the extensive use of MAO in polymerisation reactions, the chemical nature of this reagent is still not clear. The partially hydrolysed trimethylaluminium seems to consist of linear and cyclic $[MeAlO]_n$ units, with n ranging from 5 to 20. The cyclic species can also aggregate to form cages that are able to accommodate a monomeric $AlMe_3$ molecule, the latter being necessary for the activation steps. These activation steps[19] are thought to be methylation of the metallocene dichloride and

subsequent abstraction of a carbanion to generate a catalytically active cationic metallocene monomethyl complex (*Figure 1.11*). The resulting ion pair is the actual catalyst. It is possible to increase the activity of such catalysts by separating the cation and the anion. This can be achieved by substituting the 4 and 5 positions of the fluorenyl ligands of the *ansa*-complex $[Zr(C_{13}H_8C_2H_4C_{13}H_8)Cl_2]$.[20] After activation with MAO, the activity for ethene polymerisation increases by a factor of five, relative to the unsubstituted *bis*-fluorenyl zirconocene.

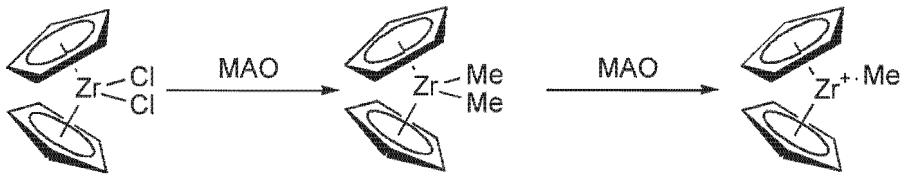


Figure 1.11: Presumed activation of a zirconocene dichloride by MAO[19]

Several industrial and academic research groups have concentrated on the study of well-defined ionic Group 4 metal complexes[16] $[Cp'_2MR]^+[L]^-$ ($Cp' = \eta^5\text{-}C_5H_{5-n}(CH_3)_n$, n = 0-5; M = Ti, Zr, Hf; R = H, alkyl; L = complex counter ion). These systems polymerise ethene and propene under mild conditions, with high selectivity and activity.

Despite the extensive and sophisticated investigations done to work out the mechanistic details of the polymerisation process, many questions remain unanswered due to the complex nature of the catalysts. Nowadays, for Group 4 compounds, it is generally accepted that a cationic d^0, 14 (or less) electron system is the active species. This view is strongly supported by the high polymerisation activity of the iso-electronic (d^0, 14 (or less) electron) neutral Group 3 and lanthanide complexes.[21] At the moment, the most widely accepted mechanism for 1-alkene polymerisation using an early-transition metal catalyst is basically the same as originally proposed in the early sixties by Cossee and Arlman (*Figure 1.12*).[22]

The polymerisation process starts with the co-ordination of an alkene at the vacant site of a cationic Group 4-alkyl complex, followed by insertion of the alkene into the metal-alkyl bond. Subsequent alkene co-ordination and insertion then leads to polymer chain growth. The polymerisation is a thermodynamically down hill process (i.e. exothermic process), due to the transformation of sp^2 C=C to sp^3 C-C bonds.[23] Chain growth can be terminated in various ways. The best-known is hydrogen transfer from the β-position of the growing alkyl chain to the active metal centre. This leads to a polymer with an alkene end-group and a metal-hydride complex, which is normally catalytically active. This process, the reverse of alkene insertion into a metal-hydride bond, is called β-hydrogen elimination.[24]

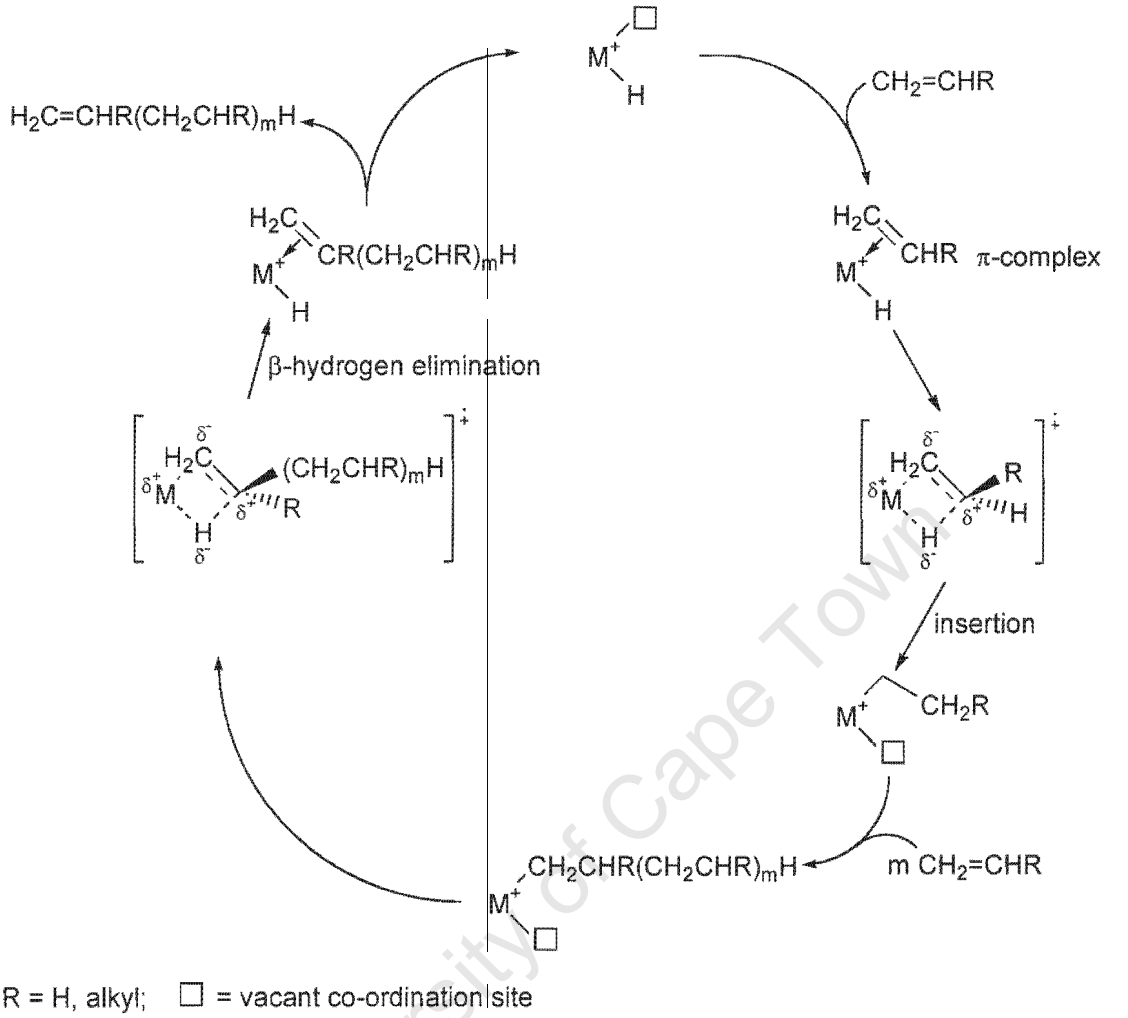


Figure 1.12: Catalytic 1-alkene polymerisation as proposed by Cossee and Arlman[22]

In 1983, Brookhart and Green and, independently, Laverty and Rooney, proposed an alternative chain growth mechanism (*Figure 1.13*). In this mechanism, electronic stabilisation of the ground state and the transition state, through interaction of the metal with one of the α-hydrogen atoms from the polymer chain (a so-called α-agostic interaction), facilitates the propagation step.[25] Alkene insertion into a metal-hydride bond and chain transfer by β-hydrogen elimination seems to occur, as proposed by Cossee and Arlman.[22] Supporting evidence for both chain propagation mechanisms has been found, indicating the complex nature of this key reaction.[26]

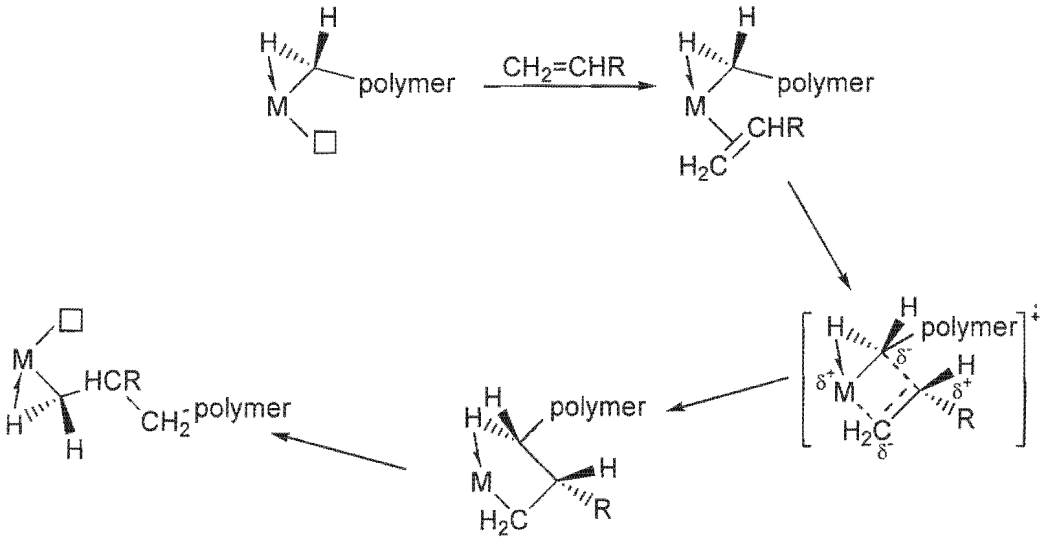


Figure 1.13: Chain propagation mechanism as proposed by Brookhart and Green, Laverty and Rooney[25]

Successful polymerisation seems to require that the catalyst is co-ordinatively and electronically unsaturated (14 electron or lower) and contains a polar M-C bond that favours a partially charged transition state. The highly electrophilic metal centre requires stabilisation by electron-donating ligands. These ligands have to meet the following criteria: they must be inert, non-exchangeable and amenable to tuning. They should also provide sufficient steric bulk in order to prevent association of the metal complex, forming bridged or dinuclear complexes. These usually give poorly soluble, catalytically inactive species. Up to now, the bis(cyclopentadienyl) ligands and their derivatives (bis(indenyl), *ansa*-bis(cyclopentadienyl) and *ansa*-bis(indenyl) systems) have been found to be by far the most successful stabilising groups for cationic Group 4, and neutral Group 3 and lanthanide complexes. These metallocene catalysts have been improved, mainly by varying the substituents on the cyclopentadienyl or indenyl ligand. This has led to the development of 'single site' catalysts, capable of polymerising a wide variety of 1-alkenes in a highly stereoselective fashion, with an activity approaching 'enzymatic rates'.[27] Recent research in this area is strongly supported by theoretical studies, providing considerable information about the fundamental steps in alkene polymerisation.[28]

1.5 Immobilised Group 4 catalysts

Solution polymerisation processes are suitable for the preparation of low-crystallinity polyalkenes such as elastomers, very-low-density ethene copolymers, and amorphous poly-1-alkenes. In these cases, the polymer product is soluble in the reaction medium and a soluble catalyst can be used.

Higher-crystallinity resins, such as isotactic polypropene or high-density polyethene, are usually prepared in continuous slurry, fluidised-bed gas phase, or bulk monomer processes. Here, the polymer is insoluble in the reaction medium. A morphologically uniform polymer particle is needed to avoid reactor fouling and to facilitate smooth operations. Reactor fouling means that the polymer is deposited on the reactor walls, thus making it impossible to run a continuous process. Polymer particles can be produced with heterogeneous catalysts and can be directly used in fabrication processes like rotational moulding, without recourse to grinding or pelletising.[29]

Metallocene catalysts in dissolved forms are unsuitable for the production of polyethene or isotactic polypropene on an industrial scale. In order to use them in the existing technical processes (by replacing the conventional Ziegler-Natta catalysts), the metallocenes have to be applied to a powdery, insoluble substrate. The reason for this is that homogeneous polymerisation catalysts form at best finely divided polymer powders, while heterogeneous catalysts can control the morphology of the polymer bead formed. As a result, the formed polymer beads are enlarged duplicates of the catalyst particles (*Figure 1.14*).[30]

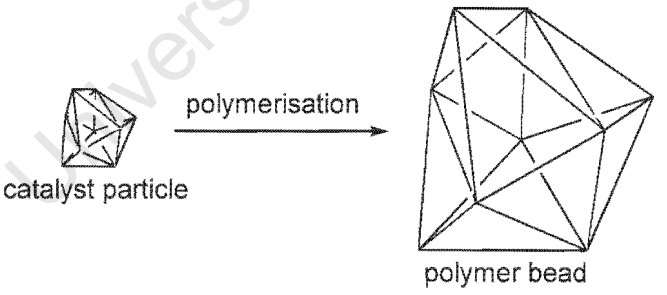


Figure 1.14: Copy of the morphology of the catalyst particle during polymerisation[30]

Catalyst immobilisation is difficult to approach at the molecular level. High surface area silica has been the most widely used support for metallocene catalysts, but other materials for immobilising the catalysts have been reported, such as alumina, magnesium dichloride and polystyrene.

Different methods of applying the metallocene to the support are known.[31] Two of them are:

i) initial absorption of MAO on the support, with subsequent addition of the metallocenes. This is the most used method. The catalysts are then washed and used in combination with additional MAO or other aluminium alkyls for the polymerisation;

ii) either absorption and immobilisation of the metallocene first, or direct bonding *via* a spacer to the support surface. Then, after addition of MAO, this catalytic system is used in the polymerisation process.

Both procedures afford different catalysts and these, in turn, produce polyalkenes with different properties.[32]

The polymers obtained by method i) are very similar to those obtained by the homogeneous system. Each metallocene on the support forms an active centre, the starting point for the growth of a polymer chain. As the active sites on the surface of each catalyst grain are identical, all chains grow uniformly, resulting in polymers with narrow molecular weight distributions.

If the metallocene is linked to the support first, different absorptions occur. Acid centres on the support also deactivate a large amount of the catalyst precursor. This different bonding leads to different active sites. Therefore, the activity is much lower than in the case of the homogeneous system, and the molecular weight distribution of the resulting polymer is much broader.

1.5.1 Inorganic supports

Inorganic support materials such as silica, alumina, magnesium dichloride, and mixtures thereof are widely used for Ziegler-Natta and Phillips catalysts.[33] 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 (*Figure 1.15*). It is interesting to see that a stereospecific catalyst, such as $[Zr(C_5H_4SiMe_2C_{13}H_8)Cl_2]$/MAO, can change its stereospecificity from syndiotactic to isotactic, because the bulky support no longer allows the inversion step in the process.[34]

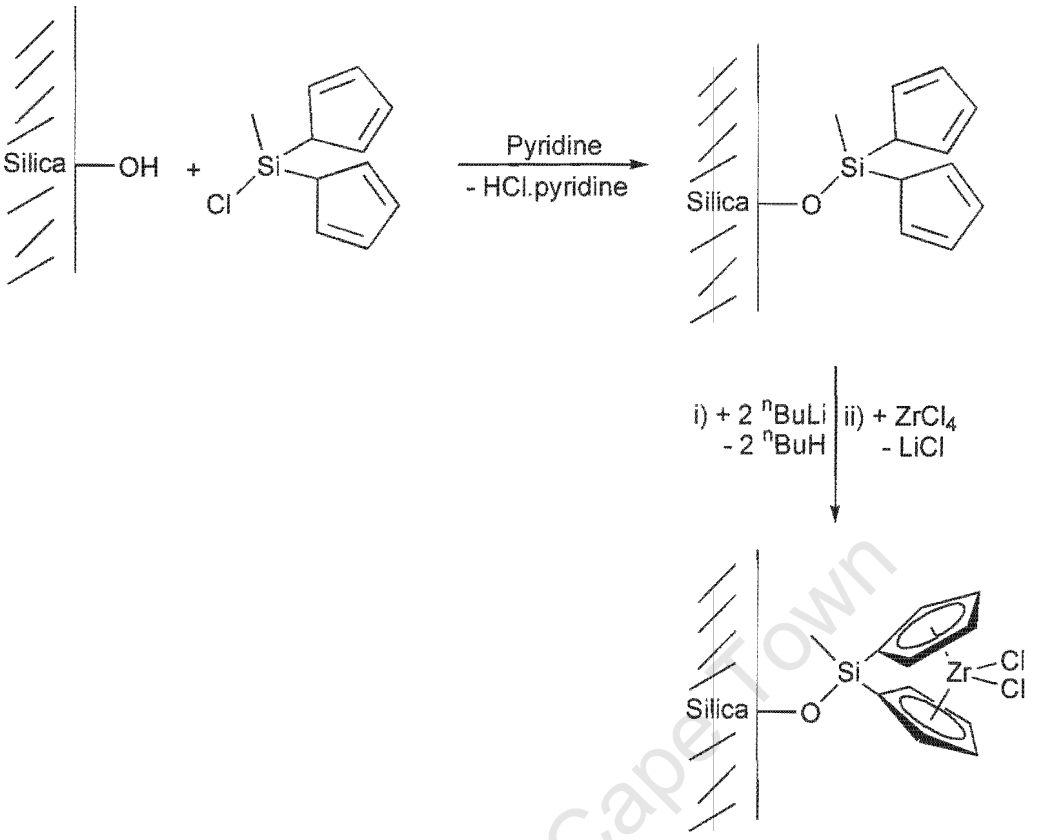


Figure 1.15: Fixation of a zirconocene catalyst on silica

1.5.2 Organic supports

The functionalisation of polymer resin beads provides an especially suitable method to tailor a heterogeneous catalytic moiety that will have similar properties to a homogeneous catalyst. Lessons learned in solution about the design of a catalytic complex may be applied more reliably to a polymer matrix than to the surface of an inorganic support, because an organic material can be designed to resemble the solution environment more closely.[35] To support a Group 4 metallocene on an inert organic substrate, the main focus has been on designing a polymer-supported ligand with which to bind the reactive metal centre.[36] This approach avoids polar components on the support surface which could decrease the catalyst activity. An example is given in *Figure 1.16*.

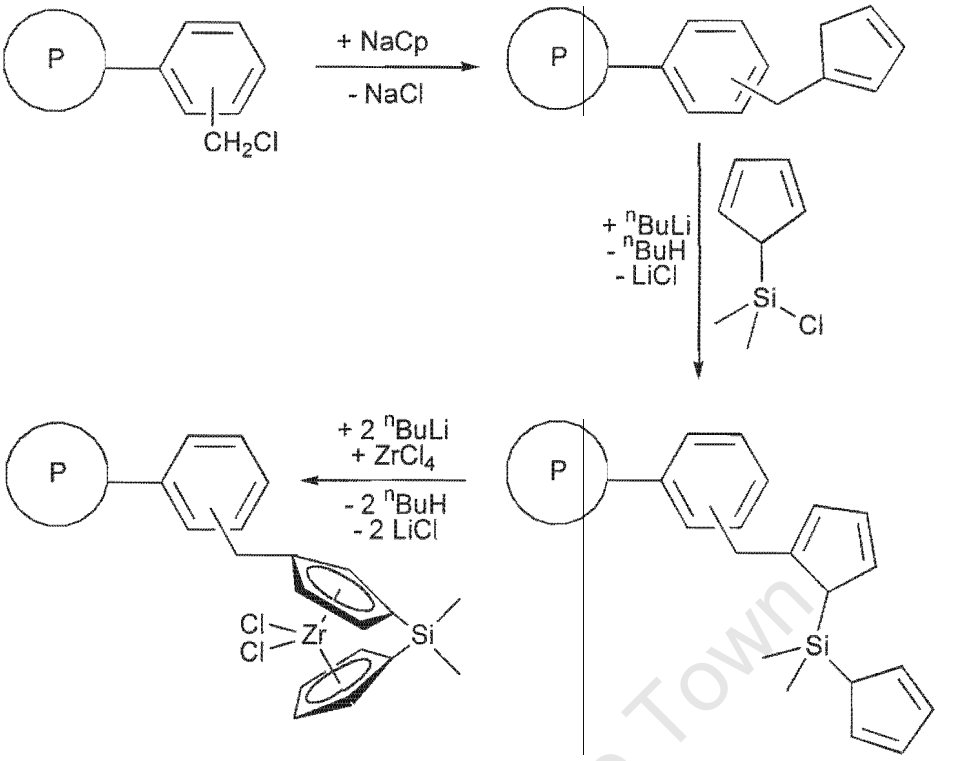


Figure 1.16: Fixation of a catalyst to polystyrene via its ligands[36]

An alternative approach is to immobilise the anionic component used to generate the active catalyst.[37] Here, the activating compound (or co-catalyst) is immobilised on lightly cross-linked polystyrene beads. These are then reacted with the metallocene to give an active supported catalyst (*Figure 1.17*). The catalytically active sites were found to be homogeneously distributed throughout the support particle. In contrast with reactions with surface-supported metallocene catalysts, the polymerisation occurs within the catalyst particle, which swells during the process. The catalysts show good activity for the slurry-phase co-polymerisation of ethene/hexene, and the spherical morphology of the catalyst was accurately replicated during polymerisation.

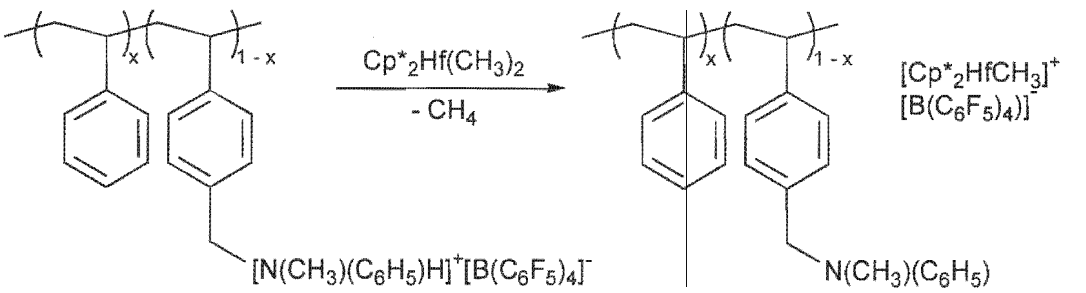


Figure 1.17: Polystyrene supported catalyst

Other current research is aimed at linking metallocenes to organic supports with a more defined structure. This work may result in heterogeneous catalysts in which the spacing of the active centres over the support can be controlled. For instance, zirconocenes supported on poly(bisindenylsiloxane) (*Figure 1.18*) or poly(bisfluorenylsiloxane) can be activated with MAO in the conventional way.[38] These catalysts gave high activities for ethene polymerisation and moderate activities for propene polymerisation. The molecular mass distributions of the polymers were rather broad, and during propene polymerisation large amounts of atactic polymer formed. Both observations might be related to the way the catalysts were formed, giving rise to a mixture of both *rac* and *meso* isomers.

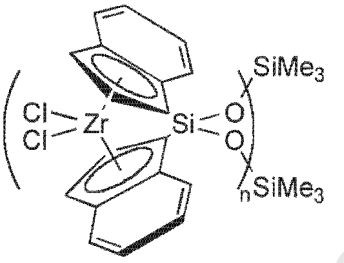


Figure 1.18: Poly(bisindenylsiloxane) supported catalysts[38]

1.5.3 Self-immobilising catalysts

Recently, the so-called self-immobilising catalysts, prepared by Alt and co-workers,[39] were reported. These homogeneous catalysts have a pendant ω-alkene group on the ligand (*Figure 1.19*). During the first stages of polymerisation, the activated catalyst acts as a co-monomer in the polymerisation process, thus heterogenising the active catalyst in the growing polymer chain. In this way, catalyst system provides its own support.[39]

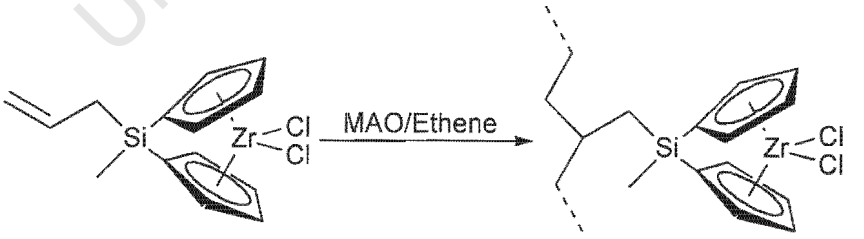


Figure 1.19: Self-immobilising catalyst containing ω-alkene functionality[39]

1.6 Objectives of the research described in this thesis

The objectives of this research are to synthesise various Group 4 metallocene catalysts and to immobilise them on dendrimers. Group 4 metallocene pre-catalysts can be attached to a dendrimer in three different ways (*Figure 1.20*):

i) linked through a σ-bond to the metal;

ii) linked through a π-bond to the metal, i.e. through the cyclopentadienyl spectator ligand; and

iii) linked through the bridge of an *ansa*-metallocene. For cationic Group 4 metallocenes, the additional option of immobilisation via the counter-ion is also possible.

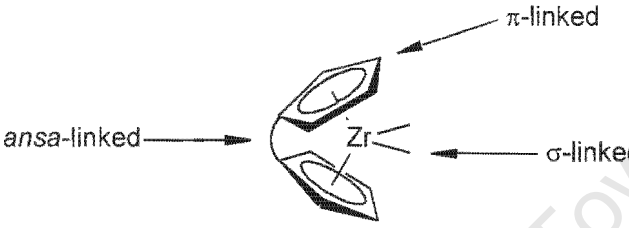


Figure 1.20: Linking positions for immobilisation in zirconocenes

The dendrimers used (*Figure 1.21*) are the carbosilane dendrimers first reported by Van Leeuwen and Van der Made.[51] These dendrimers were selected because they do not contain any polar groups that could decrease the catalyst activity. We also selected a mono-functionalised related template in order to be able to compare the properties of the immobilised Group 4 metallocenes with its homogeneous, monometallic counterpart. This mono-functionalised template (*Figure 1.21*) contains the same functional group as the dendrimers, having a trimethylsilane group representing the other 'branches' of the dendrimer.

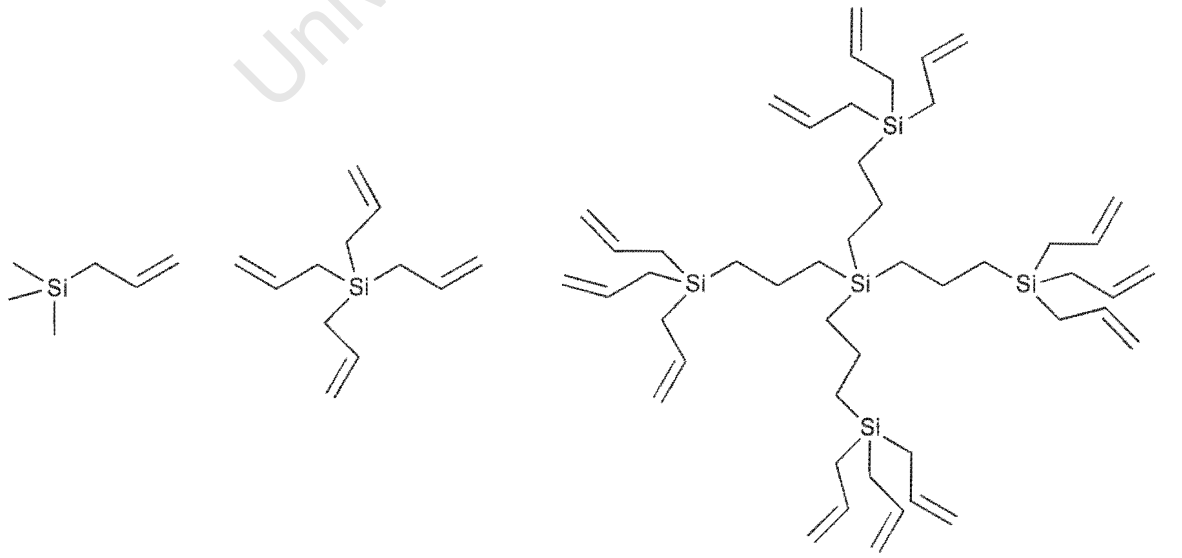


Figure 1.21: Dendrimers and the mononuclear model compound

The goal of this work was to immobilise the Group 4 metallocenes through a σ-bond, creating a metal to dendrimer bond. These compounds would then be fully characterised. Selective activation of these compounds would have to be investigated in order to generate active polymerisation catalysts, immobilised on a dendrimer. Finally, various catalytic runs would have to be performed with these active species to establish whether the polymeric products formed have different properties.

1.7 Contents of the thesis

In this chapter, I described two different areas and attempted to point out the common ground:

i) the immobilisation of homogeneous catalysts, and

ii) the use of Group 4 metallocene compounds in homogeneous alkene polymerisation reactions.

In the first part, the focus was mainly on recent developments in immobilising homogeneous catalysts on dendrimers. In the second part, the focus shifted to a general description of Group 4 metallocene catalysts, with an emphasis on the immobilisation of these. Since the field of Group 4 metallocene catalysts and that of the immobilisation of homogeneous catalysts are both extremely well-studied, this chapter provided only a general overview and is not comprehensive. The aim of the research described in this thesis is to synthesise polymerisation catalysts — active in the polymerisation of ethene and propene — that are σ-bound to a carbosilane dendrimer.

Chapter 2 describes the synthesis and characterisation of the carbosilane dendrimers used as basis for the immobilisation of the Group 4 metallocenes. These dendrimers were synthesised according to known procedures; however, the full characterisation data has not been reported before. These dendrimers have a silicon core and C3 spacers between the branching silicon atoms. The initial functional group on these dendrimers was an allyl group. This allyl group was reacted with various reagents to give dendrimers with various functional groups on the surface. The synthesis and characterisation of these functionalised dendrimers is also described here.

Chapter 3 describes the synthesis, characterisation and derivatives of lithiated dendrimers. The allyl terminated dendrimers were functionalised with thio-anisol silanes. These thio-anisole terminated dendrimers could be converted to lithiated dendrimers *in situ*, and reacted with various suitable reagents. The disadvantage of this route is that various side-products are also present, limiting the use of these lithiated dendrimers. In order to get pure lithiated dendrimers; the *in situ* generated dendrimers were reacted with tributyltin chloride to give tributyltin terminated dendrimers. These stannylated dendrimers could be used to generate the pure lithium-terminated dendrimers, through reaction with butyllithium. Dendrimers with 4 and 12 lithium atoms on the surface have been investigated. These are the largest alkyl-lithium reagents known at present.

Chapter 4 describes the synthesis and characterisation of the various mononuclear model compounds investigated. Initially the reaction of Schwartz's reagent with the model compound (allyl trimethylsilane) was performed. The various activation reactions performed are described in this chapter. A study towards the selective activation of compounds with the general formula Cp_2ZrMeR (Cp = η^5-C_5H_5; R' = alkyl) is also described in this chapter.

Chapter 5 describes the synthesis and characterisation of dendritic zirconium compounds. These are the dendrimers — described in chapters 2 and 3 — reacted with the appropriate Group 4 metallocene compounds. The synthesis of these dendritic zirconocene compounds appeared to be less straightforward than expected.

In Chapter 6, catalytic polymerisation reactions using the zirconocene compounds, described in chapters 4 and 5, are described. Several co-polymerisations of ethene and the model compound, and ethene and the allyl-terminated dendrimers are also described in this chapter.

Chapter 7 gives a final overview of the research and contains the conclusions of the thesis.

The experimental procedures for the synthesis and characterisation of the described compounds can be found in Chapter 8.

Chapter 2

Allyl-terminated carbosilane dendrimers: synthesis, characterisation and derivatives

2.1 Introduction

The rising demand for materials with improved and novel properties has switched the emphasis in polymer research from the traditional linear polymers, via the cross-linked and branched polymers to the hyperbranched or dendritic polymers. This family of highly branched three-dimensional molecules has intrigued researchers because their molecular architectures are so different from those of the traditional polymers. Numerous review articles have been published in recent years, and these are cited in the discussion that follows.

Dendrimers resemble the branching structure of trees in general shape and architecture. Dendritic macromolecules are characterised by repeating layers of building blocks (B) that 'radiate' from the central core (C).[40] The surface groups (S) contain reactive functions which are used to increase the branching until an almost globular shape with a densely packed surface is reached (*Figure 2.1*).

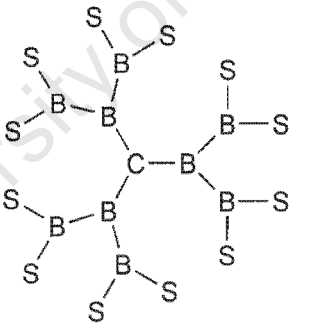


Figure 2.1: Schematic representation of a dendritic macromolecule[41]

The development of dendrimers started after the first cascade-like synthesis of branched polyamines was described by Vögtle and co-workers in 1978.[42] It then took until 1985, before two groups, headed by Tomalia[43] and Newkome,[44] published their synthetic strategies towards cascade molecules. Each group used different building blocks and strategies, but they both sought to find a systematic construction of high molecular weight, symmetrically branched, molecules.

Today, many structural classes of dendrimers are known, including dendritic polyethers,[45] polyamides,[46] polyols,[47] polyphenylenes[48] and poly(crown-ethers).[49] There are even two types of dendrimers available commercially.[43, 50]

2.2 Synthesis of allyl functionalised dendrimers

In this research it was decided to use dendrimers with an allyl functionality at the surface. The allyl functionality was chosen in order to reduce the influence of the silicon atom on the β-hydrogen, relative to the Group 4 organometallic moiety we intended to introduce as functionality. As a mono-functionalised model for the dendrimers, it was decided to use allyltrimethylsilane, abbreviated in terms of the zeroth-generation dendrimer component as **G0(allyl)$_1$**. This should result, after functionalisation, in a well-defined mononuclear organometallic complex which will have comparable properties to the complexes that result from the complexation of a Group 4 organometallic compound to a dendrimer.

The distinguishing requirement of dendrimer synthesis is the ability to synthesise very high molecular weight polymers with narrow molecular weight distributions in a controlled manner. Two fundamentally different strategies have developed for the synthesis of these dendritic macromolecules, with each method having its own advantages and disadvantages. In the divergent or starburst approach, growth of the dendrimer begins at the central core and proceeds radially outwards via a two step process. In the convergent approach, the dendrimer grows from the surface-functionalities inwards to the final core.

2.2.1 Divergent approach

The first step in the divergent approach is reaction of the core molecule with a monomer unit, which contains at least two protected branching sites. The second step involves deprotection of the introduced branching sites, which regenerates the reactive chain ends to give the next generation dendrimer. The resulting dendrimer is then used as a new core, and the reactions are repeated to give increasingly higher generations of dendrimers (*Figure 2.2*).

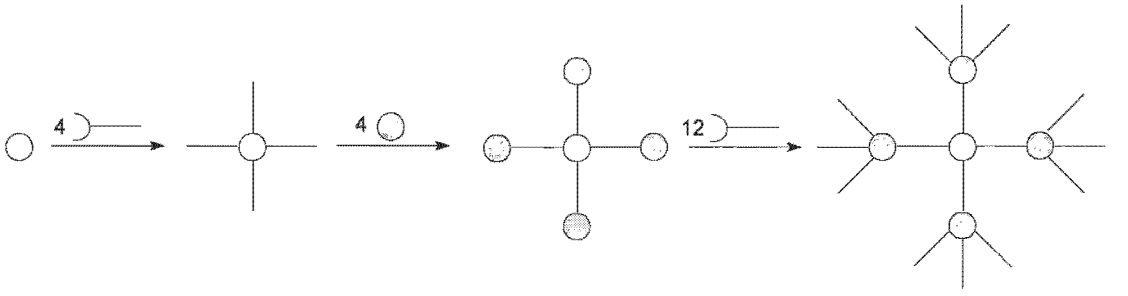


Figure 2.2: Schematic representation of divergent dendrimer growth

It should be noted that all the reactions involved in each growth step should be quantitative and without side reactions, since incomplete reactions or side reactions cause structural defects and/or coupling between dendrimers. It is obvious that the purity of each generation dendrimer is very important for the subsequent growth of the dendrimers.

We chose to synthesise our carbosilane dendrimers through a growth sequence of catalytic hydrosilylation using trichlorosilane; followed by alkenylation of the trichlorosilicon functionalities through reaction with allylmagnesium bromide.[51] Tetraallylsilane was chosen as the first generation dendrimer, **G1(allyl)$_4$**, and trichlorosilane was used as the propagation unit. Thus, a compact dendrimer could be built up with a maximum degree of branching and a minimum chance of side reactions (see *Figure 2.3*).

The synthesis of these dendrimers has been reported before;[51] however, limited experimental detail was reported. The analytical data reported was limited to a ^{1}H NMR spectrum, given as an illustration. Here we report, for the sake of completeness, the full experimental and analytical data for these dendrimers.

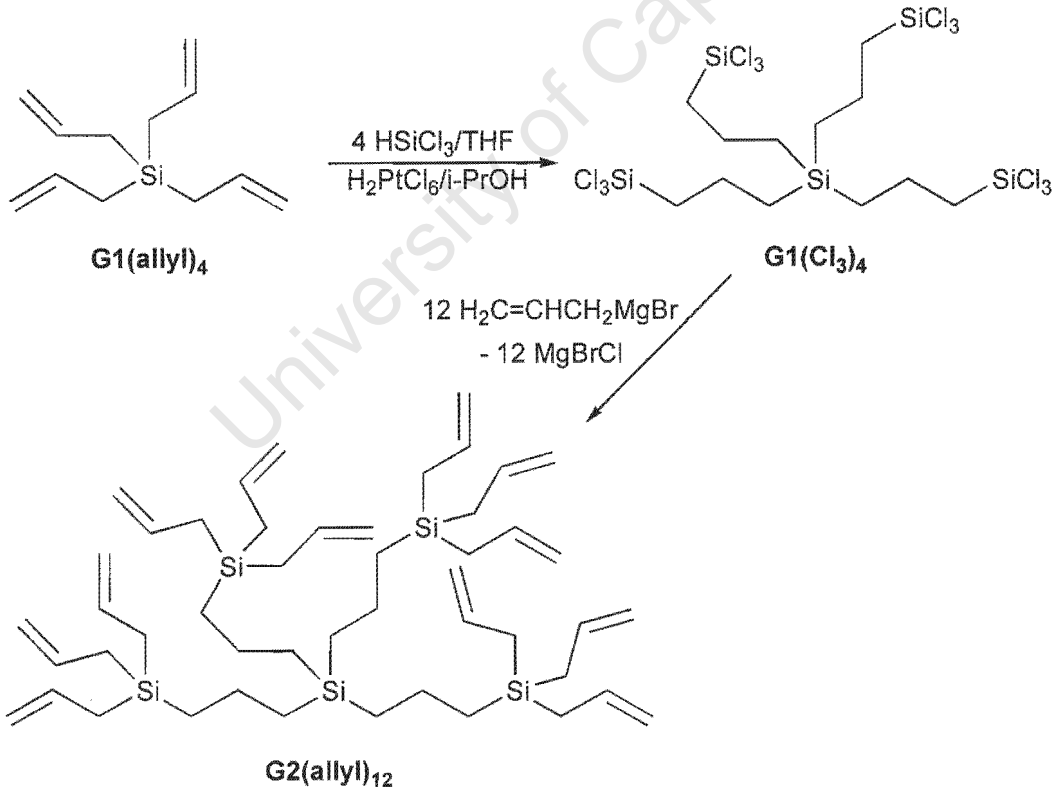


Figure 2.3: Dendrimer growth reaction: synthesis of the second-generation dendrimer

The catalytic hydrosilylation reaction, necessary to build up the above-mentioned dendrimers, is catalysed by many transition-metal complexes. The best-known catalysts for this reaction are Speier's catalyst (H_2PtCl_4 in *iso*-propanol)[52] and Karstedt's catalyst (the reaction product of H_2PtCl_4 and divinyltetramethyldisiloxane).[53] A mechanism[54] for the hydrosilylation reaction of an alkene under transition metal catalysis was first published in 1965 by Chalk and Harrod[54] (*Figure 2.4*). Initial co-ordination of the alkene to the metal was followed by *cis*-addition of the silicon-hydrogen bond. A hydride migratory insertion and elimination of the product silane completed the cycle.

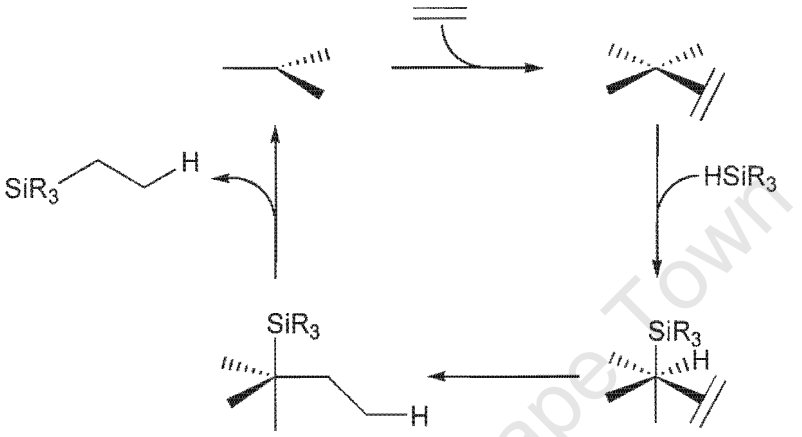


Figure 2.4: Chalk-Harrod mechanism of catalytic hydrosilylation reaction[54]

A major problem in carrying out catalytic hydrosilylation reactions of unsymmetrically substituted alkenes, is the control over regioselectivity of the Si-H addition. In the reaction of a terminal alkene $R'CH=CH_2$, with a silane R_3SiH, the α-adduct, $R'CH(SiR_3)CH_3$, and the β-adduct, $R'CH_2CH_2SiR_3$, can be formed. In the catalytic hydrosilylation of tetraallylsilane with trichlorosilane, the desired product is the all-β-adduct $Si(CH_2CH_2CH_2SiCl_3)_4$. No solvent system was specified in the original communication.[51] We followed the lead suggested by Musolf and Speier[55] and Seyferth *et al.*[56] These reports state that THF as a solvent completely suppresses the formation of the α-adduct during the catalytic hydrosilylation reaction. The product found after the catalytic hydrosilylation of tetraallylsilane with trichlorosilane in THF, showed 2 triplets and 1 multiplet in the ^1H NMR spectrum. This indicated that the desired all-β-adduct had formed. The two doublets and one multiplet, expected for the α-insertion product, $Si[CH_2CH(SiCl_3)CH_3]_4$ were absent from the ^1H NMR spectrum. When the hydrosilylation reaction was repeated without solvent, the all α-insertion product was also found. However, upon moving to higher generation dendrimers, the viscosity of these made it necessary to dilute the reaction in order to achieve proper mixing of the reagents.

The relative amounts of impurities (i.e. α-insertion products and non-reacted end-groups) can be expressed in a simple formula.* Suppose we are given a dendrimer with *P* identical reactive end groups, that undergo a chemical transformation to *n* different types of end groups. We call these end groups a_1, a_2, a_3, . . . , a_n, which will be present in the final product mixture in the proportions q_1, q_2, q_3, . . . , q_n. The composition of individual dendrimer molecules in the product mixture can be expressed as $a_1^{k1}a_2^{k2}a_3^{k3}$. . . , where *k1*, *k2*, *k3*, . . . , *kn* are the numbers of end groups in the product dendrimer bearing the groups a_1, a_2, a_3, . . . , a_n, and $k1 + k2 + k3 + \ldots + kn = P$. The mole fraction $Xa_1^{k1}a_2^{k2}a_3^{k3}$ . . . of dendrimers with composition $a_1^{k1}a_2^{k2}a_3^{k3}$ . . . is given by:

$$Xa_1^{k1}a_2^{k2}a_3^{k3}\ldots = \left(\frac{P!}{k1!k2!k3!\ldots}\right)q_1^{k1}q_2^{k2}q_3^{k3}\ldots$$

For example, for a first generation dendrimer with 5 % α- and 95 % β-insertions, we have $P = 4$, a_1 = β-insertion and a_2 = α-insertion. We find $q_1 = 0.95$ and $q_2 = 0.05$. So the mole fraction of the all-β-inserted product is $Xa_1 = (4!/4!0!)(0.95)^4(0.05)^0 = 0.815$. Likewise, we find the mole fraction of the product with one α-insertion to be 0.171; two α-insertions to be 0.0135 and three α-insertions to be 0.0005.

The reaction between tetraallylsilane, **G1(allyl)$_4$**, and excess trichlorosilane (*Figure 2.3*), catalysed by a platinum catalyst (both Speier's and Karstedt's catalysts have been used) was carried out in THF at room temperature. ^{1}H NMR and FT-IR monitoring indicated the consumption of the unsaturated group on tetraallylsilane. The absorption band at 1640 cm^{-1}, due to the ν(C=C) vibration, progressively disappeared. In the ^{1}H NMR spectra, the decrease in intensity of the multiplets attributed to the allyl functionalities was observed; as well as an increase in intensity of the resonances attributed to the newly formed propyl chain. After completion of the reaction, the product no longer contained unsaturated functionalities, as evidenced by the absence of ν(C=C) absorption bands in the FT-IR spectrum. The first generation trichlorosilicon-derivatised dendrimer **G1(Cl$_3$)$_4$** was isolated, after evaporation of excess trichlorosilane and THF *in vacuo*, in high and reproducible yield (95–100 %). Because the Si-Cl bond is reactive to water, it was decided not to attempt mass spectrometry or elemental analysis of **G1(Cl$_3$)$_4$**. Instead, chemical derivation by alkenylation, to give the second generation dendrimer; and reduction using $LiAlH_4$ (see section 2.3, page 35), led to products with satisfactory analytical data.

The compound **G1(Cl$_3$)$_4$** was completely alkenylated by a salt-elimination reaction with allyl magnesium bromide (see *Figure 2.3*). The reaction with excess Grignard was carried out under reflux in diethyl ether.

* Mr C. Meijboom is gratefully acknowledged for help with deriving this formula.

After reaction of **G1(Cl$_3$)$_4$** with excess allyl Grignard reagent, followed by aqueous work-up and purification over silica gel, the product **G2(allyl)$_{12}$** was obtained in 87 % yield. The second generation allyl-terminated dendrimer was analysed using the standard analytical techniques (FT-IR, ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy, elemental analysis and FAB mass spectrometry).

The third-generation allyl-terminated dendrimer, **G3(allyl)$_{36}$**, was synthesised from the second-generation, dodeca-allyl dendrimer **G2(allyl)$_{12}$**. Quantitative hydrosilylation with trichlorosilane was achieved in THF by using the Karstedt catalyst. Again, the all-β-insertion product was formed quantitatively. The reaction was followed using FT-IR and ^{1}H NMR spectroscopy, observing the progressive decrease of the ν(C=C) band at 1628 cm^{-1} and the disappearance of the allyl resonances in the ^{1}H NMR spectrum. The product, **G2(Cl$_3$)$_{12}$**, was analysed using FT-IR, ^{1}H and ^{13}C NMR spectroscopies, and through chemical derivation. The compound **G2(Cl$_3$)$_{12}$** was alkenylated by using excess allylmagnesium bromide in diethyl ether to give the third generation dendrimer, **G3(allyl)$_{36}$**. The latter was isolated in 83 % yield after purification by column chromatography over silica gel. The third generation dendrimer, **G3(allyl)$_{36}$**, was analysed using FT-IR, ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. The fourth- and fifth-generation dendrimers were easily synthesised, using the general methodology of catalytic hydrosilylation followed by alkenylation reactions described for the second- and third-generation dendrimers.

Dendrimer	Formula	Molecular mass	Allyl end groups
G0(allyl)$_1$[a]	$C_6H_{14}Si$	114	1
G1(allyl)$_4$	$C_{12}H_{20}Si$	192	4
G2(allyl)$_{12}$	$C_{48}H_{84}Si_5$	802	12
G3(allyl)$_{36}$	$C_{156}H_{276}Si_{17}$	2624	36
G4(allyl)$_{108}$	$C_{480}H_{852}Si_{53}$	8113	108

[a] Allyltrimethylsilane

Table 2.1: Allyl terminated dendrimers and the model-compound used in this work

No attempts to synthesise the sixth generation dendrimer were made. The sixth generation dendrimer would have been congested on the surface and the literature reported that attempts to hydrosilylate this dendrimer completely were not successful.[12] The sixth generation dendrimer would not be useful, as surface congestion could prevent functionalisation at the surface.[51]

2.2.2 Convergent approach

Another route of synthesising the carbosilane dendrimers is using the convergent route, in which the synthesis works from outside towards the core. In the convergent approach (*Figure 2.5*), there are three basic units of construction: the initial functionality that will end up on the surface of the dendrimer, the linking and branching group, and the multi-functional core (which has two or more functional groups). The surface functionality contains one functional group (C), which is reactive in the dendrimer synthesis. This functional group reacts with the branching unit. The branching unit contains two functional groups (A and B). Functional group C reacts with the multiple functional groups B of the branching unit. The functional group A, at the focal point, is converted to functionality C. This product can then be linked to either the functional groups B on the branching unit, or to the multiple functional groups B of the core molecule.

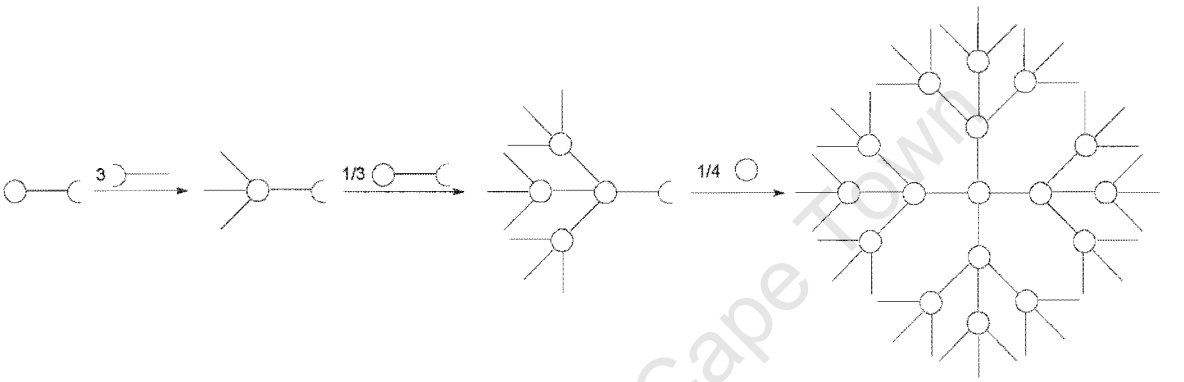


Figure 2.5: Convergent synthesis route

In this route, the monomeric 'wedge' is synthesised first. In the present work, this was done by hydrosilylating allyl chloride with trichlorosilane to give trichloro-3-chloropropylsilane, **1**, quantitatively. This product was analysed by ^{1}H and ^{13}C NMR spectroscopy and showed the expected three characteristic methylene resonances. Reaction of this compound with three equivalents of allylmagnesium bromide at low temperature resulted in the selective alkenylation of the silicon atom.

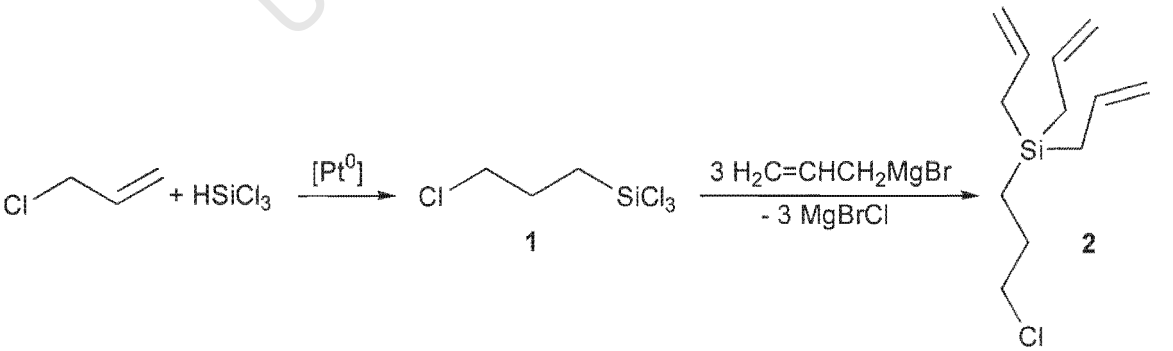


*Figure 2.6: Synthesis of the dendritic wedge **2***

Due to the increased reactivity of the silicon-chlorine bond, compared with that of the carbon-chlorine bond, a selective reaction could be achieved, providing care was taken to react the Grignard reagent at low temperature. After mixing the reagents at –78 °C and stirring at –40 °C for 30 minutes, the reaction was quenched with aqueous ammonium chloride at –40 °C. After aqueous work-up, the product, trisallyl-3-chloropropylsilane, **2**, was isolated in high yield (92 %). The product was characterised by the normal spectroscopic methods.

After reacting trisallyl-3-chloropropylsilane (**2**) with metallic magnesium, the related Grignard reagent was formed. Four equivalents of this Grignard reagent were reacted with tetrachlorosilane to form the second-generation dendrimer **G2(allyl)$_{12}$**. This second-generation dendrimer was in every aspect identical to the one previously synthesised using the divergent synthesis, as concluded from ^{1}H, ^{13}C NMR and IR spectroscopies.

Reaction of three equivalents of $ClMgCH_2CH_2CH_2Si(CH_2CH{=}CH_2)_3$, **3**, with one equivalent of trichloro-3-chloropropylsilane (**2**) at low temperature resulted in the facile formation of the second generation wedge. This could also be activated to form the Grignard, and a repetition of the previous steps could be achieved to yield the third-generation dendrimer **G3(allyl)$_{36}$**.

Thus the convergent synthesis provides an easily accessible route to the dendrimers and opens up the possibility of functionalising the dendrimers at the focal point, or using a different 'core' functionality.

2.2.3 Characterisation of the dendrimers

Many attempts were made to characterise all the dendritic compounds by IR, ^{1}H and ^{13}C NMR spectroscopies, as well as by mass spectrometry and elemental analysis. Once ^{29}Si NMR spectroscopy became available, as many compounds as possible were characterised using this tool as well. Many of the compounds, however, were too reactive, and decomposed while being analysed. For this reason, several of the compounds prepared could not be fully characterised. The specific data is given in the Experimental Chapter and the general results and trends are discussed in the following text.

IR spectroscopy

Infrared spectroscopy proved to be very useful in following the catalytic hydrosilylation reactions. Samples from the reaction mixtures were recorded neat and between NaCl plates. In all hydrosilylation reactions, the progressive disappearance of the band associated with the C=C stretching frequency at ~1630 cm^{-1} was followed. The major advantage of IR spectroscopy over ^{1}H NMR spectroscopy in following these reactions, was the increased sensitivity of the IR

spectroscopy — especially towards strongly absorbing functionalities such as the carbon-carbon double bond.

^{1}H, ^{13}C and ^{29}Si NMR spectroscopy

NMR spectroscopy has proved to be invaluable in the characterisation of the dendrimers. All dendrimers prepared were characterised by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. The ^{1}H NMR spectrum (*Figure 2.7*) of the second-generation dendrimer shows, besides the allyl resonances, three signals for the 'core' propylene groups. These are two triplets at δ 0.7 and 0.8 for the methylene groups bonded to the silicon atoms, and one multiplet at δ 1.35 ($CH_2CH_2CH_2$). The ^{1}H NMR spectrum of the second-generation dendrimer is only distinguishable from the ^{1}H NMR spectrum of the first-generation chloride-terminated dendrimer by its allyl resonances. Therefore, we could not identify which resonance was due to the methylene group attached to the core silicon atom on the basis of these spectra. In order to identify this resonance, the reaction of the first generation chloride-terminated dendrimer, **G1(Cl$_3$)$_4$**, with $LiAlH_4$ in THF,[56] was carried out to give the first-generation SiH_3-terminated dendrimer **G1(H$_3$)$_4$**.* In this dendrimer, coupling between the protons on the methylene group bonded to -SiH_3, and the hydrogens on the silicon was observed to result in a multiplet at δ 0.81. Therefore, we concluded that the triplet at δ 0.7 is due to resonances resulting from the methylene group attached to the core silicon atom. The only differences in the ^{1}H NMR spectrum between **G1(Cl$_3$)$_4$** and **G1(H$_3$)$_4$**, are the triplet attributed to SiH_3 resonances and the above mentioned multiplet of the methylene group bonded to -SiH_3.

^{13}C NMR spectroscopy was also found to be useful in characterisation of the dendrimers. Where an overlap of signals was found in the ^{1}H NMR spectra, ^{13}C NMR showed significantly different signals. These signals (mainly for the 'core' propyl chains) were often weak, due to the relative large number of terminal functionalities; however, they were clearly distinguishable. These 'core propyl chain' signals in the ^{13}C NMR spectrum were often related to the signals in the ^{1}H NMR spectrum by means of HSQC-2D experiments.

Due to the high symmetry of the molecules, the NMR spectra for the dendrimers described in this thesis are relatively simple and well-defined. ^{29}Si NMR spectra are useful in their characterisation, since they display clearly separated signals for the different types of silicon atoms in the molecules. In this regard, the assignment of the resonances corresponding to the terminal silicons with different chemical environments is relatively easy. For example, the $Si(CH_2CH{=}CH_2)_3$ atom resonates at 0.25 ppm, the $SiMe_2CH_2Cl$† resonates at 1.02 ppm, and

* This reaction is described in section 2.3 on page 36.

† See section 2.3.2, page 39.

$SiCH_2Sn$* resonates at 3–4 ppm. On the other hand, the resonances corresponding to the central and middle silicon atoms, with similar chemical shifts in the expected regions of the spectrum, are difficult to assign, as overlap is often observed.

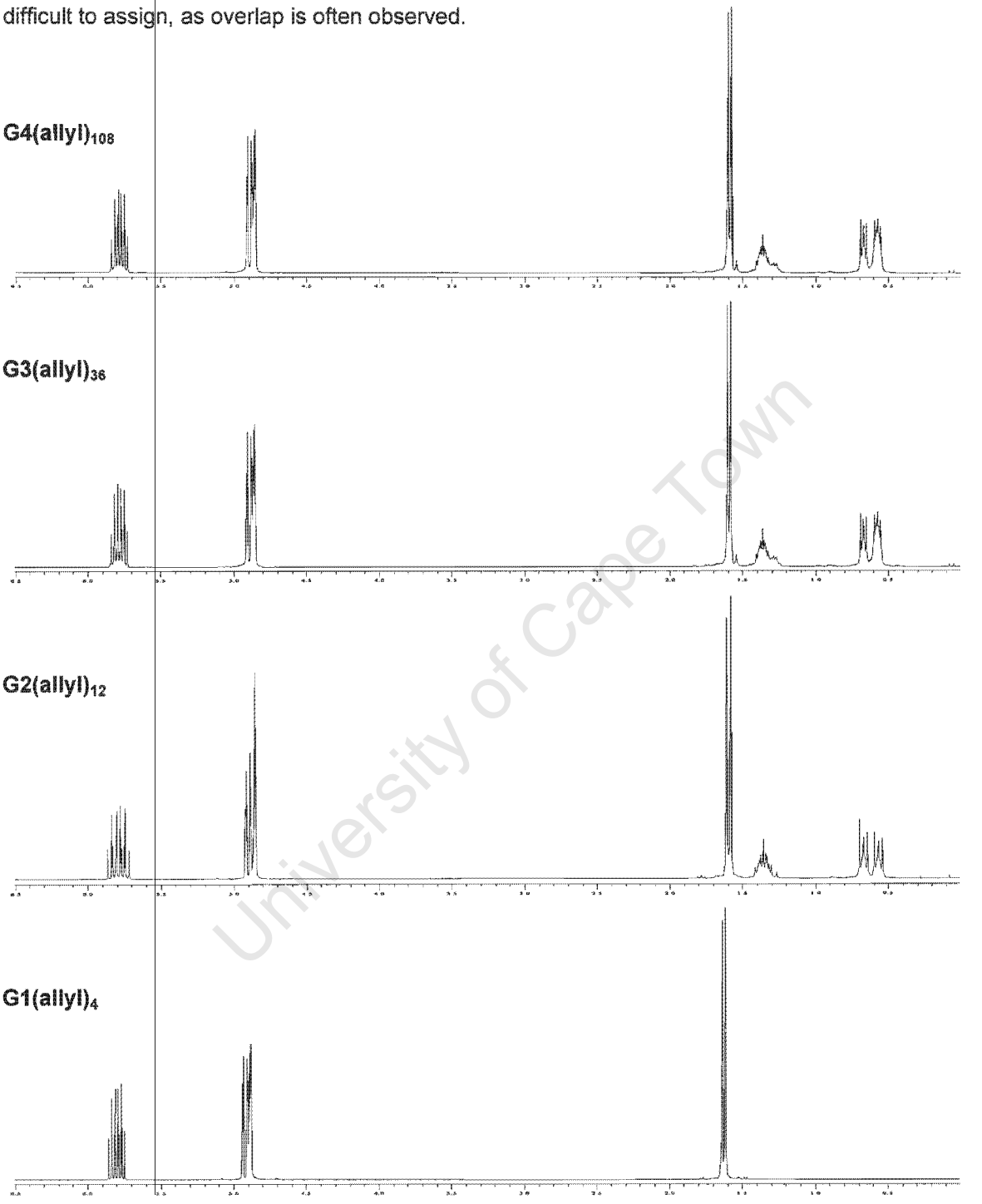


Figure 2.7: ^{1}H NMR (left) and ^{13}C (right) NMR spectra in $CDCl_3$ of the first to fourth generation dendrimers (400 MHz)

* see section 3.3.1, page 50.

Mass spectrometry

Mass spectrometry, together with NMR and IR spectroscopy, is one of the standard methods of characterisation. Analysis using mass spectrometry was attempted for all air-stable dendrimers. The molecular weights of some dendrimers were confirmed by fast atom bombardment (FAB) mass spectrometry. The results are given in the Experimental Chapter. The FAB mass spectra generally showed molecular ion peaks at the expected positions for the lower molecular weight dendrimers (i.e. the first generation and the model compounds). The elemental composition of molecular ion peaks was further confirmed by comparing their isotope patterns with the patterns generated by computer calculation. On the other hand, in the case of the higher molecular weight dendrimers, and the dendrimers with the more labile groups on the surface, only daughter peaks were observed. The FAB mass spectra were complicated by complex isotope patterns resulting from the heteroatoms.

The FAB mass spectrum of the second generation dendrimer **G2(allyl)$_{12}$**, for example, did not show a molecular ion. The absence of the parent ion peak at *m/z* = 802 can be ascribed to fragmentation in the spectrometer. However, peak clusters at *m/z* = $(M - 41)^+$, $(M - 82)^+$, $(M - 123)^+$, and $(M - 164)^+$, were observed, where M is the formula molecular weight of the dendrimer of 802 amu. The ions formed at M – 41*x* (*x* = 1–4) account for the loss of *x* allyl fragments ($\bullet CH_2CH{=}CH_2$, mass 41 amu). The isotopic distribution of **G2(allyl)$_{12}$**, after losing one allyl branch, was simulated and the simulated spectrum corresponded to the spectrum found at *m/z* = 761, indicating that the correct fragment was present.

Microanalysis

Microanalysis was attempted for all the air-stable dendrimers. Microanalytical data for the synthesised compounds is given in the Experimental Chapter. In many cases, the results obtained were the correct values, however, the higher generation dendrimers proved to be a major problem. These were all viscous oils and in some cases solvent inclusion was believed to have occured, even after drying the dendrimers under vacuum for up to 16 hours. Incomplete hydrosilylation reactions also resulted in incorrect microanalytical data. These incorrect values occur already if the alkene resonances are hardly visible in the ^{1}H NMR spectrum, making it a valuable tool for analysing the purity of the dendrimers.

2.3 Functional groups

In order to functionalise the synthesised allyl-terminated carbosilane dendrimers, a number of synthetic routes are available. We have already mentioned that catalytic hydrosilylation, using trichlorosilane, is an effective method to functionalise the dendrimer with a $SiCl_3$ group. Alkenylation and alkylations, using the various Grignard or lithium reagents, can be assumed to be applicable to the trichlorosilane functionality; though only the complete alkenylation using an allyl Grignard was performed in this work. The attempted functionalisations of the allyl-terminated dendrimer carried out in this work are shown in *Figure 2.8*, where only the first generation dendrimer is depicted.

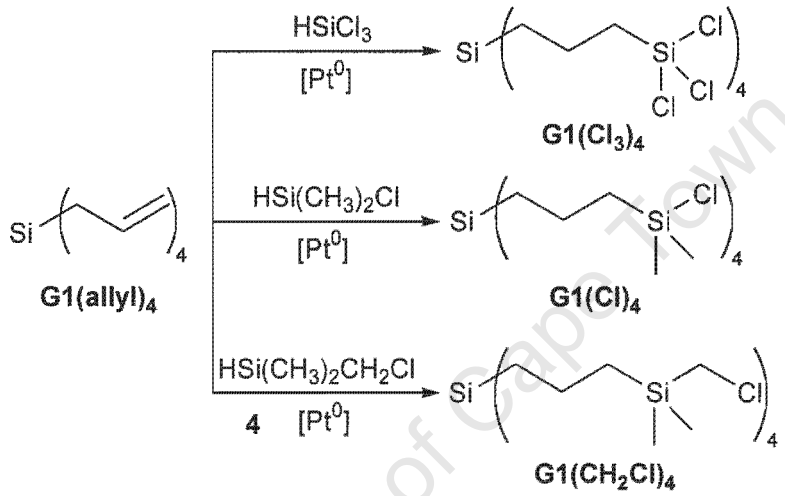
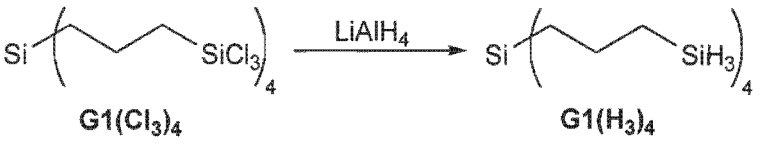


Figure 2.8: Functionalisations of the first generation dendrimer, ***G1(allyl)$_4$***

In general, the (organic) functionalisation of the allyl-terminated dendrimers was performed here by hydrosilylation reactions. These reactions were all followed by FT-IR spectroscopy.

Occasionally, lengthy reaction times were necessary in order to convert all the allyl groups on the dendrimer. These long reaction times can be illustrated by the reaction of $HSi(CH_3)_2CH_2Cl$, **4**, with the third-generation allyl-terminated dendrimer, **G3(allyl)$_{36}$**. This reaction had to be heated under reflux for about ten days before conversion of the last 5 % of the allyl groups was achieved (interestingly, about 90 % of the allyl groups were converted after 16 hours of heating under reflux). It is important to try and convert that last 5 % of the allyl groups — as we indicated on page 28; 5 % unreacted allyl groups means that about 81 % of the dendrimer is without allyl functionalities (not 95 %). Because the dendrimers containing one allyl group behave almost identically to those without allyl functionalities, separation by column chromatography proved unsuccessful in removing the remaining allyl-functionalised dendrimers.

Reduction of the $SiCl_3$ group, using lithium aluminium hydride, was successful and resulted in the SiH_3-functionalised dendrimers (*Figure 2.9*). These dendrimers were obtained in good yields after aqueous work-up. The SiH_3-functionalised dendrimers were stable to air, but reactive to water in the presence of Brønsted bases. The work-up of these dendrimers involved quenching the excess $LiAlH_4$. Care was taken to use a large excess of dilute acid for this step, in order to prevent the mixture from getting alkaline. As described on page 32, this dendrimer was mainly used to distinguish between the two different CH_2Si signals in the ^1H NMR.



G1(Cl$_3$)$_4$ **G1(H$_3$)$_4$**

Figure 2.9: Reduction of $SiCl_3$ terminated dendrimer

2.3.1 Chlorodimethylsilane functionality and its reactions

The success of the hydrosilylation of the allyl-functionalities is related to the acidity of the proton on the silane. Hydrosilylation using Speier's catalyst is rather limited. The hydrosilylation using $HSiCl_3$ and $HSi(CH_3)_2CH_2Cl$ are successful, but $HSi(CH_3)_2Cl$ can not be (quantitatively) reacted with an allyl functionality using Speier's catalyst, even at elevated temperatures (120 °C).

However, we successfully used Karstedt's catalyst[53] in the catalytic hydrosilylation of dendrimers with chlorodimethylsilane. The product of the hydrosilylation of tetraallylsilane, **G1(allyl)$_4$**, with chlorodimethylsilane was purified by crystallisation. The product, initially a viscous oil, crystallises at –40 °C from pentane to give $Si[CH_2CH_2CH_2Si(CH_3)_2Cl]_4$, **G1(Cl)$_4$**, which was identified by ^1H and ^{13}C NMR spectroscopy as well as by chemical derivation.

The second generation dendrimer **G2(Cl)$_{12}$** was synthesised in an analogous manner, starting from the second generation allyl-terminated dendrimer **G2(allyl)$_{12}$**.

The reactive silicon-chloride bond in the dendrimer derivatives was reacted with lithium aluminium hydride to give the tetranuclear $-Si(CH_3)_2H$ functionalised dendrimer **G1(H)$_4$**. This functionality can be used in further hydrosilylation reactions, to attach an organometallic allyl-functionalised group. The silicon-hydrogen bond is stable to oxygen, but reactive to water, in the presence of Brønsted bases. The **G1(H)$_4$** dendrimer was analysed by ^1H and ^{13}C NMR spectroscopy as well as by IR spectroscopy, mass spectrometry and elemental analysis.

The chlorodimethylsilane-terminated dendrimer can be regarded as a dendritic equivalent to chlorotrimethylsilane. Chlorotrimethylsilane is an extensively used alcohol protecting group in organic synthesis.[57] We decided to examine the possibility of using the chlorodimethylsilane as a dendritic protecting group, by reacting it with an alcohol in the presence of an organic base. Thus, we reacted 4.1 equivalents of $HOCH_2C_6H_3[OCH_2CH_2CH_2Ru(\eta^5\text{-}C_5H_5)(CO)_2]_2$ — **Rp3G1OH**[58] — with one equivalent of the first generation chlorodimethylsilane terminated dendrimer, **G1(Cl)$_4$**, in the presence of excess triethylamine (*Figure 2.10*). After aqueous work-up, followed by chromatography over silica gel, the organoruthenium dendrimer, **G1(Rp3G1)$_4$**, was isolated in 63 % yield. The ^{1}H NMR spectrum (*Figure 2.11*) was helpful here as separate signals for the silyl-propyl chains indicated that the reaction took place on all four dendritic arms. The integration of the signals was a further confirmation that tetra-functionalisation had occurred. It has been suggested in that dendrimers such as these might be used as an immobilisation phase in combinatorial chemistry. The present work shows that a functionalised alcohol can easily be immobilised on the surface of the dendrimer.

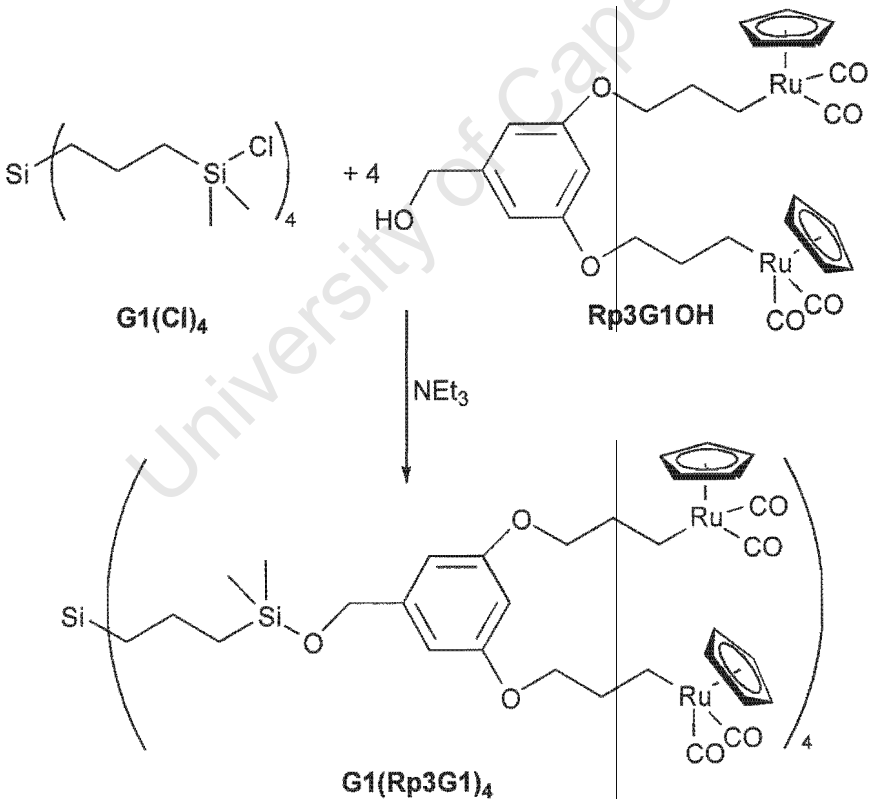


Figure 2.10: Reaction of the chlorodimethylsilyl terminated first generation dendrimer ***G$_1$(Cl)$_4$*** *with* ***Rp3G1OH***

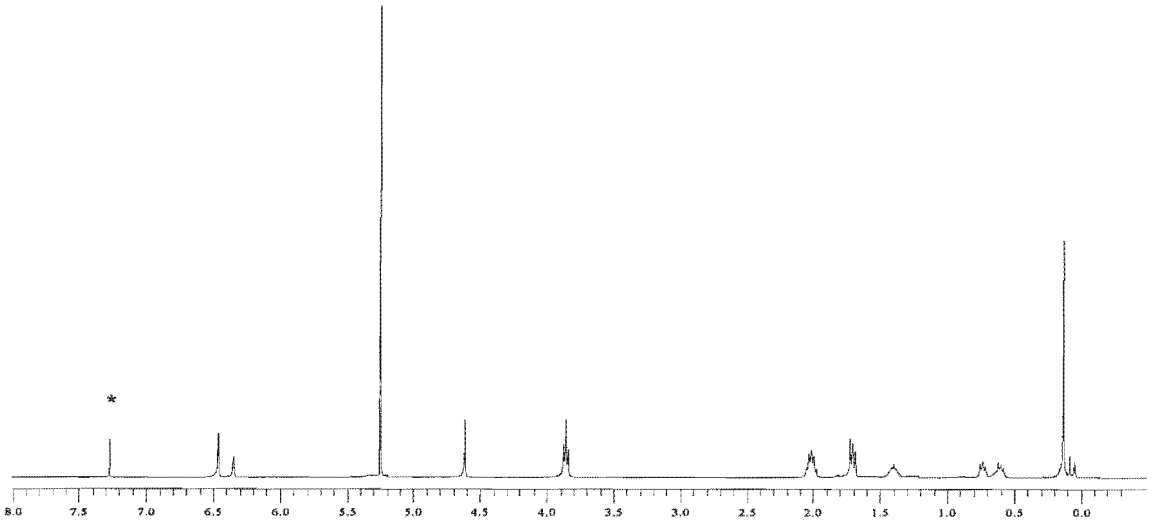


*Figure 2.11: ^{1}H NMR spectrum of **G1(Rp3G1)$_4$** in $CDCl_3$, * denotes $CHCl_3$ impurities in the solvent*

The reaction of NaCp in THF with the four-directional dendrimer **G_1(Cl)$_4$** was also successful.[59] The desired cyclopentadienyl-functionalised organosilicon dendrimer, **G_1(Cp)$_4$**, was obtained in 73 % after aqueous work-up. The ^{1}H NMR spectrum of this dendrimer in $CDCl_3$ shows the typical pattern of resonances of a cyclopentadienyl moiety σ-bonded to a silicon atom at δ 6.6 and 6.5.[60] The typical dendrimer resonances corresponding to the methyl and methylene protons were also present. The expected integrated ratio for all these signals was a further confirmation that a successful tetra-functionalisation of the dendritic core had been achieved.

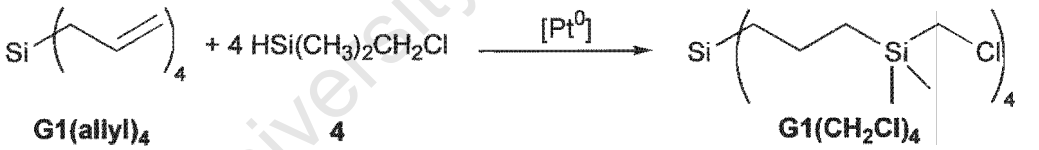
The chlorodimethylsilyl terminated dendrimer, **G1(Cl)$_4$**, was also reacted with $K[CpFe(CO)_2]$.[59] The desired iron-carbonyl dendrimer **G1(Fp)$_4$** was obtained as a colourless oil, after purification by column chromatography. This dendrimer contains an iron-silicon σ-bond. The attachment of the iron-carbonyl unit can easily be observed in the IR spectrum. Evidence for the complete functionalisation of the dendrimer was provided by the ^{1}H and ^{13}C NMR spectra. The planned reaction of **G1(Cl)$_4$** with the carbonyl anions of ruthenium, tungsten and molybdenum have not been performed due to the expected reactivity of the M-Si bond.[61] Instead, reactions of these metal carbonyl anions with the chloromethyl-terminated dendrimers have been performed and will be described on page 41.

Dendrimer functionality	δ_H of $Si[CH_2CH_2CH_2-]_4$	δ_H of functional groups
$-SiCl_3$	0.28 (8, m), 1.01 (8, t), 1.33 (8, m)	-
$-SiH_3$	0.59 (8, m), 0.82 (8, m), 1.44 (8, m)	3.48 (12, t)
$-Si(CH_3)_2Cl$	0.68 (8, m), 0.80 (8, m), 1.58 (8, m)	0.28 (24, s)
$-Si(CH_3)_2H$	0.55 (8, m), 0.62 (8, m), 1.35 (8, m)	0.03 (24, d), 3.81 (4, m)
$-Si(CH_3)_2[CpFe(CO)_2]$	0.59 (8, m), 0.85 (8, m), 1.42 (8, m)	0.32 (24), 4.68 (20)
$-Si(CH_3)_2[C_5H_4]$	0.56 (8, m), 0.88 (8, m) 1.35 (8, m)	-0.09 (24, s) 3.40 (4, br), 6.4-6.6 (16)
$-Si(CH_3)_2CH_2Cl$	0.59 (8, m), 0.70 (8, m), 1.35 (8, m)	0.09 (24, s), 2.76 (8, s)
$-Si(CH_3)_2CH_2I$	0.55 (8, m), 0.70 (8, m), 1.35 (8, m)	0.10 (24, s), 1.99 (8, s)

Table 2.3: ^1H NMR data of various first generation dendrimers

2.3.2 (Chloromethyl)dimethylsilane functionality and its reactions

The catalytic hydrosilylation of tetraallylsilane, **G1(allyl)$_4$**, with (chloromethyl)dimethylsilane, **4**, (*Figure 2.12*) was successful using the Karstedt's catalyst[53] in THF. (Chloromethyl)dimethyl-silane[62] (**4**) is easily obtained by reduction of commercially available chloro(chloromethyl) dimethylsilane with $LiAlH_4$. The catalytic hydrosilylation reaction was followed by IR spectroscopy, monitoring the allylic C=C stretching frequency at 1618 cm^{-1}. After 72 hours of heating to reflux in THF, the mixture was worked up. The product was the desired (chloromethyl)-dimethylsilane-functionalised first generation dendrimer, **G1(CH$_2$Cl)$_4$**. ^1H NMR spectroscopy revealed that all allylic double bonds had reacted. The spectrum (*Figure 2.13*) also revealed the CH_2Cl signal at δ 2.76 and the $Si(CH_3)_2$ signal at δ 0.09, as well as the signals attributed to the tetrapropylsilane core functionality.



G1(allyl)$_4$ **4** **G1(CH$_2$Cl)$_4$**

*Figure 2.12: Synthesis of the first generation –$Si(CH_3)_2CH_2Cl$ terminated dendrimer **G1(CH$_2$Cl)$_4$***

Similarly, the catalytic hydrosilylation of allyltrimethylsilane, **G0(allyl)$_1$**, with (chloromethyl) dimethylsilane, **4**, was successful and gave 3-[(chloromethyl)dimethylsilyl]propyl-trimethylsilane, **G0(CH$_2$Cl)$_1$**, in 67 % yield. The yield was decreased during work-up due to the volatility of the disilane. The zeroth generation analogue of the (chloromethyl)dimethylsilane-terminated dendrimer was analysed satisfactorily by ^1H and ^{13}C NMR spectroscopy, as well as by IR spectroscopy, mass spectrometry and elemental analysis.

The second generation dendrimer, **G2(CH$_2$Cl)$_{12}$**, was obtained in similar fashion to the first generation dendrimer, **G1(CH$_2$Cl)$_4$**, and was analysed satisfactorily using the above-mentioned techniques. The main problem encountered in the synthesis of these dendrimers was, again, to obtain full conversion of the allylic double bonds. This appeared to be difficult, even though the reaction was strongly exothermic. To moderate the exothermic process, we mixed the allylic dendrimer with the catalyst in THF and slowly added a slight excess of the silane. Heating to reflux was commenced only once the evolution of heat had subsided. Extended heating under reflux appeared to be necessary in order to react the last few percent of the allylic double bonds.

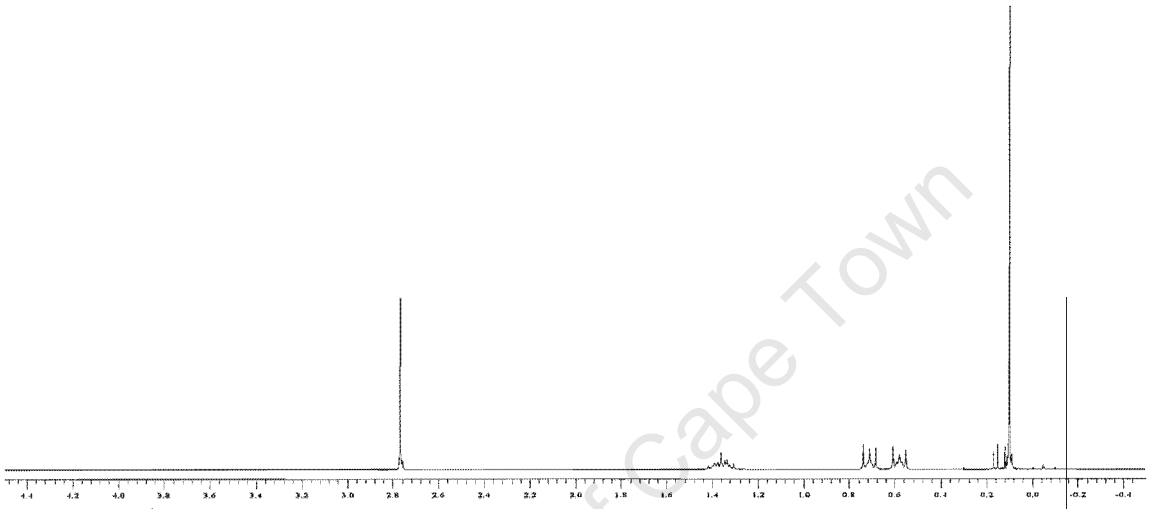


*Figure 2.13: ^{1}H NMR spectrum in CDCl$_3$ of **G1(CH$_2$Cl)$_1$***

The mass spectrum of the zeroth generation dendrimer **G0(CH$_2$Cl)$_1$** showed the parent ion and fragmentation as expected. In the mass spectrum of the first generation (chloromethyl)dimethylsilane-terminated dendrimer, **G1(CH$_2$Cl)$_4$**, no parent ion (mass 627 amu) was visible due to fragmentation in the mass spectrometer. However, a molecular mass peak cluster with the isotope pattern of a trichloro species was apparent at *m/z* = 477. The loss of a fragment of mass 150 is accounted for by the loss of one of the four branches of the dendrimer (•CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$Cl, mass 150 amu.). On the other hand, the second generation dendrimer, **G2(CH$_2$Cl)$_{12}$**, completely fragmented in the mass spectrometer and no identifiable fragments were found in the mass spectrum.

Reaction of the first generation (chloromethyl)dimethylsilane-functionalised dendrimer, **G1(CH$_2$Cl)$_4$**, with tetramethyl-cyclopentadienyllithium (Cp''Li) or -sodium in THF under reflux was not successful (*Figure 2.14*). We attributed this to the relative inertness of the chlorine on the methylene functionality. This chloro group is stabilised by the silicon atom, which removes electron density from the chloro group. However, by heating the dendrimer in dry acetone, in the presence of sodium iodide, under reflux, the chloro group was replaced by the more reactive iodo

group (*Figure 2.14*). This illustrates the relative stability of the chloro group in this compound, as generally a primary chloro group is instantaneously replaced by an iodo group at room temperature. This is a standard test for alkylchlorides:[63] primary chlorides react within 5 seconds, secondary chlorides need several minutes and tertiary chlorides need heating under reflux. The dendrimer, however, had to be heated under reflux for more than 20 minutes. The iodomethyl-substituted dendrimer, **G1(CH$_2$I)$_4$**, was easily identified by its ^{1}H NMR spectrum. A difference in the shift of the peak assigned to the CH_2X (X = Cl, I) protons, from δ 2.76 to δ 2.00, was observed in the ^{1}H NMR spectrum.

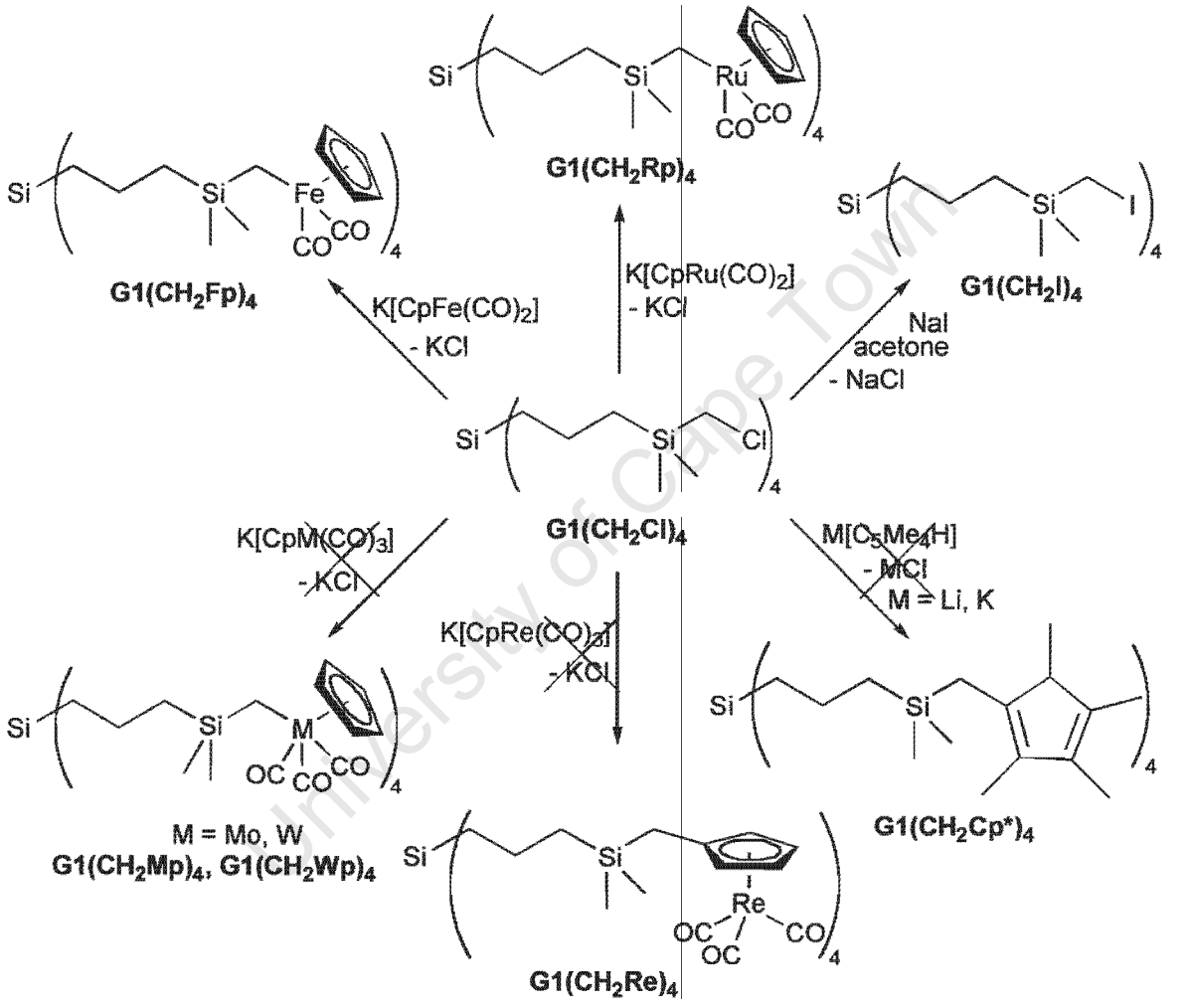


Figure 2.14: Some reactions of the first generation –Si(CH$_3$)$_2$CH$_2$Cl terminated dendrimer ***G1(CH$_2$Cl)$_4$***

Reaction of the (chloromethyl)dimethylsilane terminated dendrimer, **G1(CH_2Cl)$_4$**, with the strong cobaloxime nucleophile was not successful. This reaction was attempted under standard reaction conditions and no nucleophilic substitution occurred. Reactions with K[$CpFe(CO)_2$][64] and K[$CpRu(CO)_2$][64] were successful, and gave **G1(CH_2Fp)$_4$** and **G1(CH_2Rp)$_4$** (*Figure 2.14*). However, prolonged reaction times — at least 18 h, whereas the reaction with a 'normal' alkyl halide takes about an hour to go to completion — were needed in order to drive this reaction to completion. The reactions of K[$CpW(CO)_3$],[64] K[$CpMo(CO)_3$],[64] or K[$CpRe(CO)_3$], with the (chloromethyl)dimethylsilane-terminated dendrimer **G1(CH_2Cl)$_4$** were not successful (*Figure 2.14*). These reactions were expected to give the dendrimers **G1(CH_2Wp)$_4$**, **G1(CH_2Mp)$_4$**, and **G1(CH_2Re)$_4$**. However, these carbonyl anions appeared to be insufficiently strong nucleophiles. The reaction of these carbonyl metal anions with the iodomethyl-terminated dendrimer, **G1(CH_2I)$_4$**, are expected to be successful, but only model reactions have been performed to date.

2.4 Conclusions and future

Allyl terminated carbosilane dendrimers were prepared and analysed using the standard analytical techniques. For the sake of completeness, the synthesis and analysis were reported, though the dendrimer synthesis had been communicated previously. Allyl terminated dendrimers could be built up using both a convergent and a divergent sythesis route.

The allyl terminated dendrimers were functionalised by catalytic hydrosilylation reactions. Using this method, the dendrimers were functionalised with a $SiCl_3$, $Si(CH_3)_2Cl$, or a $Si(CH_3)_2CH_2Cl$ group. These groups were subsequently converted to other functionalities using standard reactions. It is important that these reactions run to completion, otherwise incomplete dendrimers are obtained. A formula has been reported that gives the possibility of calculating the molar fractions of incompletely functionalised dendrimers.

The chlorodimethylsilyl-functionalised dendrimer was reacted with $LiAlH_4$, CpNa, KFp and Rp3G1OH. These reactions resulted in the expected functionalisations on the dendrimers. The (chloromethyl)dimethylsilyl functionalised dendrimers were reacted with Cp''Li and Cp''Na. These reactions were, however, unsuccessful and we could not isolate a dendrimer with a Cp* functionality on the surface. In the conclusions and future section of the next chapter, we propose an alternative sythesis to the Cp*-functionalised dendrimers.

Reactions of the (chloromethyl)dimethylsilyl-functionalised dendrimers with a range of metal carbonyl anions were also performed. Only when the anions were strong nucleophiles, such as K[$CpM(CO)_2$] (M = Fe and Ru), a reaction occurred and the functionalised dendrimers were

isolated. In the case of the weaker nucleophiles, $K[CpM(CO)_3]$ (M = Mo, W and Re), no reaction or inclomplete reactions were observed.

The (chloromethyl)dimethylsilyl terminated dendrimers were reacted with NaI in acetone under reflux conditions to give the (iodomethyl)dimethylsilyl terminated dendrimers. The iodo group is more reactive than the chloro group. The reaction of these dendrimers with the metal anions $[CpM(CO)_3]$ has not been performed yet, but it is expected to result in the metal carbonyl-functionalised dendrimers. Several preliminary reactions (not reported here) indicated that these metal carbonyl anions can react with the (iodomethyl)trimethylsilane.

Chapter 3

Synthesis, characterisation and derivatives of lithiated dendrimers

3.1 Introduction

In order to attach a suitable zirconocene moiety to a dendrimer, it appeared to be necessary to generate lithiated dendrimers. The considerations for generating these dendrimers were:

- Blocking of possibilities of β-hydrogen elimination
- Electronically stabilising the compound

On the basis of these two considerations we developed a route to di-alkyl zirconocenes that allow selective activation. The development of the zirconocene chemistry is described in Chapter 4. In this chapter we will describe how we developed the formation of polylithiated dendrimers on the basis of the above considerations.

There are two principal options for the introduction of a metal atom into an organic moiety. One of them is to use another organometallic reagent as a carrier for the metal M. This metal (typically Li, Na, K) is exchanged for a mobile electrofugal group Z in the target molecule, and Z is transferred metathetically to the reagent. This reaction is a versatile and convenient route to the formation of 'carbanionic' reagents, most of the time generated as intermediates. This reaction is called permutational interconvertion.

$$R_3C\text{-}Z + M\text{-}R' \longrightarrow R_3C\text{-}M + Z\text{-}R'$$

The most straightforward and rational approach is, however, a direct replacement of the leaving group Z by reaction with elemental metal, in a reductive replacement reaction.

$$R_3C\text{-}Z + 2\,M \longrightarrow R_3C\text{-}M + Z\text{-}M$$

In either category, the favourite leaving groups Z are hydrogen, the halogens, and metalloids such as mercury and tin. The standard procedures for the preparation of organometallic species are based on the replacement of such elements. These methods are complemented by the more restricted methods that involve the cleavage of carbon-oxygen, carbon-sulfur, or carbon-carbon bonds.

In summary, the most used methods are:

- The replacement of halogen by lithium or lithium base
- Cleavage of ethers and thioethers by lithium or lithium base
- Replacement of hydrogen by lithium or lithium base
- Replacement of a metal by lithium or lithium base

Few organic compounds containing two or more lithium atoms have been reported in the literature up to now.[65] Most of the known triply, quadruply or multiply metallated molecules are either those of the tetralithiomethane[66] type, or are polylithiated alkenes, arenes or π-stabilised systems (for example $LiCHPh\text{-}SiMe_2\text{-}CHPhLi$[67]). The polylithium* compound in *Figure 3.1* is the first known triply metallated organic compound in which the metallated carbon atoms are not stabilised by π-systems.[68]

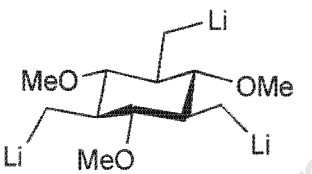


Figure 3.1: The first trilithiated compound[68]

Polylithiated compounds have great synthetic potential as multifunctional building blocks, but were not available, mainly due to lack of appropriate synthetic routes. Also, decomposition of polylithioalkanes by β-elimination of lithium hydride (e.g. 1,3-dilithiopropane decomposes at –60 °C to allyllithium)[69] hinders their preparation and isolation.

3.2 Deprotonation of allyl-terminated dendrimers

The first reactions we tried in an attempt to obtain lithiated dendrimers were based on the reported deprotonation reaction of allyltrimethylsilane[70] by Schlosser's superbase (a combination of n-butyllithium and potassium *tert*-butoxide). We decided to generate allyl-type organoalkali metal species, as these can be prepared with particular ease via deprotonation reactions.[71] Allyl-type organopotassium compounds are most attractive species for organic synthesis. They do not only offer regioselectivity, but also provide stereocontrol. The stereocontrol can be brought about in two ways. Either the original configuration of the alkene precursor may be delivered, via the allylpotassium reagent, unchanged to the final product; or one may allow torsional equilibration at

* The illustrations of mono- and polylithiated compounds are not indicative of the real structures of these compounds in solution or in the solid state. Instead, they reflect the structures on the basis of their reactivities.

the stage of the organometallic intermediate. The equilibrium of the reaction lies in general strongly towards the *exo* side, as shown in *Figure 3.2*.

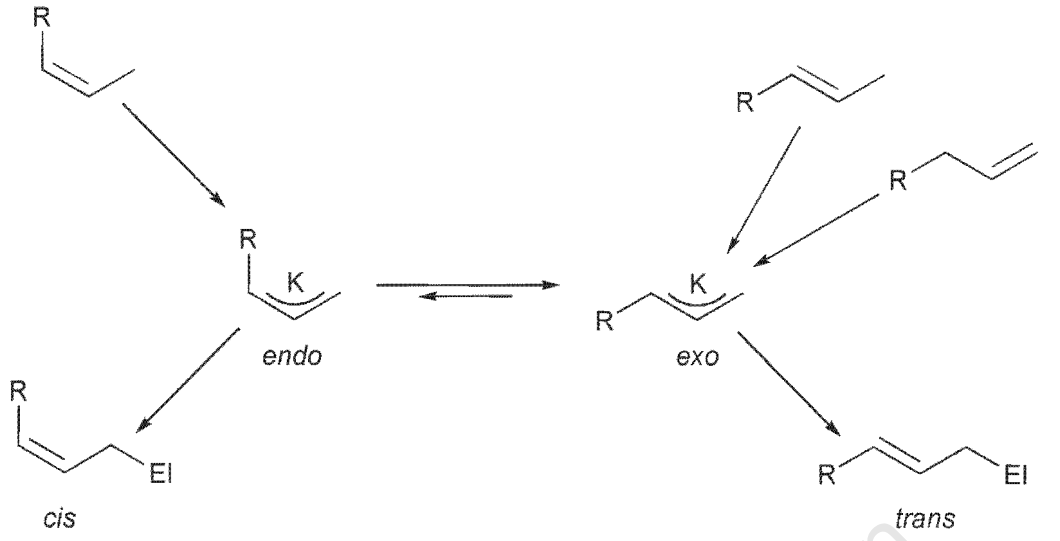


Figure 3.2: Cis-trans *isomerisation of allylpotassium reagents and their products*

Schlosser's superbase appeared to be the reagent of choice for the metallation of allylic silanes. Besides allyltrimethylsilane,[70] silanes such as *cis*- and *trans*-2-butenyltrimethylsilane,[72] *cis*- and *trans*-2-hexenyltrimethylsilane,[72] trimethyl-2-methylallylsilane, [73] butoxydimethyl-2-methylallylsilane[73] and (diisopropylamino)dimethyl-2-methylallylsilane[73] have been deprotonated using Schlosser's base.

Upon deprotonation of allyltrimethylsilane, **G0(allyl)$_4$**, by Schlosser's base in hexane/diethyl ether, a faint yellow solution formed. This solution was quenched with chlorotrimethyl silane, upon which a large amount of white solid precipitated. After aqueous work-up, ^{1}H and ^{13}C NMR spectroscopy revealed that $(CH_3)_3SiCH{=}CHCH_2Si(CH_3)_3$, **5**, had formed (*Figure 3.3*). It was clear from the spectra that a single isomer had formed, and the coupling constant of 18.3 Hz indicated that the *trans*-isomer had formed selectively.[74] The yield of 100 % indicated that the reaction was a fast, selective and complete reaction.

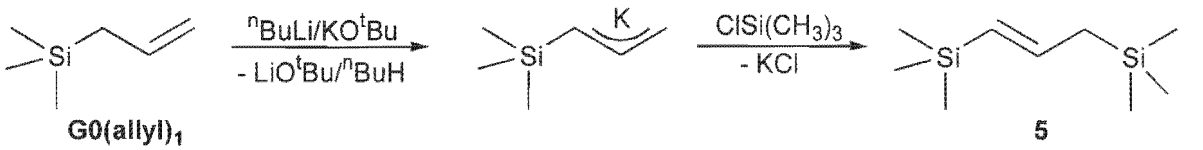


Figure 3.3: Deprotonation of allyltrimethylsilane, ***G0(allyl)$_4$***

These results indicated that it might be possible to deprotonate allyl-terminated dendrimers using the same reaction. The reaction was repeated with **G1(allyl)$_4$**, the first generation allyl terminated dendrimer, and 5 equivalents of Schlosser's base. The mixture was quenched, after 3.5 hours at room temperature, with D_2O. After work-up, however, it appeared that approximately 43 % of the allyl groups had isomerised, as was concluded from ^1H and ^{13}C NMR spectra. The isomerised groups have a coupling constant of 18 Hz, i.e. they are the *trans*-isomers. Upon repeating the reaction and quenching after 16 h at room temperature, the amount of isomerised allyl-groups increased to 61 %. Even heating to reflux for 16 hours did *not* increase the percentage of isomerised (and therefore metallated) allyl funtionalities to over 81 %. With a convertion of 81 %, a product distribution as given in *Table 3.1* is expected on the basis of the formula on page 27. These experiments reveal that it is difficult to completely deprotonate allyl-terminated dendrimers (*Figure 3.4*).

G1(allyl)$_4$

Figure 3.4: Deprotonation and deuteration of the first generation dendrimer

Product	%
$Si(CH=CHCH_2D)_4$	43
$(CH_2=CHCH_2)Si(CH=CHCH_2D)_3$	40
$(CH_2=CHCH_2)_2Si(CH=CHCH_2D)_2$	14
$(CH_2=CHCH_2)_3Si(CH=CHCH_2D)$	2
$(CH_2=CHCH_2)_4Si$	0.1

Table 3.1: Theoretical product percentages in a mixture of G1 dendrimers with 81 % conversion of the functionalities

A possible explanation for this behaviour has been given in the literature. 1,5-Hexadiene reacts five times faster than 1-hexene with Schlosser's superbase in tetrahydrofuran (THF), resulting in the formation of the corresponding allyl-type organopotassium compounds. The acceleration suggests an extra co-ordination of the metal by the 'passive' second ene-moiety. In THF, the reaction of 1,ω-dienes, having moderate chain lengths, stops cleanly at the monometallation; even if the reagent is employed in large excess. In contrast, the dimetallated species of 1,5-hexadiene is formed preferentially when the reactants are suspended in hexane. This selectivity is observed even when less than stoichiometric amounts of Schlosser's base are used.

The monometallation products probably form a mixed aggregate with unconsumed superbase in hydrocarbon media. Within this aggregate, the second hydrogen-metal interconversion can be accomplished at a much faster rate than the first one (*Figure 3.5*). This reactivity has been observed with 1,ω-dienes with chain lengths of up to 11 carbon atoms.

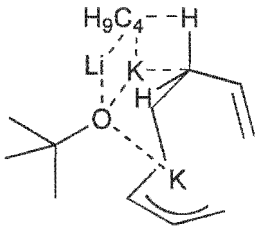


Figure 3.5: Postulated mixed aggregate of super-base and 1,7-octadiene

Following these arguments, it might be reasonable to propose that the large mixed-metal aggregate proves sterically too bulky to accommodate the closely placed four allyl groups of the fisrt-generation dendrimer. Therefore, it might be argued that double deprotonation of **G1(allyl)$_4$** is fast, resulting in a dipotassium compound. The resulting lithium-*tert*-butoxide might then co-ordinate to the potassium in an ether-like fashion, resulting in an aggregate large enough to sterically block the protons on the remaining allyl groups (*Figure 3.6*). This would also explain why the degree of deprotonation increases with time and temperature.

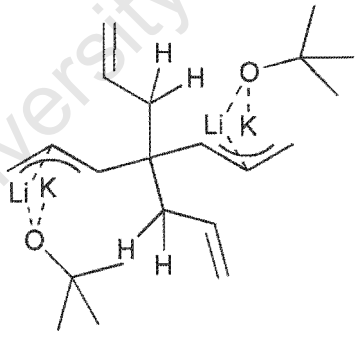


Figure 3.6: Proposed aggregate of Schlosser's base with tetraallylsilane, ***G1(allyl)$_4$***

Taking the above into consideration, we decided to try and deprotonate tetraallylsilane, **G1(allyl)$_4$**, with a combination of n-butyllithium and *N,N,N',N'*-tetramethylethylenediamine (TMEDA). The added TMEDA polarises the carbon-metal bonds and thus facilitates the deprotonation reaction. Before that, TMEDA breaks up the butyllithium hexamers into far more reactive, smaller units, mainly dimers. These two effects taken together provide powerful activation of the *n*-butyllithium

reagent, as well as sufficiently small, sterically less-hindering reactants. Lappert and co-workers[75] have recently deprotonated diallylsilanes using this combination of n-butyllithium and TMEDA.[75]

Upon addition of four equivalents of *n*-butyllitium to a mixture of one equivalent of **G1(allyl)$_4$** and four equivalents of TMEDA in pentane, a white solid precipitated slowly over a period of 16 hours. The reaction mixture was quenched with excess chlorotrimethylsilane and worked-up in a similar way to the previous attempts. ^{1}H and ^{13}C NMR revealed, however, that once again the tri-metallated species was present in the reaction mixture. The conclusion we draw from this experiment is that even the TMEDA-stabilised allyllithium branches in the dendrimer are probably sterically too demanding to allow deprotonation of the last allyl group.

3.3 Silylmethyllithium-terminated dendrimers

As mentioned above, the dendrimer and model compound must be stabilised against unwanted side-reactions after reaction with the zirconocenes, such as subsequent β-hydrogen or β-methyl elimination. We therefore decided on $RSiMe_2CH_2Li$ as the 'monomer-unit', resulting in the model compound $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_2CH_2Li$, **G0(CH$_2$Li)$_1$**, and the first-generation lithiated dendrimer $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Li]_4$, **G1(CH$_2$Li)$_4$**. The added advantage of the dimethylsilyl group is that the generated lithium reagent is stabilised by the silicon atom.[76] The model compound **G0(CH$_2$Li)$_1$** (*Figure 3.7*) was conveniently synthesised from the zeroth generation chloride dendrimer, $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_2CH_2Cl$, **G0(CH$_2$Cl)$_1$**, by reductive replacement with lithium in diethyl ether at 0 °C. The compound **G0(CH$_2$Li)$_1$** was generated and used *in situ*. A description of this reaction is reported in chapter 4. No attempts to isolate **G0(CH$_2$Li)$_1$** have been made. After reaction of the lithium reagent, separation from the (possible) dimeric side-product was readily achieved by washing the product with pentane. The reaction of the model chloride **G0(CH$_2$Cl)$_1$** with lithium metal to form **G0(CH$_2$Li)$_1$** was performed in diethyl ether. The synthesis of the well-known $(CH_3)_3SiCH_2Li$[77] (**6**) is performed in pentane if isolation of the lithium reagent is desired.

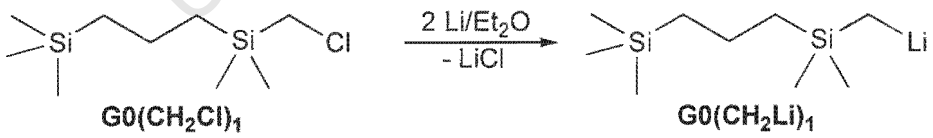


*Figure 3.7: Synthesis of the model compound **G0(CH$_2$Li)$_1$***

Reaction of **G1(CH$_2$Cl)$_4$**, the first-generation chloride dendrimer $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Cl]_4$, with metallic lithium in diethyl ether did show the formation of a white precipitate. The white solid was separated from the colourless solution by filtration. When the solution was quenched with water and titrated against acid, however, there appeared to be no alkaline compounds, i.e. no

active lithium reagent was present. Upon removal of the solvent, only $Si[CH_2CH_2CH_2Si(CH_3)_3]_4$, **G1(CH$_3$)$_4$**, was recovered, as concluded from ^1H and ^{13}C NMR spectroscopy (*Figure 3.8*). It appears that the corresponding lithium reagent had formed, partly or completely; and subsequently reacted to form the observed trimethylsilyl-terminated dendrimer, **G1(CH$_3$)$_4$**. There is a possibility that the (partly) lithiated dendrimer reacted with the solvent, diethyl ether.[71] No attempts were undertaken to analyse the white precipitate.

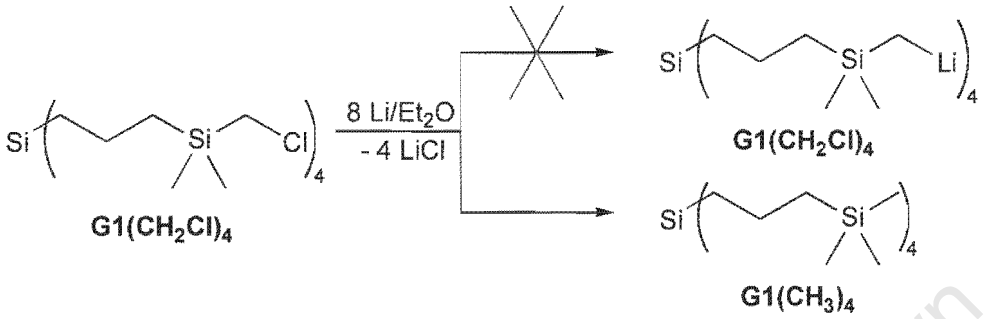


*Figure 3.8: Reaction of **G1(CH$_2$Cl)$_4$** with metallic lithium*

It is highly unlikely that deprotonation of the produced $Si[CH_2CH_2CH_2Si(CH_3)_3]_4$, **G1(CH$_3$)$_4$**, would lead to the generation of the desired lithiated dendrimer. Peterson[78] reported in 1967 that deprotonation of tetramethylsilane and n-butyltrimethylsilane was possible with n-butyllithium activated by TMEDA. This reaction, however, gave yields of 36 % and 46 % after 3 and 4 days! It is clear from this report[78] that full deprotonation of $Si[CH_2CH_2CH_2Si(CH_3)_3]_4$, **G1(CH$_3$)$_4$**, would be more than likely to fail.

3.3.1 Lithiated dendrimers generated *in situ*

For the synthesis of known di(lithiomethyl)silanes, a limited number of reports are available in the literature. The synthesis of di(lithiomethyl)dimethylsilane from di(chloromethyl)dimethylsilane and metallic lithium has a reported yield of 30 % as a consequence of elimination of LiCl after mono-metallation.[79] A high-yield synthesis of LiCHPh-$SiMe_2$-CHPhLi was reported by Akkerman and Bickelhaupt.[80] This preparation is based on the reductive cleavage of the C-S bonds of PhSCHPh-$SiMe_2$-CHPhSPh with lithium. Subsequently, a recent report by Strohmann and co-workers described the high yield synthesis of a series of di(lithiomethyl)silanes[81] and tetra(lithiomethyl)silanes[82] by reductive cleavage of C-S bonds with lithium dihydronaphthylide.

Following this method, the dendrimer $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5]_4$, **G1(CH$_2$SPh)$_4$**, was synthesised. This dendrimer is accessible via catalytic hydrosilylation of tetraallylsilane, **G1(allyl)$_4$**, with the known $HSi(CH_3)_2CH_2SC_6H_5$[83], **7**, (*Figures 3.9* and *3.10*). Due to the high stability of the (phenylthiomethyl)dimethylsilane, **7**, (distilled at 109 °C/vac), the hydrosilylation

reaction could be run at 120 °C, leading to reaction times of approximately 2 hours. The first generation dendrimer, **G1($CH_2SPh)_4$**, was isolated by distilling off the excess **7**, followed by filtration. Yields are typically around 95 % for all generation dendrimers.

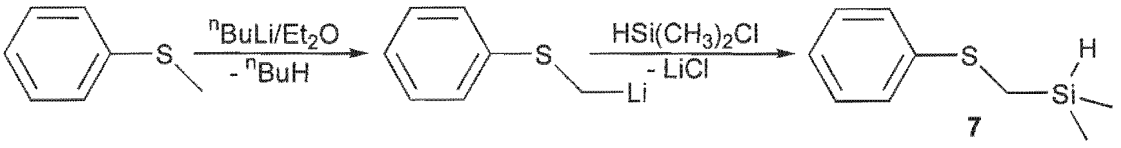


Figure 3.9: Synthesis of (phenylthiomethyl)dimethylsilane, ***5***[83]

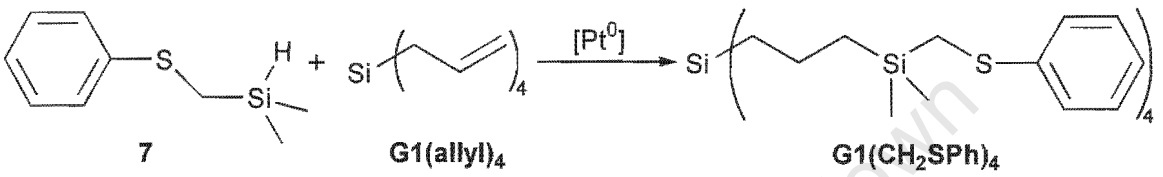


Figure 3.10: Synthesis of ***G1($CH_2SPh)_4$***

Initial reaction of the phenylthiomethyl-terminated first-generation dendrimer **G1($CH_2SPh)_4$** with a slight excess of lithium dihydronaphthylide ($LiC_{10}H_8$) at –41 °C, followed by quenching with chlorotrimethylsilane, showed the main characteristics of this reaction. The reaction proceeded rapidly and completely to give the desired deuterated dendrimer $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2D]_4$, **G1($CH_2D)_4$**, as concluded from the ^1H and ^{13}C NMR spectrum of the product after isolation. Besides the deuterated dendrimer, however, four equivalents of DSC_6H_5 were formed, as well as eight equivalents of naphthalene! Removal of the malodorous thiol was achieved by washing the product with dilute aqueous base, and the naphthalene was removed by repeated column chromatography. The repeated chromatography, however, reduced the yield of final product to 9 %. The NMR spectra confirmed, however, that full conversion had taken place. The signals attributable to the different branches appeared at the same chemical shift, confirming that full conversion had, indeed, taken place.

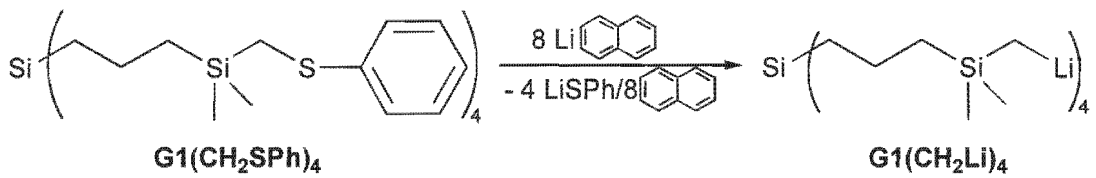


Figure 3.11: Reaction of ***G1($CH_2SPh)_4$*** *with lithium dihydronaphthylide*

The generation of both non-polar alkanes and carbosilanes through reductive lithiations has led to various separation problems being described in the literature.[84] Several approaches to solve this problem have been applied,[84] such as sublimation, crystallisation followed by chromatography, and steam-distillation. The major drawback of these techniques is their inappropriateness for dealing with air- and moisture-sensitive products. We unsuccessfully tried using a catalytic amount of naphthalene. After several attempts we formulated a successful system. in this system approximately 25 mol% naphthalene is used, in solution, with an excess of lithium at 0 °C. The dendritic phenylthiomethyl compound is added slowly, making sure there is always the green/blue colour of the lithium dihydronaphthylide present in solution. The reaction has to be run at the relative high temperature of 0 °C in order to maintain a reasonable rate of regeneration of lithium dihydronaphthylide. These reactions take about 1 hour to run to completion. Fortunately, the generated lithium reagent is stable enough in THF to 'survive' for this time.

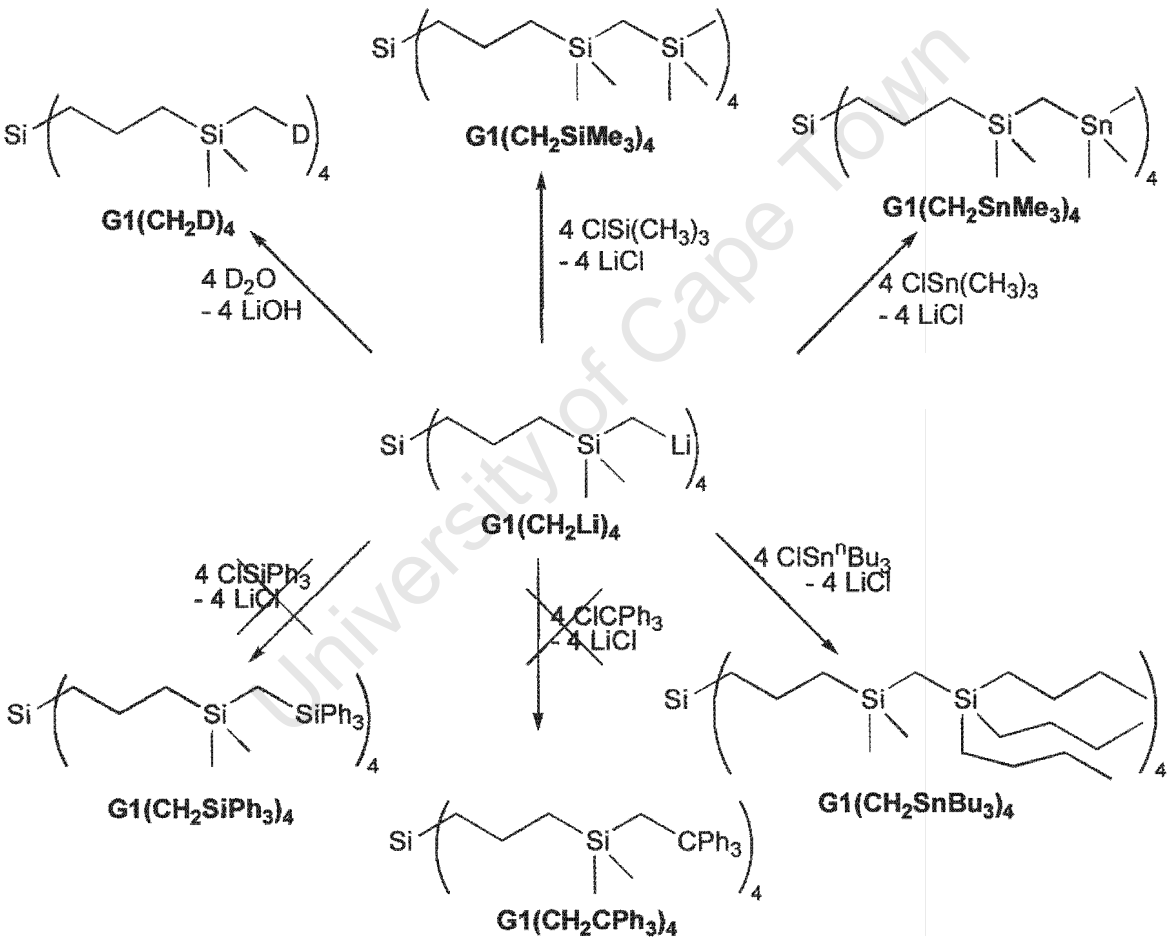


Figure 3.12: Reactions of the first generation lithiated dendrimer

The dendritic lithium reagent $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Li]_4$, **G1(CH$_2$Li)$_4$**, was analysed by quenching the *in situ* formed reagent with D_2O, $ClSi(CH_3)_3$, $ClSn(CH_3)_3$, or

$ClSn(CH_2CH_2CH_2CH_3)_3$ (*Figure 3.12*). The products were separated from the salts formed, by extraction into hexane. Separation from the thiol HSC_6H_5 — formed by hydrolysis from $LiSC_6H_5$ — was achieved by washing the hexane solution with dilute aqueous base. Drying under vacuum at ±150 °C removed most of the naphthalene. The resulting mixture contained ~ 90 % of the desired dendrimer and was purified by column chromatography over silica gel, eluting with hexane. The generated dendrimers, $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2D]_4$ (**G1(CH_2D)$_4$**), $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Si(CH_3)_3]_4$ (**G1(CH_2SiMe_3)$_4$**), $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Sn(CH_3)_3]_4$ (**G1(CH_2SnMe_3)$_4$**), and $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Sn(CH_2CH_2CH_2CH_3)_3]_4$ (**G1(CH_2SnBu_3)$_4$**) (*Figure 3.12*) were analysed satisfactorily by ^1H, ^{13}C and ^{29}Si NMR spectroscopy, and by mass spectrometry and elemental analysis.

The second generation (phenylthiomethyl)-terminated dendrimer, **G2(CH_2SPh)$_{12}$**, was synthesised using the same methodology of hydrosilylating the C=C double bond. Reaction of the second generation dendrimer, **G2(CH_2SPh)$_{12}$**, with lithium dihydronaphthylide resulted in the formation of the second generation lithiated dendrimer, **G2(CH_2Li)$_{12}$** — as was concluded from the formation of the second generation tributyltin-terminated derivative, **G2(CH_2SnBu_3)$_{12}$**, after quenching with $ClSn(CH_2CH_2CH_2CH_3)_3$. Satisfactory data for this second generation dendrimer was obtained. To our knowledge, these are the first examples of lithiated dendrimers; and the second generation dendrimer is the largest lithium reagent reported up to now. Strohmann and coworkers[82] have reported a lithium reagent with up to four lithium atoms in its structure, and it is conceivable that yet larger structures can be synthesised using this methodology.

The radical anion-induced reductive metallation of phenylthioethers appears to be a general method for the lithiation of dendrimers. It is a very easy and quick method, provided that the final product is unreactive towards the side-products of the reaction ($LiSC_6H_5$, $C_{10}H_8$ and lithium dihydronaphthylide) and that a work-up involving column chromatography is possible. The above discussion shows, however, that it is difficult to isolate the lithiated dendrimer itself using this route, or to use the lithiated dendrimer for the synthesis of air-sensitive compounds.

3.3.2 Isolation of lithiated dendrimers

With these considerations in mind, we investigated a slightly different route, starting from the above-mentioned tributyltin-terminated dendrimer. Alkyltributyltin compounds are known to be convenient precursors for the generation of alkyllithium reagents via permutational metal-metal exchange.[85] In general, the organo-element/lithium (element = B, Se, Sn, Sb, Te, Hg, Tl, Pb and Bi) exchange reactions proceed in a clean and quick fashion. The following features are common to this type of reactions:[86]

i) The reactions usually proceed rapidly, even at low temperatures.

ii) These reactions are equilibrium reactions; therefore, good yields are only achieved when the negative charge in the organolithium compound that is formed is stabilised better than in the lithium-reagent.

iii) The exchange takes place only in the case of elements having valence electron shells that can be expanded to a decet, necessary for the formation of the intermediary ate-complexes.* The exchange takes place easier with fourth- and fifth-row elements than with second- and third-row elements.

The permutational tin-lithium exchange reaction was initially reported by Peterson[87] to be unsuccessful for the synthesis of trimethylsilylmethyllithium in hexane, the addition of TMEDA resulting in a yield of ca. 25 % after 24 hours. In 1980, however, Seitz and Sapata[88] reported the high yield (>90 %) synthesis of trimethylsilylmethyllithium (**6**) from (trimethylsilylmethyl)tributyltin and butyllithium in THF. The side product of the reaction, tetrabutyltin, can easily be removed by extraction into hexane.

$$(CH_3)_3SiCH_2Sn^nBu_3 + {}^nBuLi \longrightarrow (CH_3)_3SiCH_2Li + Sn^nBu_4$$

Following this method,[88] we attempted the synthesis of 'clean' $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Li]_4$, **G1(CH$_2$Li)$_4$** (*Figure 3.13*). A solution of $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Sn(CH_2CH_2CH_2CH_3)_3]_4$, **G1(CH$_2$SnBu$_3$)$_4$**, in THF was treated with 4.0 equivalents of *n*-butyllithium at 0 °C (*Figure 3.14*). The yellow mixture slowly decolourised. After 30 minutes the solvent was evaporated and the mixture of a white solid and a clear liquid was extracted with pentane. ^{1}H NMR spectroscopy on the isolated solid product in benzene-d^6/THF-d^8 indicated that the lithiated dendrimer had formed. The resonances due to the tributyltin moiety had disappeared and a singlet at *ca.* –1.8 ppm, integrating for 8 protons, was evident. This signal was attributed to the CH_2Li moiety in the dendrimer. The value of –1.8 ppm is in accordance with literature values for trimethylsilylmethyllithium (**6**).[78, 89, 90] The rest of the spectrum showed the normal resonances for a first generation dendrimer, with triplets at 0.7 and 0.8 ppm and a multiplet at 1.3 ppm for the propyl chain, as well as a singlet at 0.03 ppm attributable to the dimethylsilyl group (*Figure 3.13*). Further evidence for the formation and isolation of the lithiated dendrimer was provided by quenching NMR samples with D_2O and $ClSi(CH_3)_3$. After quenching, ^{1}H NMR spectra identical to those obtained from the previously isolated $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2D]_4$, **G1(CH$_2$D)$_4$**, and $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Si(CH_3)_3]_4$, **G1(CH$_2$SiMe$_3$)$_4$**, were observed.

* These lithiumpentaalkyl stannate complexes have been spectroscopically observed: H.J. Reich and N.H. Phillips, *J. Am. Chem. Soc.*, 1986, **108**, 2102.

It is important in these reactions that *exactly* four equivalents of butyllithium are used, as any excess of butyllithium co-aggregates with the dendrimer upon work-up. It is subsequently not possible to separate the aggregated butyllithium from the lithiated dendrimer. Also, any excess butyllithium can form lithium pentabutylstannate by reaction with the formed tetrabutyltin. This compound can also not be separated from the lithiated dendrimer and gives rise to difficulty in the analysis of the product.

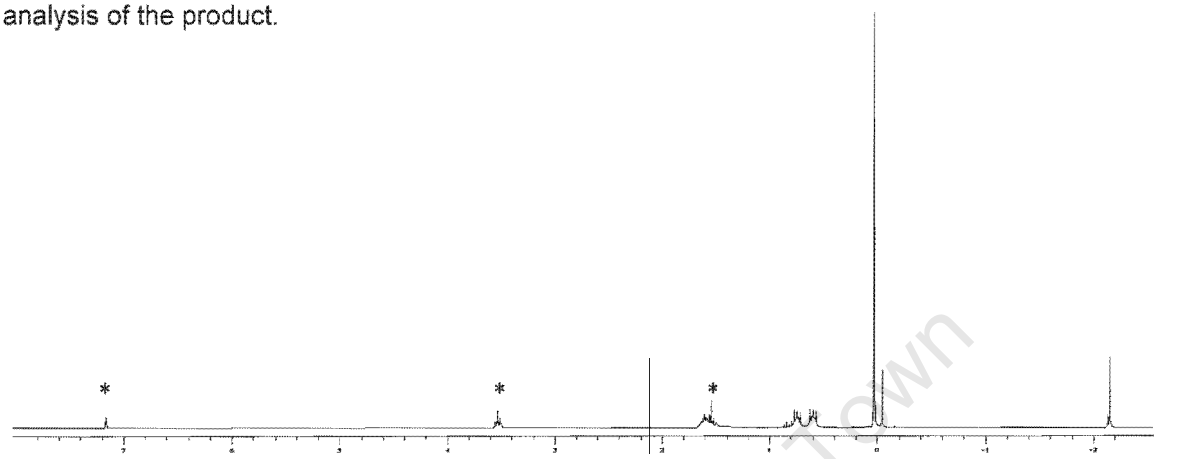


*Figure 3.13: ^{1}H NMR spectrum of **G1(CH$_2$Li)$_4$** in C_6D_6/THF-d8, * denotes protio impurities in the solvent*

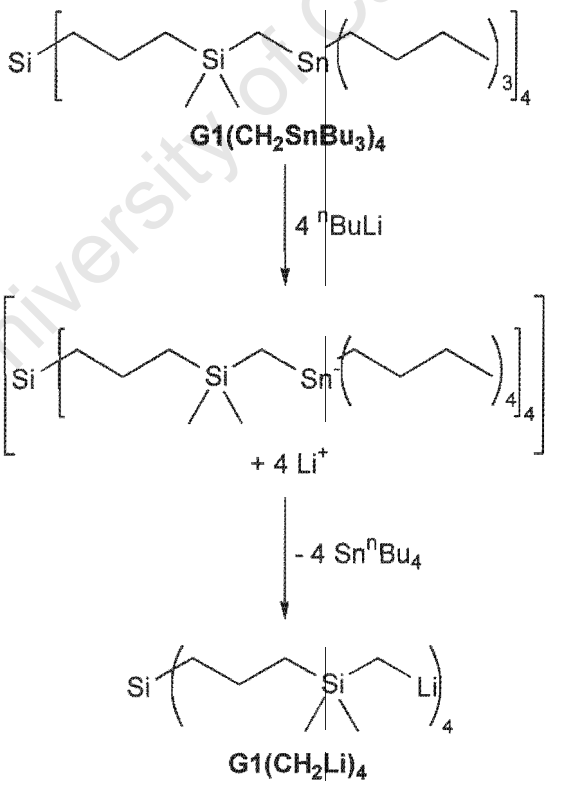


*Figure 3.14: Synthesis of lithiated dendrimer **G1(CH$_2$Li)$_4$***

The pyrophoric dendrimer is insoluble in pentane, benzene and diethyl ether. This behaviour can be rationalised through the observation that trimethylsilylmethyllithium, **6**, does not exist as a monomer (as initially reported by Connolly and Urry),[89] but rather as higher-number aggregates. Trimethylsilylmethyllithium (**6**) behaves as a normal alkyllithium species in solution, i.e. it forms electron-deficient polymeric species.[90] At the same time, the steric effect of the trimethylsilyl-group is evident, in that (**6**) is a tetramer rather than the hexamer in benzene[90] and in 2-methylpentane solution.[91] For normal alkyllithium reagents (ethyl-, *n*-butyl-, *iso*-propyl-, *tert*-butyl and trimethylsilylmethyllithium) in pure hydrocarbon solvents, there is '... no evidence for a degree of aggregation lower than *fourfold*'[92] (my emphasis). Upon addition of organic bases such as diethyl ether, THF, or triethylamine, the hexameric organolithium reagents dissolve as tetrasolvated tetramers. Data given for lithiomethyltrimethylsilane, **6**, and triethylamine[92] suggests that for this reagent the normal behaviour applies.

In the light of the above literature data on trimethylsilylmethyllithium, **6**, it is not surprising that the dendritic lithium reagent is insoluble in pentane and benzene. The difficulty of solubilising the dendritic lithium reagent in diethyl ether is also explained. In order to dissolve, the aggregation of the groups around the lithium atoms needs to dissociate, otherwise crosslinking would prevent dissolution.

We also attempted the synthesis of the di-methyllithiosilane $Me_2Si(CH_2Li)_2$. For the synthesis of this compound we attempted the same route, already used for the litiated dendrimers. Reaction of two equivalents of phenylthiomethyllithium with one equivalent of dichlorodimethylsilane gave the expected bis(phenylthiomethyl)dimethylsilane.[81] This compound could then be converted to the bis(tributyltinmetthyl)dimethylsilane following the procedure described for the phenylthiomethyl terminated dendrimers.

After reacting this compound with two equivalents of n-butyllithium, only the mono-lithiated silane was observed in the 1H NMR spectrum. An inseparable mixture of n-butyllithium, the stannylated silylmethyllithium, and tetrabutyltin was obtained. It was reported by Kauffmann[86] that the stannyl/Li exchange reaction of $Me_2Si(CH_2SnPh_3)_2$ with PhLi exclusively gives the mono-exchanged product. No further attempts at the synthesis of di(lithiomethyl)silanes

Attempts at the synthesis of $Si[CH_2CH_2CH_2Si(CH_3)(CH_2SC_6H_5)_2]_4$ and $Si[CH_2CH_2CH_2Si(CH_2SC_6H_5)_3]_4$ and, via these, at $Si[CH_2CH_2CH_2Si(CH_3)(CH_2Li)_2]_4$ and $Si[CH_2CH_2CH_2Si(CH_2Li)_3]_4$, were hampered by difficulty in isolating the di- and tri(phenylthio-methyl)silanes $HSi(CH_3)(CH_2SC_6H_5)_2$ and $HSi(CH_2SC_6H_5)_3$. These silanes could be synthesised by the reaction of two and three equivalents of $LiCH_2SC_6H_5$ with the appropriate chlorosilane. The

silanes could also be identified in the crude reaction mixture by ^{1}H-NMR spectroscopy. However, the boiling point of these silanes at 10^{-3} mm Hg appeared to be around 200 °C. At this temperature, a redistribution reaction occurs with silanes, which resulted in a mixture of $HSi(CH_3)(CH_2SC_6H_5)_2$, $H_2Si(CH_2SC_6H_5)_2$, $H_3Si(CH_2SC_6H_5)$ and $Si(CH_3)_2(CH_2SC_6H_5)_2$, as was concluded from the ^{1}H NMR spectrum of the product. Column chromatography of the silanes resulted in hydrolysis of the sensitive Si-H bond, resulting in siloxanes. Separation via crystallisation did not work either, since the silanes were both oils at –40 °C. We did not attempt to synthesise these tetrakis[di(phenylthiomethyl)silane]- and tetrakis[tri(phenylthiomethyl)silane]-dendrimers further.

3.4 Conclusions and future

Our attempts at the synthesis of lithiated dendrimers is described in this chapter. The initial reaction of Schlosser's superbase with allyltrimethylsilane, **G0(allyl)$_1$**, was successful and gave, after quenching the reaction, the expected product. The reaction with the first generation allyl terminated dendrimer **G1(allyl)$_4$**, however, did not give full deprotonation of the four allyl groups. A maximum of 81 % of allyl groups could be deprotonated, resulting in a mixture of compound that contains only 43 % of the appropriate product.

We then turned our attention to the reductive cleavage reaction of C-S bonds. Hydrosilylation of allyl terminated dendrimers with $HSi(CH_3)_2CH_2SC_6H_5$, **7**, was successful and gave the corresponding phenylthiomethyl terminated dendrimers. These dendrimers could be reacted with excess lithium dihydronaphthalyde to give the lithiomethyl-terminated dendrimers. A number of model reactions were performed with **G1(CH$_2$Li)$_4$**. One of the products of these model reactions was the tributyltin-terminated dendrimer **G1(CH$_2$SnBu$_3$)$_4$**.

The tin-terminated dendrimer **G1(CH$_2$SnBu$_3$)$_4$** could be reacted with four equivalents of n-butyllithium to give a mixture of **G1(CH$_2$SnBu$_3$)$_4$** and tetrabutyltin. The dendrimer **G1(CH$_2$SnBu$_3$)$_4$** was positively identified by ^{1}H and ^{13}C NMR. The second generation dendrimer was synthesised using the same methodology.

The lithiated dendrimers can be used as building blocks for a number of organometallic dendrimers. As mentioned in chapter 2, the synthesis of Cp* functionalised dendrimers was not successful. Functional groups can be introduced during the synthesis of Cp* and its derivatives by reacting the intermediate tetramethylcyclopentenone with the appropriate alkyllithium or alkyl Grignard reagent.[93] This route opens up the possibility of reacting an excess of tetramethyl-cyclopentenone with the *in situ* generated lithiated dendrimer to form Cp* functionalised dendrimers.

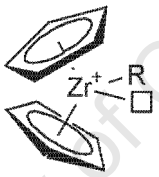
The synthesis of di(lithiomethyl)silanes by the stannyl/lithium exchange reaction was not successful. It is possible to observe these lithiated silanes by NMR spectroscopy when they are synthesised from the tellurium-derivative.[81, 82] Tellurium is more electronegative than tin, therefore the telluride/lithium exchange reaction is faster, and the equilibrium lies more to the side of the product. It is anticipated that the appropriate dendrimers can be synthesised by hydrosilylating the allyl terminated dendrimers with $HSi(CH_2TeBu)_2$, The product from this reaction can then be subjected to telluride/lithium exchange reactions to give the lithiated dendrimer.

Chapter 4

Mononuclear zirconocenes, related compounds and their activation reactions

4.1 Zirconocene precursors

Polymerisation catalysts of Group 4 metallocenes are purported to be cationic metallocenes containing one alkyl or hydride ligand and a vacant co-ordination site (*Figure 4.1*). Numerous reports on the generation of cationic Group 4 metallocenes for polymerisation of alkenes are available.[16] These reports have one thing in common: the starting materials are *symmetric* Group 4 metallocenes of the type Cp_2MR_2 (Cp = η^5-C_5H_5 or derivative thereof; M = Ti, Zr, Hf; R = Cl, H, CH_3). The zirconocenes attached to a dendrimer, however, would be *asymmetric* zirconocenes of the type Cp_2ZrRR' (Cp = η^5-C_5H_5; R = Cl, CH_3; R' = dendrimer). The goal of the present research was to obtain an active polymerisation catalyst attached to a dendrimer. Attachment of a neutral zirconocene to the dendrimer, followed by selective activation of the zirconocene, appeared to be the most straightforward method of achieving this.



R = H, -CH_3, polymer; A^- = counter-ion

□ = vacant co-ordination site

Figure 4.1: Cationic zirconocene, active in the polymerisation of 1-alkenes

In order to investigate whether a zirconocene can be selectively activated after attachment to a dendrimer, we decided to study the behaviour of mononuclear model compounds first. In this way, the properties of the compounds and the reactions of the metallocenes attached to a dendrimer might be predicted. We were specifically interested in looking at the following aspects:

i) Ease of reaction: e.g., it is necessary for the reactions to be fast and clean in order to obtain pure dendritic zirconocenes.

ii) Selectivity of activation: after attachment of the zirconocene to the dendrimer, it would not be useful if, upon activation for a catalytic reaction, the zirconocene disconnected from the supporting dendrimer.

iii) Clean reactions: dendritic zirconocenes are expected to be highly air- and moisture-sensitive compounds; therefore, simple purification procedures are essential to minimise handling (and hence decomposition) of the compounds.

As described in Chapter 1, a metallocene can be attached to a dendrimer in three different ways (*Figure 4.2*). We define these as:

i) σ-bound: the zirconocene is bound to the dendrimer via a σ-bond between the zirconium and the organic group.

ii) π-bound: the zirconocene moiety is bound to the dendrimer through one of its Cp ligands.

iii) *ansa*-bound: in case of an *ansa*-metallocene, the bond between the dendrimer and the zirconocene is on the bridge between the two Cp ligands.

A fourth possibility, a bond between the dendrimer and the zirconocene *via* a η^3-allyl group, is not useful as the η^3-allyl group would deactivate the zirconocene for polymerisation reactions.

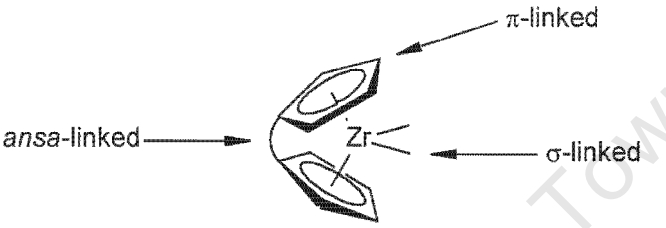


Figure 4.2: Ways in which a zirconocene can be linked to dendrimers

The aim of the research is to bind Group 4 metallocenes through the σ-link (*Figure 4.2*), thereby creating a metal-to-dendrimer bond. Various strategies are available for linking Group 4 metallocenes to organic groups.[94] Some of the strategies are:

- Salt elimination or salt metathesis reactions: in these reactions an alkyl-metal reagent (typically a lithium or Grignard reagent) reacts with a Zr-Cl bond to form an alkyl-zirconium bond.
- Hydrometallation: the direct insertion of a carbon-carbon double bond into a Group 4 hydride.
- Alcoholysis: the reaction of a Group 4 metal-alkyl bond with an alcohol to form a Group 4 alkoxide.

The alcoholysis reaction is not useful as it introduces a metal to heteroatom bond, which de-activates the system for future polymerisation reactions (this feature has been used to observe co-ordination of alkenes to cationic zirconocenes).[95] On the basis of this argument, we decided to investigate the hydrometallation reaction and the salt elimination reaction in order to determine whether they could lead to the required complexes.

4.2 Hydrometallation reactions

Schwartz's reagent, $[Cp_2Zr(H)Cl]_n$, **9**, is a well-known reagent in organic synthesis for the functionalisation of alkenes.[96] The compound is commercially available, but the well-documented synthesis is both easy and fast to perform. Schwartz's reagent (9) is synthesised by reducing zirconocene dichloride, **8**, with $LiAlH_4$ in THF.[97] After reaction of four equivalents of Cp_2ZrCl_2, **8**, with $LiAlH_4$ in THF, a mixture of Schwartz's reagent, **9**, and zirconocene dihydride forms (*Figure 4.3*). Washing this mixture with dichloromethane, converts the zirconocene dihydride to zirconocene hydrochloride, **9**. It is essential that this washing is done rapidly, as the dichloromethane slowly converts **9** back into **8**.

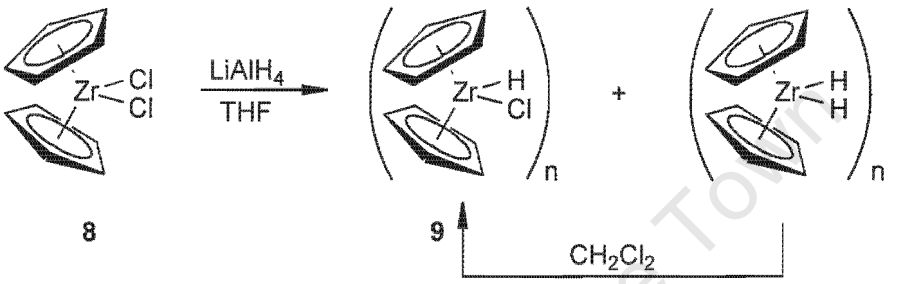


Figure 4.3: Synthesis of Schwartz's reagent

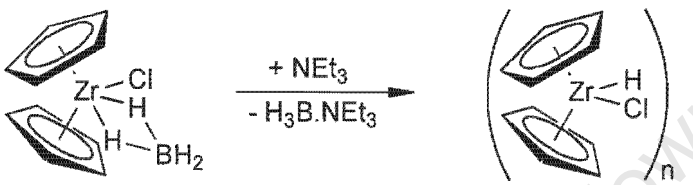
In order to obtain the hafnium analogues of these compounds, $[Cp_2Hf(H)Cl]_n$, **10**, was synthesised. The hafnium analogues of cationic zirconocene complexes are assumed to be less reactive than the zirconium species — leading to a stabilisation of the activated complexes towards β-H elimination reactions. The polymeric $[Cp_2Hf(H)Cl]_n$, **10**, precipitated instantaneously in the reaction of Cp_2HfCl_2 with $LiAlH_4$ in THF at 0 °C.[98] The product thus obtained was then used for hydrohafnation reactions. Neither hydrometallation reagent is soluble in common organic solvents due to their oligomeric character.[99] $[Cp_2Hf(H)Cl]_n$ (**10**) is, like $[Cp_2Zr(H)Cl]_n$ (**9**), highly moisture and oxygen-sensitive. However, whereas the $[Cp_2Zr(H)Cl]_n$, **9**, was slightly light sensitive, $[Cp_2Hf(H)Cl]_n$ showed no sign of decomposition during prolonged exposure to light. The titanium analogue of these compounds was not synthesised, as it is known to be thermally unstable.

Alternative synthesis

We used an alternative route to obtain crystalline zirconocene chlorohydride, **9**. Though the reagent has been used extensively in organic synthesis, no structure determination has been performed on the compound. This is mainly due to the oligomeric nature of the reagent, which results in an amorphous powder during formation. The alternative route we used, employs the well-known abstraction of BH_3 from a BH_4 group on zirconium by triethylamine.

The starting material, $Cp_2Zr(BH_4)Cl$, **11**, was conveniently synthesised through the redistribution reaction of Cp_2ZrCl_2 (**8**) and $Cp_2Zr(BH_4)_2$ in THF. ^1H and ^{13}C NMR spectroscopy revealed that pure $Cp_2ZrCl(BH_4)$, **11**, was isolated after recrystallization. Attempts to react the appropriate stoichiometric amounts of $LiBH_4$ and Cp_2ZrCl_2 (1:1) resulted in the formation of the bis(borohydride) in reduced yield.

We mixed $Cp_2ZrCl(BH_4)$, **11**, with triethylamine in THF (*Figure 4.4*). Slowly, a white precipitate formed. Some crystalline material was obtained, through this new route to Schwartz's reagent, **9**, but these crystals were not suitable for X-ray diffraction.



11 **9**

Figure 4.4: Alternative synthesis of Schwartz's reagent

Analysis

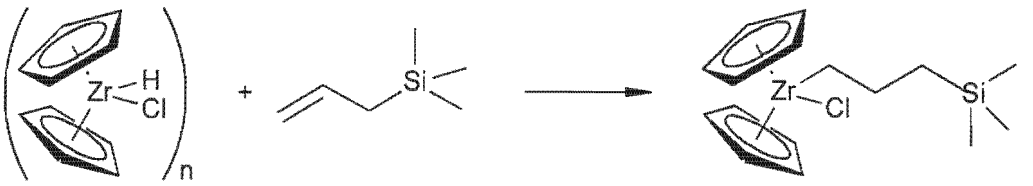
Both Schwartz's reagent, **9**, and its hafnium analogue **10** are insoluble in normal organic solvents. Therefore, the purity of these two reagents was determined by reacting them with an excess of dry, degassed acetone, resulting in the formation of mononuclear, soluble, chloroisopropoxy zirconocene. The zirconocene dihydride reacts with acetone to form diisopropoxy zirconocene, which can be distinguished in the ^1H and ^{13}C NMR spectra from the chloroisopropoxy zirconocene (see Experimental Chapter).

4.2.1 Hydrometallation of allyltrimethylsilane

The product of the hydrozirconation reaction with allyltrimethylsilane, **G0(allyl)$_1$**, (*Figure 4.5*) in toluene resulted in a clear yellow oil which was very soluble in common organic solvents and highly oxygen- and moisture-sensitive. The analogous hydrohafnation product is a colourless oil and exhibits the same behaviour. The products were purified by extraction into pentane, leaving the pure $(CH_3)_3SiCH_2CH_2CH_2(Cp_2MCl)$ (M = Zr: **G0(ZrCl)$_1$**, Hf: **G0(ZrCl)$_1$**) after evaporation of the pentane. Both products are thermally stable and can be stored for a long period (several months) under an inert atmosphere at room temperature without apparent decomposition.

Hydrozirconation of allyltrimethylsilane (**G0(allyl)$_1$**) was also performed in benzene, THF, and CH_2Cl_2. This resulted in the same product, as was concluded from ^1H and ^{13}C NMR spectroscopy, and by chemical derivation. The products from hydrozirconation or hydrohafnation

appeared to be the expected hydrometallation complexes $(CH_3)_3SiCH_2CH_2CH_2(Cp_2MCl)$ (M = Zr, Hf). The reaction in THF was faster than the reaction in benzene, due to the more polar character of the solvent. This resulted in better solubility of the reactive $Cp_2Zr(H)Cl$ monomer because of solvent co-ordination. Reaction in CH_2Cl_2 was even faster; but a competitive reaction of zirconocene hydrochloride with dichloromethane to form zirconocene dichloride (**8**) also occurred in this solvent, resulting in a lower yield.[97]



9 **G0(allyl)$_1$** **G0(ZrCl)$_1$**

Figure 4.5: Hydrozirconation of allyltrimethylsilane, ***G0(allyl)$_1$***

In order to gain additional information about the product of the hydrozirconation reaction, several derivatives were made. The hydrozirconation product of allyltrimethylsilane, **G0(allyl)$_1$**, was reacted with bromine: after the appropriate work-up, the organic product appeared to be 1-bromopropyl-3-trimethylsilane; as was concluded from ^{1}H NMR spectroscopy. After reaction of the hydrozirconation product with iodine in THF, the inorganic product was isolated. This appeared to be a mixture of zirconocene diiodide,[100] zirconocene dichloride (**8**) and zirconocene iodochloride,[101] as was concluded from ^{1}H NMR spectroscopy. We did not attempt to isolate the organic product

4.2.2 Attempted activation reactions

Neutral Group 4 metallocenes are not active catalysts in the polymerisation reaction of 1-alkenes. It is therefore necessary to activate these compounds for polymerisation. In our model system, we showed that hydrozirconation of allyltrimethylsilane, **G0(allyl)$_1$**, was successful. In order to activate the hydrozirconation product, it was necessary to abstract the chloride from $(CH_3)_3SiCH_2CH_2CH_2(Cp_2ZrCl)$, **G0(ZrCl)$_1$**.

A simple but key realisation in the development of cationic Group 4 metallocene chemistry[102] was the fact that non-coordinating, non-reactive counterions such as $[B(C_6H_5)_4]^-$ and $[CH_3B(C_6F_5)_3]^-$ were required for the formation of active catalysts. Anions such as $CF_3SO_3^-$ and BF_4^- either co-ordinate strongly or react with $[Cp_2M(R)]^+$ (R = alkyl, aryl) or $[Cp_2M(R)(THF)]^+$.[102, 103] A useful reagent for the activation of zirconocene species is $[Cp'_2Fe][B(C_6H_5)_4]$ (Cp' = η^5-$C_5H_4CH_3$), **12**, which is thermally stable and reacts with Cp_2ZrR_2 (R = $-CH_3$, $-CH_2C_6H_5$) complexes in THF, CH_2Cl_2 and toluene. A major disadvantage of this reagent is that it does not react with

$Cp_2Zr(R)Cl$. $Ag[B(C_6H_5)_4]$, **13**, is effective only in 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.[102, 103]

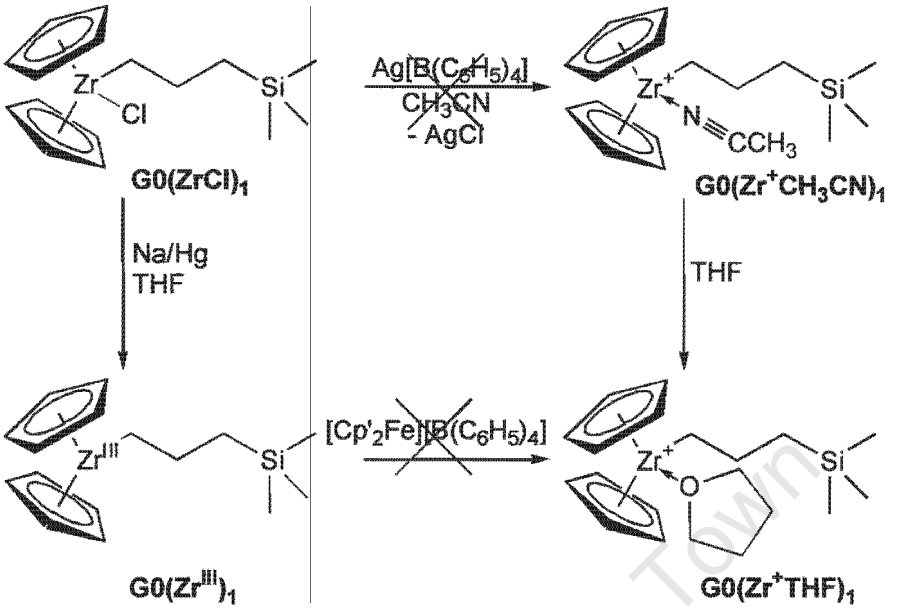


Figure 4.6: Mononuclear model complex and several possible activation routes through chloride abstraction

Chloride abstraction

One of the promising routes to selective activation of zirconocene alkylchlorides is the abstraction of chloride with Ag^+, displacing the chloride with the weakly co-ordinating $[B(C_6H_5)_4]^-$. The reaction with $Ag[B(C_6H_5)_4]$, **13**, was reported to be successful only in the strongly co-ordinating acetonitrile.[102, 103] We repeated the literature reaction of $Cp_2Zr(CH_3)_2$, **14**, with $Ag[B(C_6H_5)_4]$, **13**. This resulted in the reported cationic zirconocene complex $[Cp_2ZrCH_3(NCCH_3)_2][B(C_6H_5)_4]$. However, after reaction of the compound $(CH_3)_3SiCH_2CH_2CH_2(Cp_2ZrCl)$, **G0(ZrCl)$_1$**, with $Ag[B(C_6H_5)_4]$, **13**, no evidence for the cationic zirconocene complex was observed in the ^1H NMR spectrum. The crude reaction mixture showed a signal attributable to the phenyl groups of $B(C_6H_5)_4^-$, but the integration of that signal was too small. The signal attributed to the phenyl rings may be due to slight solubility of $Ag[B(C_6H_5)_4]$, **13**, in deuterated acetonitrile. After crystallisation, an unidentified Zr(IV) species was present. Jordan and Echols[104] have reported that the reaction of Cp_2ZrCl_2 (**8**)with two equivalents of $Ag[B(C_6H_5)_4]$, **13**, was unsuccessful. They repeated the reaction with Cp_2ZrI_2 and this resulted in the dicationic zirconocene $[Cp_2Zr(CH_3CN)_3][B(C_6H_5)_4]_2$.[104] This reaction suggested that it might be useful to exchange the chloride for an iodide in the model compound $(CH_3)_3SiCH_2CH_2CH_2(Cp_2ZrCl)$, **G0(ZrCl)$_1$**.

However, upon reacting $(CH_3)_3SiCH_2CH_2CH_2(Cp_2ZrCl)$, **G0(ZrCl)$_1$**, with boron triiodide, only zirconocene diiodide was observed in the ^1H and ^{13}C NMR spectra.

Alkylation followed by alkyl abstraction

One of the alternative routes to activate the mononuclear system of the type Cp_2ZrRCl is the methylation of the complex with one equivalent of methyl Grignard or methyllithium reagent; followed by methyl abstraction by $B(C_6F_5)_3$[105] in benzene.[106] In our experiments, it appeared that the product of the reaction of $(CH_3)_3SiCH_2CH_2CH_2(Cp_2ZrCl)$, **G0(ZrCl)$_1$**, with MeMgI or MeLi was thermally very unstable and the product could only be handled at or below –20 °C, provided it was used within 1 day. This observation is consistent with the reported instability of the alkene insertion product of zirconocene dihydride[107] and with the decomposition of the Cp_2ZrCl_2/BuLi system (Negishi system)[108] to give 'zirconocene' (Cp_2Zr). Above –20 °C, the $Cp_2Zr(CH_3)$-$CH_2CH_2CH_2Si(CH_3)_3$, **G0(ZrMe)$_1$**, decomposed to form a dark, blue-purple zirconium(II) complex. This complex was not further analysed as it was insoluble in most common solvents. It is reported in the literature that the alkene insertion products of zirconocene dihydride decompose to form 'Cp_2Zr(II)', alkene and alkane.[107] After reacting the hydrozirconation product with MeLi at –20 °C, the product was reacted with $B(C_6F_5)_3$ at –20 °C. This yielded a mixture of $[Cp_2ZrCH_2CH_2CH_2Si(CH_3)_3]^+[MeB(C_6F_5)_3]^-$, G0($Zr^+$) and $[Cp_2ZrCH_3]^+[(CH_3)_3SiCH_2CH_2CH_2$-$B(C_6F_5)_3]^-$, as was concluded from the ^1H and ^{13}C NMR spectra (*Figure 4.7*).

The trimethylsilane group in $(CH_3)_3SiCH_2CH_2CH_2(Cp_2MCl)$ does not stabilise the β-hydrogen on the Zr-propyl group. This is necessary to prevent decomposition of the dialkylzirconocene. It was anticipated, that the hydrozirconation product of vinyltrimethylsilane could result in a complex that was stabilised, due to the close proximity of the trimethylsilane moiety. However, upon hydrozirconating vinyltrimethylsilane, the product showed multiple trimethylsilane resonances in the ^1H NMR spectrum and a signal with two satelites at δ 4.35. The latter chemical shift is typical for a silicon hydride. Presumably, some reaction involving the trimethylsilane group occurs, resulting in a Si-H bond. This line of research was consequently not pursued.

It is possible that there is not enough steric hindrance from the trimethylsilyl-propyl group to cause selective abstraction of the methyl group. We anticipated that alkylation resulting in the weakest known Zr-C bond, followed by selective abstraction, would be an alternative route. It has been reported[109] that the one-electron oxidation of $Cp_2Zr(CH_3)(CH_2C_6H_5)$ by $[Cp'_2Fe][B(C_6H_5)_4]$ resulted in the selective formation of $[Cp_2ZrCH_3]^+$. Also, the bond-dissociation energy of the Zr-$CH_2C_6H_5$ bond is reported[110] to be the lowest of the Zr-C bonds, i.e. the Zr-$CH_2C_6H_5$ bond is the weakest zirconium-alkyl bond reported in literature. Therefore, we attempted to activate the reaction product of $Cp_2Zr(Cl)CH_2CH_2CH_2Si(CH_3)_3$, **G0(ZrCl)$_1$**, and $K(CH_2C_6H_5)$.[111] The synthesis

of $Cp_2Zr(CH_2C_6H_5)CH_2CH_2CH_2Si(CH_3)_3$, **G0(ZrBz)$_1$**, was performed in toluene at –40 °C. The ^1H NMR spectrum, run at room temperature, revealed that some decomposition products were already forming.

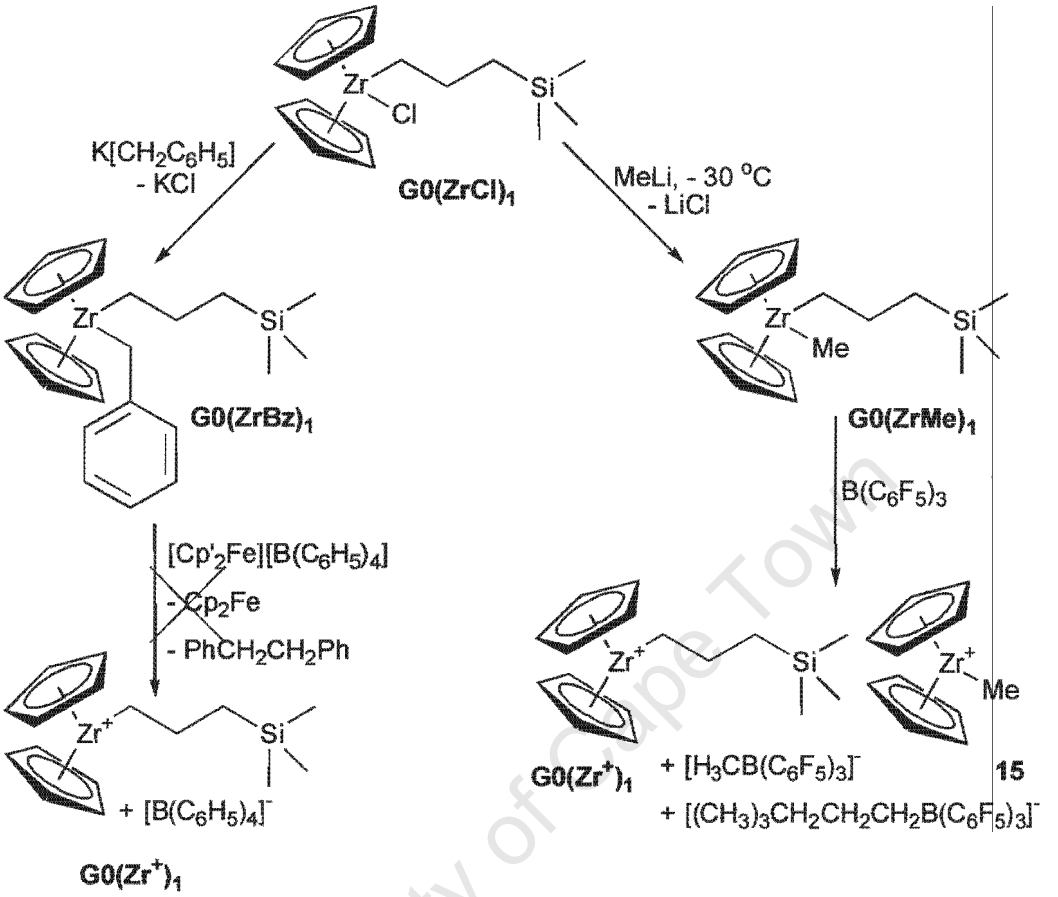


Figure 4.7: Mononuclear model complex and two possible activation routes through alkylation followed by alkyl abstraction

^1H and ^{13}C NMR spectroscopies showed that the reactions of *in situ* generated $Cp_2Zr(CH_2C_6H_5)CH_2CH_2CH_2Si(CH_3)_3$ with $[Cp'_2Fe][B(C_6H_5)_4]$, **12**, in toluene at –30 °C did not give any product after 16 hours (*Figure 4.7*). We then decided to increase the temperature of this mixture to 0 °C, and monitor whether there was any resultant reaction. After 4 hours, however, no reaction was observed (the formation of Cp'_2Fe can visually be easily observed). When heated to room temperature, a dark purple solution was observed, with a white precipitate. The dark purple compound appeared to be 'zirconocene' (Cp_2Zr). The white precipitate comprised a mixture of compounds with ^1H NMR resonances in the phenyl region, possibly a tetraphenylborate salt. After repeating the reaction with $B(C_6F_5)_3$ as activating agent, the same results were obtained, i.e. decomposition of the precursor $Cp_2Zr(CH_2C_6H_5)CH_2CH_2CH_2Si(CH_3)_3$, **G0(ZrBz)$_1$**. The conclusion drawn from these experiments is that it is not possible to activate a zirconocene compound with

two alkyl groups containing β-hydrogens. The competitive decomposition reactions of these compounds make it difficult to isolate them or even to observe the desired cationic product spectroscopically. When these zirconocenes are bound to a dendrimer, the competitive decomposition reactions of the dendrimer-bound zirconocenes are clearly undesirable.

Activation using MAO

Methylaluminoxane (MAO)[112] is the best-known agent for the activation of metal complexes in the homogeneous polymerisation of 1-alkenes. One of the major problems with MAO is that it does not have a well-defined structure, and therefore it is not clear what exactly the mechanism of activation is when using this reagent. MAO formed by controlled reaction of trimethylaluminium with water, under elimination of methane, is thought to be a mixture of oligimers.[113] The basic oligomer can associate to form cage structures. These cage structures then complex additional trimethylaluminium. Cryoscopic measurements in benzene show MAO to have a molecular mass of between 1000 and 1500 g/mol. Usually, an excess of MAO is needed, covering an Al/M ration of 400–20 000. The optimum Al/M ration depends on the metallocene used, and on the experimental conditions.[114]

The aluminoxane cocatalysts have at least two functions: alkylation of the metallocene component, which takes place within seconds, even at –60 °C; and formation of the active species by abstraction of a methyde anion (*Figure 4.8*). The resulting active species is thought to be a 14 electron cationic alkylmetallocenium ion, formed by dissociation of the metallocene aluminoxane complex.[102, 115] The [alumoxane-Me]$^-$ anion is regarded as weakly or non-coordinating.[116] Nearly every zirconocene is active, forming a single-site catalyst.[117] The created cationic zirconocene created contains a vacant co-ordination site that is available for the incoming 1-alkene. The problem in identifying these steps is that a large excess of MAO (typically 500–10 000 equivalents) is required in order to get an active polymerisation catalyst. This large excess is necessary to drive the equilibrium of the abstraction reaction towards the product: the cationic methyl zirconocene.

Assuming the above depiction of the activation to be correct, we performed a number of polymerisations with MAO as the activating agent. The idea was to abstract the newly formed methyl group by using MAO, creating a cationic zirconocene. For these polymerisations, we hydrozirconated allyltrimethylsilane, **G0(allyl)$_1$**. A known amount of **G0(ZrCl)$_1$** (typically 20 μmol) was dissolved in a small volume of toluene. This was added to a solution of MAO (400 equivalents) in toluene, after saturating the MAO solution with ethene. The polymerisation was run at 0 °C. Immediately after adding the zirconocene, a darkening of the solution was observed,

indicating that a cationic zirconocene had formed. After approximately 30 seconds, the precipitation of voluminous amounts of polyethene was observed.

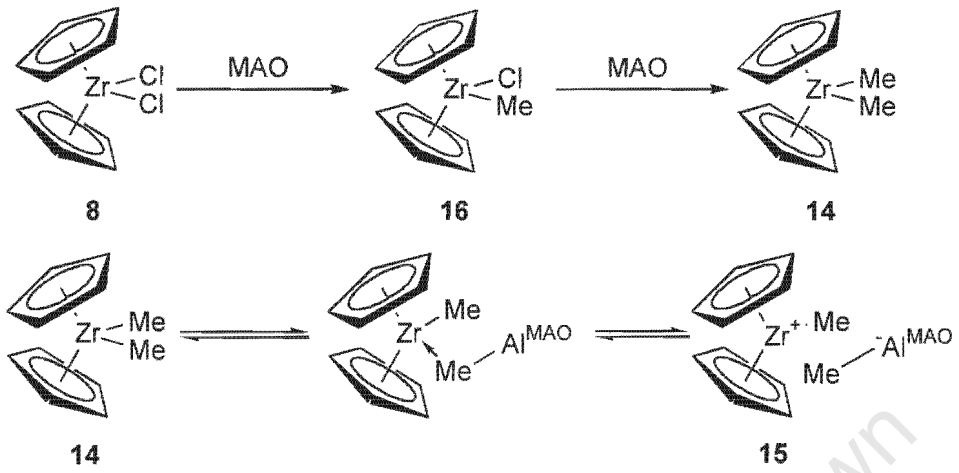


Figure 4.8: Activation reactions of metallocenes with MAO

In order to find out whether the propyltrimethylsilane unit was incorporated in the polymer, we performed the following experiment. Using the above polymerisation conditions, the reaction was quenched after 30 seconds with *iso*-propanol. Quenching of the reaction was performed at that time because up to that moment the polymeric material was still soluble. The organic products were extracted into chloroform, and analysed using ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum showed, besides the typical resonances attributable to straight-chain alkanes, a strong resonance at δ 0.07. We believe that this resonance was due to the trimethylsilyl group, thus indicating that during activation the propyltrimethylsilane was incorporated in the polymer. There is still the possibility that the propyltrimethylsilyl anion was abstracted from the zirconocene; In that case, upon quenching, propyltrimethylsilane would have been obtained. This material is, however, volatile and would have evaporated during work-up of the polymeric material.

4.3 Cationic allyl zirconocene

We were trying to define a zirconocene system that could be linked to a dendrimer *and* would be active for the polymerisation of alkenes. From this point of view, we decided to synthesise the cationic allyl zirconocene. This complex itself is not active in alkene polymerisation reactions; however, it has the potential of being linked to a dendrimer by hydrosilylation reactions, creating an active cationic complex (*Figure 4.9*).

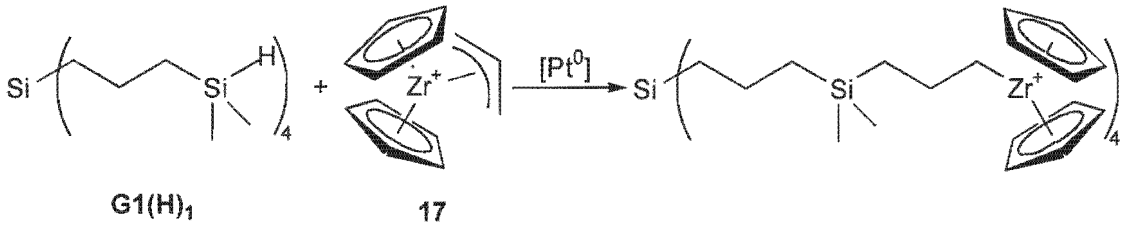


Figure 4.9: Proposed route for connecting a cationic allyl-zirconocene to a dendrimer

In order to arrive at the cationic allyl zirconocene $[Cp_2Zr(C_3H_5)(THF)][B(C_6H_5)_4]$, **17**, we reacted diallyl zirconocene[118] with $[HNBu^n_3][B(C_6H_5)_4]$, **18**, in THF at –40 °C. Instantaneous precipitation of a white solid was observed. The solid was isolated by filtration and washed with THF to remove the amine, and unreacted starting material. Spectroscopic analysis (^1H and ^{13}C NMR) of the white solid product in CD_3CN revealed that a mixture of cationic allyl zirconocenes had been isolated. Interestingly, the complexes appeared to be two different species in a 4:5 ratio of σ-bound and π-bound allyl groups (*Figure 4.10*). The formation of the two isomers of cationic allyl zirconocene was anticipated because in the starting material, diallyl zirconocene, the allyl groups are believed to be different — one allyl group is believed to be bound in a σ-fashion and the other is believed to be π-bound. These modes of bonding were concluded from IR spectroscopic studies.[118] The protonating agent either reacts with both allyl groups, having a small preference for the σ-bound group; or there is a redistribution reaction, isomerising the allyl groups after reaction.

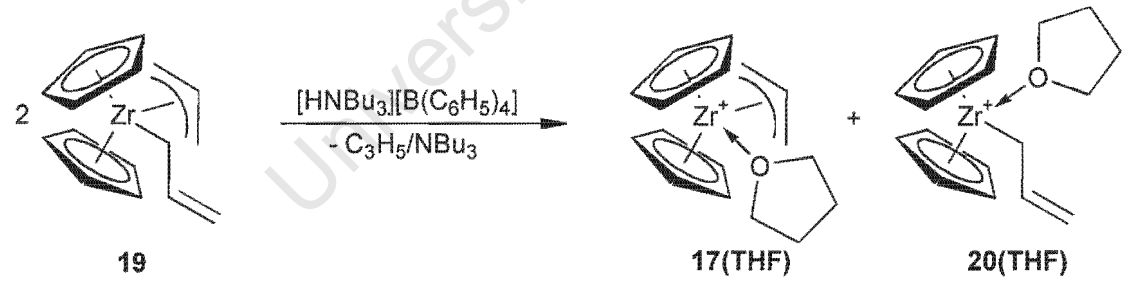


*Figure 4.10: Synthesis of cationic allyl zirconocenes **17(THF)** and **20(THF)***

The mixture of the cationic allyl zirconocene compounds **17(THF)** and **20(THF)** in THF was reacted with the first generation dimethylsilane terminated dendrimer, $Si[CH_2CH_2CH_2Si(CH_3)_2H]_4$, **G1(H)$_4$**, in an attempt to generate a tetra-zirconium species (as in *Figure 4.9*). This reaction appeared to be unsuccessful, as several products were found. These multiple products could result from β-hydrogen elimination from the hydrosilylated product, though the THF should have stabilished these products. Another possibility is the dehydrogenative polymerisation of the

dendrimers, in which case the cationic zirconocene had reacted with the available Si-H bonds after insertion. We did not pursue these reactions further, due to the side reactions mentioned above.

4.4 Sterically congested zirconocene systems

We then decided to focus on zirconocenes that do not contain any β-hydrogen atoms. As reported earlier in this chapter, dialkyl zirconocene complexes that contain β-hydrogen atoms give rise to a number of problems, including thermal instability. In addition, cationic zirconocene complexes that contain β-hydrogen atoms are likely to undergo β-hydrogen elimination reactions to give a cationic zirconocene hydride and an alkene (*Figure 4.11*).

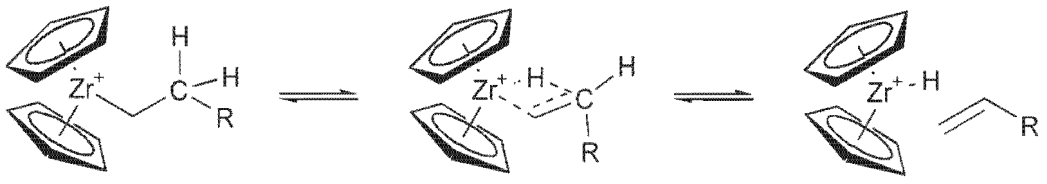
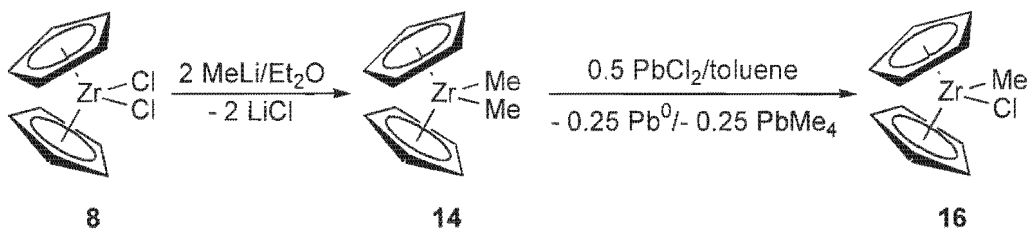


Figure 4.11: β-Hydrogen elimination reaction in a cationic alkyl zirconocene

With these considerations in mind, we decided to generate dialkyl zirconocenes that were sterically congested at the β-position. We tuned our attention to methylalkyl zirconocenes with a methyldimethylsilyl group ($-CH_2Si(CH_3)_2R$) as the alkyl group. The group R in the general formula $Cp_2Zr(CH_3)CH_2Si(CH_3)_2R$ could then be used to attach the dialkyl zirconocene to a dendrimer. The reasoning behind investigating this class of zirconocenes was that the bulky dimethylsilyl group could give selective activation after reaction with alkyl abstraction reagents such as $B(C_6F_5)_3$.[106]

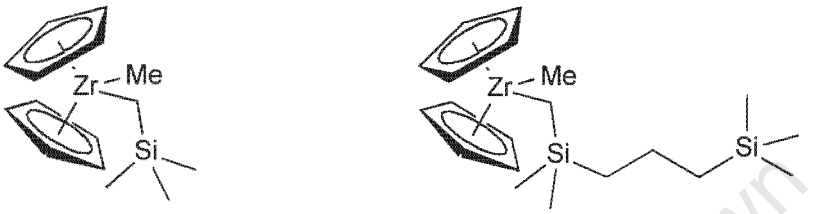
Reaction of zirconocene dichloride, **8**, with excess methyllithium in diethyl ether afforded dimethyl zirconocene, **14**,[119, 120] in 80 % yield (*Figure 4.12*). The dimethylzirconocene, **14**, was purified by sublimation, and analysed by ^1H and ^{13}C NMR spectroscopy. Reaction of dimethylzirconocene, **14**, with lead(II)chloride in toluene afforded the chloromethylzirconocene, **16**,[120, 121] in 78 % yield. This route led to a higher yield than the reaction of zirconocene dichloride, **8**, with one equivalent of methyl Grignard in dichloromethane.



8 **14** **16**

*Figure 4.12: Synthesis of chloromethylzirconocene, **16***

Reaction of chloromethylzirconocene, **16**, with one equivalent of the appropriate lithium reagents $LiCH_2Si(CH_3)_3$, **7**,[77] and $LiCH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3$, **G0(CH$_2$Li)$_1$** respectively, afforded the asymmetrically substituted zirconocenes (*Figure 4.13*) in reasonable yields (~80 %). It would have been advantageous to attach either a Si-H or an allylsilane functionality to the zirconocene. However, upon trying to convert either $ClCH_2Si(CH_3)_2H$ or $ClCH_2Si(CH_3)_2CH_2CH{=}CH_2$ into the respective lithium reagents, various side reactions occurred, such as deprotonation of the allyl group, and reaction of the produced lithium reagent with the acidic Si-H bond. It appeared to be impossible to generate either $LiCH_2Si(CH_3)_2H$ or $LiCH_2Si(CH_3)_2CH_2CH{=}CH_2$.



21 **G0(CH$_2$ZrMe)$_1$**

*Figure 4.13: Asymmetric methylzirconocenes **21** and **G0(CH$_2$ZrMe)$_1$***

Both asymmetric dialkyl zirconocene compounds were positively characterised by ^1H and ^{13}C NMR spectroscopy. Attempts to obtain satisfactory elemental analyses were not successful, due to the sensitivity of the dialkyl zirconocenes towards oxygen and water. The elemental analyses of several compounds corresponded well, however, to the oxygenated and hydrolysed products.

4.4.1 Activation of asymmetric zirconocenes

The asymmetric zirconocenes, **21** and **G0(CH$_2$ZrMe)$_1$**, (*Figure 4.13*) described above have to be activated in order to be able to polymerise alkenes. For our purposes, we required this activation to be selectively directed towards abstraction of the methyl group. The need for selective abstraction was motivated by the fact that these zirconocenes had to be attached to the dendrimer through the silyl group and that we therefore required this group to remain attached to the zirconocene.

Reaction of the model compounds (*Figure 4.13*) with excess $B(C_6F_5)_3$ resulted in the *selective* abstraction of the methyl group (*Figure 4.14*),[122] as was concluded from both ^1H and ^{13}C NMR spectroscopy. In order to conclude this, we also needed the ^1H and ^{13}C NMR data for $[Cp_2ZrCH_3]^+$, **15**, and $[Cp_2ZrCH_2Si(CH_3)_3]^+$, **22**. The Zr-C signal in the ^{13}C NMR spectra provided the clearest distinction between these two compounds. The ^{13}C signal for $[Cp_2Zr\underline{C}H_3]^+$ (**15**) was found at δ 45 whereas the ^{13}C signal for $[Cp_2Zr\underline{C}H_2Si(CH_3)_3]^+$ (**22**) appeared at δ 70. This large

difference in shift is due to the electron-withdrawing properties of the silicon atom. Analytical data pertaining to the cationic zirconocenes can be found in the Experimental Chapter.

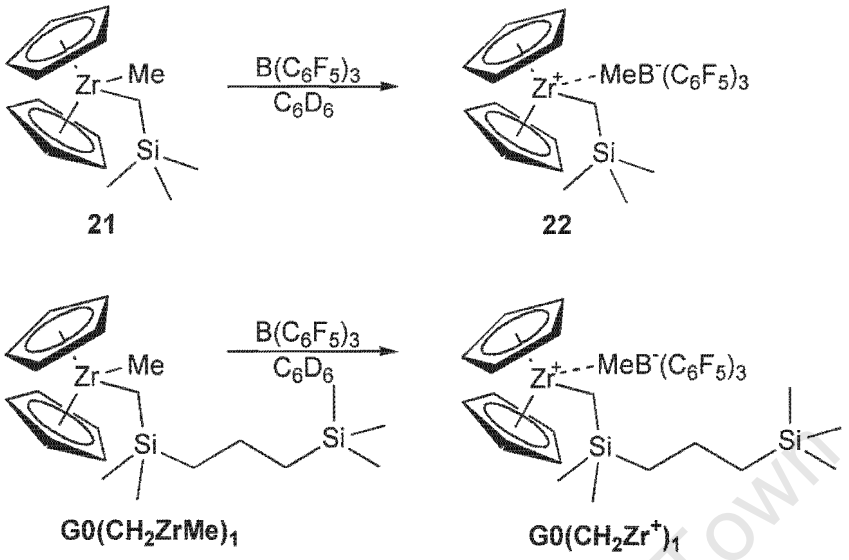


*Figure 4.14: Selective activation of the asymmetric zirconocenes **21** and **G0(CH$_2$ZrMe)$_1$***

The compound $[Cp_2ZrCH_3]^+$, **22**, was easily obtained[106] by reacting dimethylzirconocene, **14**, with an excess $B(C_6F_5)_3$ in benzene at room temperature. The yellow cationic methyl zirconocene, **15**, was formed instantaneously. As starting material for $[Cp_2Zr\underline{C}H_2Si(CH_3)_3]^+$, **22**, the reaction of zirconocene dichloride, **8**, with excess $LiCH_2Si(CH_3)_3$, **6**, was performed. The compound $Cp_2Zr[CH_2Si(CH_3)_3]_2$, **23**, was isolated as large off-white crystals after work-up.

Upon reacting $Cp_2Zr[CH_2Si(CH_3)_3]_2$, **23**, with excess $B(C_6F_5)_3$ in deuterobenzene, the formation of a yellow-brown oil was observed. Upon analysis by ^1H and ^{13}C NMR spectroscopy, it appeared that there was nothing more than a residue of starting material present in the solution. Apparently, a solvent-separated ion pair was formed — and these are known to have low solubility in benzene. When the NMR spectrum of this compound was measured in the more polar C_6D_5Br, a mixture of unidentified zirconocenes was observed, indicating that decomposition might have occurred.

The activation of the asymmetric methyl zirconocenes was, however, successful and it appeared unnecessary to have the data for the activation reaction of $Cp_2Zr[CH_2Si(CH_3)_3]_2$, **23**, for comparison. The clear difference in the ^{13}C NMR resonances, due to the alkyl groups on zirconium, made it possible to conclude that selective activation of this class of compounds was possible. The reactions of chloromethylzirconocene, **16**, with the lithiated dendrimers are

described in the next chapter, along with the hydrozirconation reactions of the various dendrimers.

4.5 Conclusions

In this chapter, the synthesis of a number of monometallic zirconocene molecules is described. Analysis of all these compounds was hampered by the unavailability of equipment to perform elemental analysis and mass spectrometry on air and moisture-sensitive compounds. We investigated zirconocenes that can be attached to a dendrimer in such a way that these zirconocenes can be activated selectively.

Initially we looked at the hydrozirconation reaction of allyltrimethylsilane, **G0(allyl)$_1$**. This gave the model compound for hydrozirconated dendrimers. Then we unsuccessfully attempted several activation reactions of **G0(ZrCl)$_1$**. These reactions can be devided into two groups:

i) direct abstraction of the chloride, and

ii) alkylation of the zirconocene, followed by abstraction of the newly formed alkyl group.

Activation of the systems was achieved, but not the desired selective activation.

We then turned our attention to asymmetric zirconocenes containing a bulky CH_2SiMe_2 group. This is in line with the previous chapter, where we reported the synthesis of lithiated dendrimers containing a $SiMe_2CH_2Li$ functionality. These zirconocene derivatives were readily synthesised from $Cp_2ZrMeCl$, **16**, and the appropriate lithium reagent. The asymmetric zirconocenes were activated by $B(C_6F_5)_3$. This reagent abstracts selectively the methyl group, indicating that the dendrimer-bound zirconocenes can be activated selectively as well.

Chapter 5

Polynuclear zirconocenes, related compounds and their activation reactions

5.1 Introduction

On the basis of the results described in the previous chapters, we decided to generate two types of polynuclear zirconium compounds:

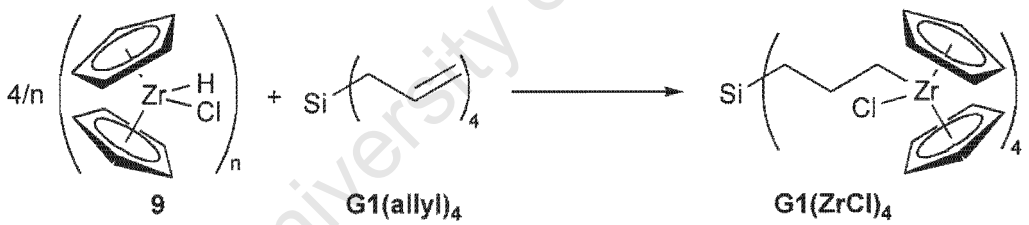
i) hydrozirconation products of the allyl-terminated dendrimers, and

ii) reaction products of the lithiomethyl-terminated dendrimers with $Cp_2ZrClMe$.

The results of these reactions are described in this chapter. The hydrozirconation products were mainly intended to be model compounds, whereas we hoped that the product of the salt-elimination reaction of the lithiomethyl-terminated dendrimers and $Cp_2ZrClMe$ would give catalyst precursors.

5.2 Hydrometallation reactions

The reaction of $[Cp_2Zr(H)Cl]_n$, **9**, with tetraallylsilane, **G1(allyl)$_4$**, (*Figure 5.1*) resulted in the tetra-insertion product $Si[CH_2CH_2CH_2(Cp_2ZrCl)]_4$, (**G1(ZrCl)$_4$**), as was concluded from ^1H and ^{13}C NMR spectroscopy.



9 **G1(allyl)$_4$** **G1(ZrCl)$_4$**

*Figure 5.1: Hydrozirconation of tetraallylsilane, **G1(allyl)$_4$***

During this reaction, a distinct solvent effect was observed. The reaction of these compounds in THF took about two hours to run to completion. The same reaction in benzene took 48 hours. This made it possible to monitor the reaction of $[Cp_2Zr(H)Cl]_n$, **9**, with **G1(allyl)$_4$**. It appeared to be possible to identify all four possible insertion products. However, upon reaction of 1 equivalent of tetraallylsilane, **G1(allyl)$_4$**, with 1 equivalent of $[Cp_2Zr(H)Cl]_n$, **9**, in benzene, a mixture of insertion products was obtained — and not just the mononuclear organometallic complex. It might be possible to obtain the mononuclear insertion product by repeating the reaction in toluene at low temperature. From the ^1H NMR spectrum of the 1:1 reaction product it can be concluded that the products do not undergo β-H elimination, as this would equilibrate to the mono-insertion product.

It can also be concluded from this spectrum that a fast ligand redistribution reaction, as reported for Cp_2ZrXY (X, Y = F, Cl, Br, I or Me), is not likely to occur.

The tetrazirconium species **G1(ZrCl)$_4$** could be isolated as a yellow, crystalline solid. However, no crystals suitable for X-ray crystallography could be obtained. This was mainly due to the reactive nature of the tetrazirconium species towards oxygen and moisture. It appeared to be not possible to grow suitable crystals inside the glovebox, mainly due to the vibrations present.

The reaction of the second generation dendrimer, **G2(allyl)$_{12}$**, with an excess of the hydrometallation reagent, $[Cp_2Zr(H)Cl]_n$, **9**, in benzene, resulted in the expected insertion products $Si\{CH_2CH_2CH_2Si(CH_2CH_2CH_2[Cp_2ZrCl])_3\}_4$, **G2(ZrCl)$_{12}$**, after 72 hours at ambient temperature. The ^{13}C NMR signals of the inner carbon atoms were hard to resolve because of the ratio of 12 carbon atoms for the outer propyl group versus 4 for the inner propyl group. Therefore, signals from the latter C atoms were not observed in the ^{13}C NMR spectrum run at 200 MHz.

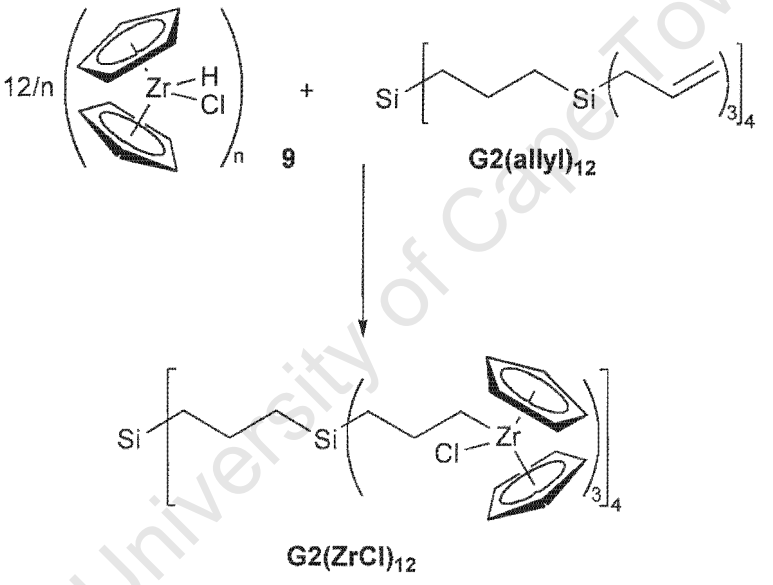


*Figure 5.2: hydrozirconation of **G2(allyl)$_{12}$***

Both the tetranuclear and the dodecanuclear zirconium compounds **G1(ZrCl)$_4$** and **G2(ZrCl)$_{12}$** were used as catalyst precursors for the polymerisation of ethene. These polymerisation reactions are described in Chapter 6: Catalytic reactions.

5.3 Reaction of lithiated dendrimers with chloromethylzirconocene

The reaction of the lithiomethyl-terminated dendrimers (described in Chapter 3) with chloromethylzirconocene, **16**, is depicted in *Figure 5.3*. This reaction, however, appeared to be more difficult than the simple depiction in this figure. The lithiomethyl-terminated dendrimer **G1(CH$_2$Li)$_4$** was generated *in situ*, by reaction of the tributyltin-derivatised dendrimer **G1(CH$_2$SnBu$_3$)$_4$** with 4 equivalents of *n*-butyllithium; and reacted with 4.1 equivalents of $Cp_2ZrMeCl$, **16**. The product was then extracted into pentane and crystallised from pentane at –30 °C. Analysis using ^1H and ^{13}C NMR spectroscopy, however, revealed large amounts of tetrabutyltin. Tetrabutyltin is supposed to be an inert liquid that freezes at –97 °C. However, after several recrystallisations of the product from pentane, significant amounts of tetrabutyltin were still observed in the NMR spectra.

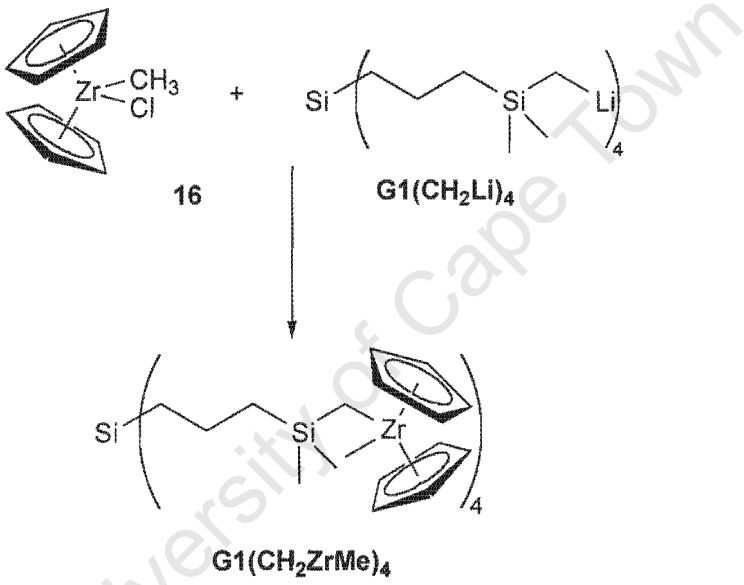


*Figure 5.3: Expected reaction of lithiated dendrimer with $Cp_2ZrMeCl$, **16***

We repeated the reaction, washing the lithiated dendrimer several times with pentane (see Chapter 3) before adding the zirconocene. This produced better analytical data. The ^1H and ^{13}C NMR spectra were consistent with the expected products. However, in all cases, peaks that could be assigned to tetrabutyltin were found in the spectra. The mixture of the tetranuclear zirconium compound and tetrabutyltin was reacted with an excess of $B(C_6F_5)_3$; yet ^1H and ^{13}C NMR spectroscopy revealed a mixture of compounds. We were not able to identify the expected tetracationic zirconium species in this mixture.

5.4 Conclusion

Polynuclear zirconium species with 4 (**G1(ZrCl)$_4$**)and 12 (**G2(ZrCl)$_{12}$**) zirconocene units on the surface of a dendrimer can be synthesised using hydrozirconation reactions. These compounds are extremely sensitive to oxygen and moisture due to the reactive Zr-C bond. These zirconocene-terminated dendrimers can be isolated as yellow, crystalline solids, but up to now we have not been able to obtain crystals suitable for X-ray crystallography.

The reactions of lithiomethyl-terminated dendrimers with $Cp_2ZrClMe$, **16**, were not satisfactory. We have come close to the goal of generating dendrimers with zirconocene moieties on the surface that can be activated selectively. However, it appeared that small amounts of impurities in the lithiomethyl-terminated dendrimers make it very difficult to isolate the reaction product.

Chapter 6

Catalytic reactions

6.1 Introduction

The importance of well-defined single-site metallocene catalysts for alkene polymerisation has been well established in the last 20 years. A major breakthrough towards industrial application of single site metallocene and related complexes for catalytic alkene polymerisation has been the discovery that methyl aluminoxane (MAO) is an excellent co-catalyst. A second key step in catalyst development has been the preparation of a wide variety of (*ansa*)-metallocenes. This opened the way to precise stereocontrol of alkene insertion during the polymerisation process.

In this chapter an exploration of the catalytic alkene polymerisation potential of the various complexes described in the previous chapters is described. The neutral complexes have been reacted with two different cation-generating species, MAO and tris(pentafluorophenyl)borane. These 'activation' reactions have been described in previous chapters, here we limit the discussion to the catalytic reactions of these 'activated' compounds. The use of allyl-terminated dendrimers as monomer and co-monomer is also described.

Early transition metal based alkene polymerisation catalysts are extremely reactive materials. They react rapidly with oxygen, water and other contaminants in the solvent and monomer feed that contain active hydrogen or contain Lewis basic components. Without proper precautions the reactivity of the catalytically active species will rapidly decrease due to the above mentioned impurities, or even no catalytic activity might be observed as the active catalyst may have been consumed before the catalytic process starts.

Rigorous removal of oxygen, water and other active contaminants from the polymerisation reactor, solvent and monomer is essential for reproducible experiments. With MAO activated catalysts this condition is realized by very large excesses of MAO, which is a very effective impurity scavenger. For borane-activated complexes the problem of removing impurities is hard to solve. In these experiments the catalyst itself acts as a scavenger and it is clear that for these systems it will be difficult to obtain reproducible data. To the borane-activated systems we added tri-octylaluminium. The trioctylaluminium acted as a general scavenger, as well as an aluminium standard to the borane activated systems. This way, the borane and the MAO activated systems were comparable, as they were having the same concentrations in both zirconium and aluminium.

6.2 Attempted polymerisation reactions of the model compound and dendrimers

In general, the polyalkenes obtained with classical or modern Ziegler-Natta catalysts are built from regular 1-alkenes. This gives apolar polymers that are sometimes difficult to be used for particular applications (*e.g.* dying or mixing with polar polymers). A commercially very attractive extension of the range of applications of polyalkenes could be realised when it would be possible to build-in polar functions at wish. (Co)polymers containing polar substituents are very promising for use in industry because of improved adhesive properties, affinity for dyes and compatibility with other polar polymers (*e.g.* polyacrylates), compared to regular polyalkenes. This area of partly functionalised polyalkenes is commercially so attractive that it seems very probable that industrial research has already focused on the oligomerisation and polymerisation of functionalised 1-alkenes. However, so far reports and patents on these polymers have scarcely been published. This may indicate the high complexity of the subject.

Early transition metal-catalysed alkene polymerisation of polar alkenes can be devided in two parts:

i) polymerisation of α,β-unsaturated ketones and esters such as acrylates[123] and caprolactones,[124] and

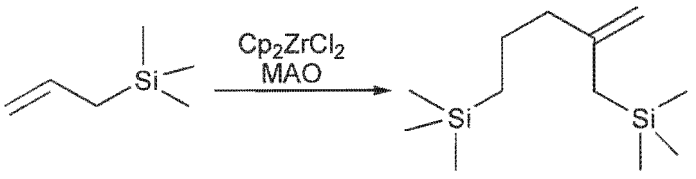
ii) polymerisation of 1-alkenes containing a protected polar function.[125]

The polymerisation of acrylates and lactones has been well-established. In general, mixtures of polymers are obtained with a very narrow molecular weight distribution. However, (co)polymerisations with functionalised 1-alkenes are still largely unsuccessful, with one exception reported by Waymouth *et al.*[125]

Here we report our findings on the use of the dendrimers as (co)monomers in the polymerisation reaction. Our initial findings were on allyltrimethylsilane, the model compound, as a monomer in the homo-polymerisation reaction catalysed by *in-situ* generated $[Cp_2ZrMe][MeB(C_6F_5)_3]$ or a mixture of Cp_2ZrCl_2 and MAO. Waymouth *et al.* Have reported that 1-alkenes containing a bulky polar functionality (tert-butyldimethylsilyloxy, diisopropylamine) can be polymerised using $[Cp^*_2ZrMe][MeB(C_6F_5)_3]$ or $[Cp^*_2ZrMe][B(C_6F_5)_4]$ ($Cp^* = \eta^5$-C_5Me_5) as catalysts.[125] Interestingly, monomers with sterically less demanding polar substituents could not be polymerised. Including a trimethylsilyl group in a polymer gives the opportunity to functionalise the polymer after polymerisation through C-Si bond cleaving reactions.

An attempt was made to polymerise allyltrimethylsilane, **G0(allyl)$_1$**. The catalyst, Cp_2ZrCl_2, **8**, was added to a mixture of 200 equivalents of allyltrimethylsilane and 400 equivalents of MAO at 0 °C. This reaction was stirred for 1 h at 0 °C and then quenched with *iso*-propanol. After aqueous

work-up, a colourless oil was recovered. This oil appeared to be the dimer of allyltrimethylsilane, as was concluded from ^{1}H and ^{13}C NMR spectroscopy (see *Figure 6.1*).



G0(allyl)$_1$ **24**

Figure 6.1: Catalytic dimerisation reaction of allyltrimethylsilane

After the second insertion of allyltrimethylsilane into the Zr-C bond, apparently a β-hydrogen elimination occurs, resulting in the C=C double bond in the molecule. No traces of trimer or tetramer were observed in the NMR spectra.

An explanation might be related to the observation by Jordan and coworkers that the structure of $Cp'Zr(CH_2CH_2SiMe_3)(L)^+$ (Cp' = η^5-C_5H_5Me; L = Cl^-, THF, PMe_3, CH_3CN) has an agostic interaction between the Zr^+ and the *C*Si atom.[126] They found that the spectroscopic and rectivity properties of these silyl-substituted cations differ from those of the non-silylated alkyl analogues[127] $Cp'_2Zr(CH_2CH_2R)(L)^+$ (Cp' = η^5-C_5H_5Me; R = H, Me, Et, Ph, CMe_3; L = Cl^-, THF, PMe_3, CH_3CN). In these $Cp'_2Zr(CH_2CH_2R)(L)^+$ complexes, in general, there appears to be a β-H agostic interaction, giving rise to the structure as presented in *Figure 6.2, left*.[127]

R = H, Me, Et, Ph, CMe_3

Figure 6.2: Agostic interaction in $Cp_2Zr^+CH_2CH_2R$ (left)[127] and $Cp_2Zr^+CH_2CH_2SiMe_3$ (right)[126]

In compounds of the type $Cp'Zr(CH_2CH_2SiMe_3)(L)^+$, however, a structure more like in *Figure 6.2, right*, was found. This structure was confirmed by X-ray crystallographic analysis.

The stabilisation of the Zr^+ centre in $Cp'Zr(CH_2CH_2SiMe_3)(L)$+ complexes by agostic Zr···CSi interactions is very similar to the stabilisation of carbocation centres by suitably oriented SiR_3 substituents. This effect has been ascribed to overlap of the back lobe of the Si-C bond with the empty (or reacting) p-orbital on the carbocation as illustrated in *Figure 6.3*. Theoretical studies show that $H_3SiCH_2CH_2CH_2^+$ favors a distorted structure in which the close $H_3SiC\cdots C^+$ contact reflect stabilisation of the C^+ centre by the electron rich $CSiH_3$.[128]

Figure 6.3: Stabilisation of a carbocation by an trialkylsilyl group

Following this line of reasoning, it might be possible that the agostic interaction with the β-hydrogen in the compound is complemented with an interaction with one, or possibly two, CSi groups. Thus the bis-inserted complex (*Figure 6.4*) might be sufficiently stabilised to sterically prevent insertion of a third allyltrimethylsilane. At the same moment, the possibility to undergo β-hydrogen elimination is still present, favoring this process.

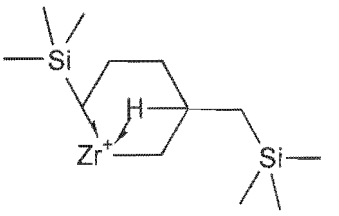


Figure 6.4: Proposed intermediate in the catalytic dimerisation of allyltrimethylsilane

The dimer of allyltrimethylsilane is sterically too big to be used as a monomer in the polymerisation of alkenes. Therefore, co-polymerisation of allyltrimethylsilane, **G0(allyl)$_1$**, and ethene was also unsuccessful. On the basis of these considerations we come to propose the following mechanism for the catalytic dimerisation of **G0(allyl)$_1$** (*Figure 6.5*)

After adding allyltrimethylsilane to *in situ* generated $[Cp_2ZrMe][MeB(C_6F_5)_3]$, however, immediately a blue-purple solution formed. In the ^1H NMR spectrum multiple zirconium species were observed as well as multiple trimethylsilyl containing compounds. Multiple C=C double bond species were also present. It was clear that the cationic zirconium compound decomposed after insertion of the C=C double bond. It might be possible that a transfer of the trimethylsilyl group from the (inserted?) allyltrimethylsilane to the cationic zirconium takes place. This Zr-Si$(CH_3)_3$ species would then decompose to form (ultimately) zirconocene (Cp_2Zr). We do not have a satisfactory explanation for this marked contrast between the behaviour of *in situ* generated $[Cp_2ZrMe][MeB(C_6F_5)_3]$ and Cp_2ZrCl_2/MAO in the presence of allyltrimethylsilane. In general it is assumed that the catalytically active species in both mixtures is the same, *i.e.* $[Cp_2ZrMe]^+$ or, after β-hydrogen elimination, $[Cp_2ZrH]^+$. The assumption that the cationic zirconocene is the same might point to the role of the co-catalyst ($MeB(C_6F_5)$ or MAO) in these reactions. MAO being a weaker Lewis base than the borane, might indicate that the borane (or borate) is actually the

species causing the decomposition of allyltrimethylsilane (or its product) in the borane activated system.

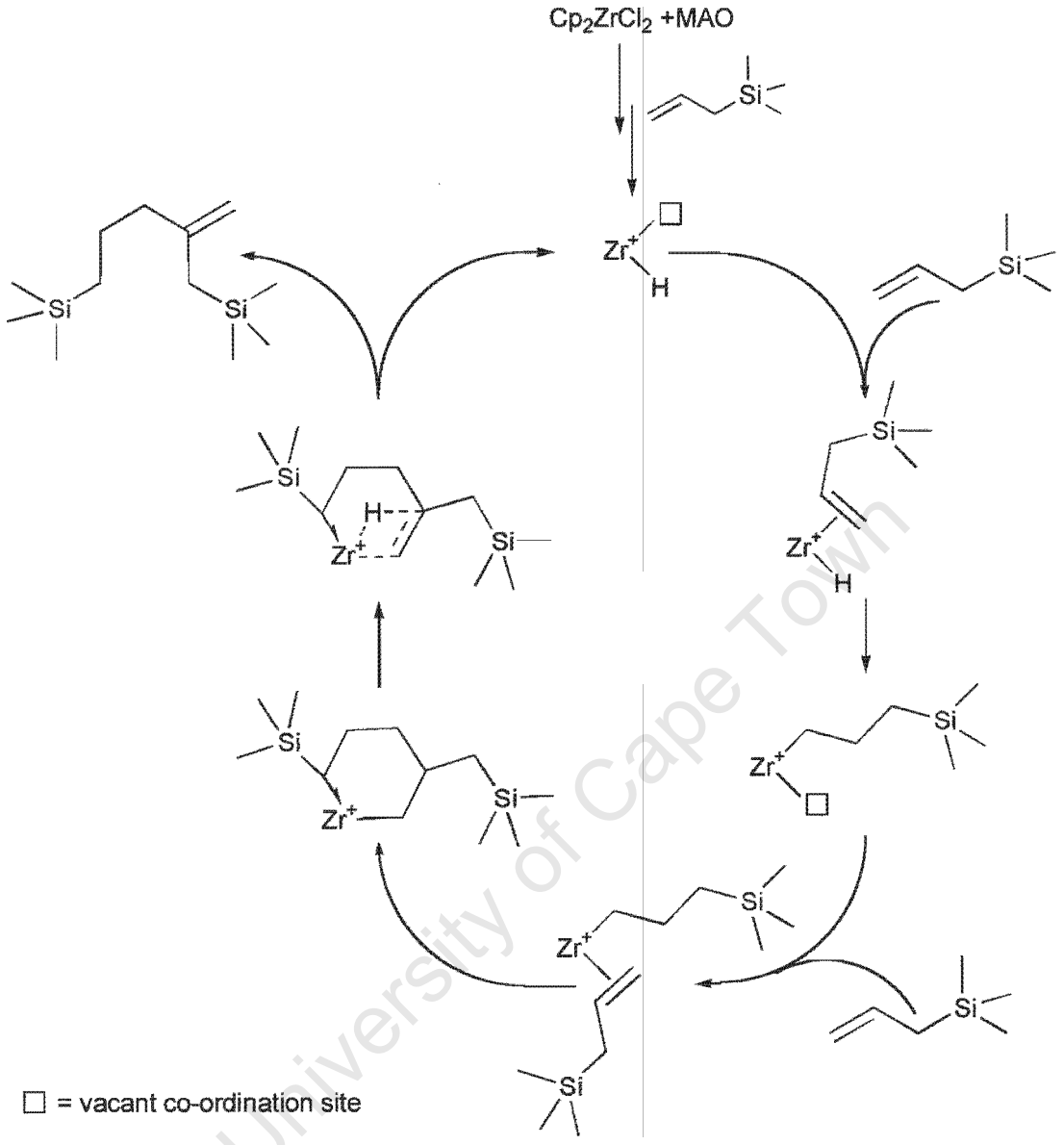


Figure 6.5: proposed mechanism for the dimerisation of allyltrimethylsilane, ***G0(allyl)$_1$***

When using tetraallylsilane **G1(allyl)$_4$**, or the second generation dendrimer, **G2(allyl)$_{12}$**, as monomer in a polymerisation reaction, a different behaviour was observed. After mixing either **G1(allyl)$_4$** or **G2(allyl)$_{12}$** with MAO (500 equivalents) in toluene at 0°C, the catalyst Cp_2ZrCl_2, **8**, was added and the mixture stirred for 1 h. Quenching, followed by aqueous work-up, however, gave the starting materials **G1(allyl)$_4$** and **G2(allyl)$_{12}$** back. It is possible, however, that the catalyst is still active, but not able to activate the propene functionalities on these two dendrimers. When this reaction was repeated, however, under an atmosphere of ethene, the same behaviour

was observed, *i.e.* no reaction occurred. We explain this unexpected behaviour by assuming that a stable π-allyl-complex is being formed, which is known to be an inactive catalyst for the polymerisation of alkenes (see *Figure 6.6*).

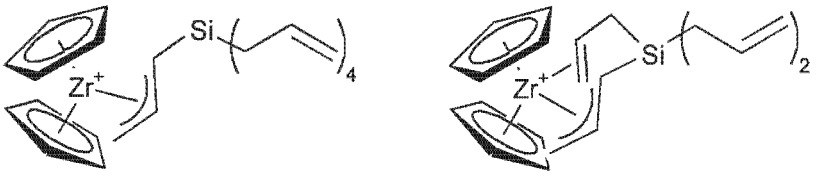


*Figure 6.6: Two possible cationic allyl compounds being formed in the reaction of cationic zirconocenes and tetraallylsilane (**G1(allyl)$_4$**)*

Attempts to generate π-allyl-complexes of cationic zirconocene on the dendrimer by mixing *in situ* generated $[Cp_2ZrMe][MeB(C_6F_5)_3]$ led to the same behaviour as with the model compound. We could therefore not draw a definite conclusion as to why cationic zirconocenes are not active in the polymerisation and co-polymerisation of allyl-terminated dendrimers.

6.3 Polymerisations using hydrozirconation products

In order to see whether the zirconocenes that are being formed as result of hydrozirconation reactions remain attached to the dendrimers, and, more importantly, whether they give different products, we have performed several experiments. The synthesis of these zirconocenes attached to the model compound and to the dendrimers has been discussed in Chapter 4 (model compound) and Chapter 5 (poly-zirconium species). In Chapter 4, a discussion is also given about activation using MAO. Here we will limit the discussion to the results of the polymerisation reactions.

Polymerisation reactions using ethene as a monomer have been performed. Care was taken to keep all conditions identical in order to be able to compare the polymeric materials after reaction. The temperature was kept constant at 0 °C by cooling the outside of the polymerisation vessel in an ice/water bath. Ethene was bubbled through a vigorously stirred solution of 500 equivalents of MAO in toluene for 30 min in order to saturate the solution with the gas. A freshly prepared catalyst solution was added and the polymerisation reaction was run for 1 h. Care was taken to ensure the same *zirconium* concentration in the solution, in order to be able to compare activities and polymer properties. As standard catalysts, the reactions were also repeated with Cp_2ZrMe_2, **14**, and Cp_2ZrCl_2, **8**. The conditions for polymerisation conditions are summarised in *Table 6.1*.

	MAO activated	Borane activated
Total volume	30 cm^3	30 cm^3
Solvent	toluene	Toluene
Amount Zr	20 μmol	40 μmol
[Zr]/[Al]	400	800
Aluminium compound	MAO	$Al[(CH_2)_7CH_3]_3$
temperature	0 °C	0 °C
time	1 h	1 h

Table 6.1: Polymerisation conditions

After work-up, the polyethene samples were recovered as white powders. The melting points of all samples were between 132 and 135 °C. IR revealed that, indeed, straight chain alkanes were formed. The polyethene samples were analysed by gel permeation chromatography (GPC). It appeared that the samples had comparable Mn and Mw. From these results we conclude that the zirconium moiety is removed from the dendrimer either during the activation process, or early in the polymerisation reaction. The analytical data of the polymers obtained from the catalytic polymerisation of ethene using mononuclear, tetranuclear and dodecanuclear catalyst precursors are given in *Table 6.2*.

Precat.	Yield	Mp (°C)	Mn	MP	Mw	Mz	Mz+1	Polydisp.
Cp_2ZrCl_2		135	71878	212199	494837	1465517	2569699	6.88
$G0(ZrCl)_1$		137	62037	229094	477291	1438572	2526688	7.63
$G1(ZrCl)_4$		135	43038	233164	377930	1268235	2400260	8.76
$G2(ZrCl)_{12}$		132	56542	843488	599384	1749277	2847420	10.61

Table 6.2: Analytical data of the polymers

It is clear from the results given in Table 6.2 that the polydispersity of the polymer samples increases with increasing number of branches on the dendrimer. This behaviour can be due to the zirconocene moiety being decomplexed from the dendrimer, or dendritic polymer. The nature of the catalytically active species changes upon decomplexation, causing the polydispersity to increase.

Some notes on polymerisation

Early transition metal based polymerisation catalysts are extremely reactive materials. They react rapidly with oxygen, water and other contaminants in the solvent and monomer feed. These catalysts also react with active hydrogen and Lewis basic compoounds in the solvent and

monomer feed. Without proper precautions this reactivity will rapidly lead to catalyst deactivation and, in some cases, no catalytic activity could be observed. It is imaginable that the catalyst can be consumed by impurities in the monomer feed or the solvent, before the reaction starts.

Rigorous removal of oxygen, water and other reactive contaminants from the polymerisation reactor, solvent and alkenes is essential for reproducible results. With MAO activated catalysts this condition is realised by using a large excess of MAO. Though the MAO reacts rapidly with water and oxygen, compounds such as THF are not being consumed by reaction with MAO.For single component catalysts such as the Cp_2ZrMe_2/MAO system, we decided to add trioctylaluminium to the mixture as an internal scavenger

It would be advantageous to have a dedicated solvent purification system and polymerisation set-up, however this was not the case. Incidentally, polymerisation reactions did not occur and the reproducibility of the reactions described in this chapter was rather low. All reactions reported here were repeated at least three times.

6.4 Conclusions

Several polymerisation reactions, using the dendrimers described in chapter 2 as monomers, were attempted. These reactions resulted in a quantitative recovery of the dendritic starting materials. When using allyltrimethylsilane, **G0(allyl)$_1$**, as a monomer, a dimer of this material was isolated in 100 % yield. A mechanism for the dimerisation of **G0(allyl)$_1$** is proposed in this chapter.

When using a mixture of the hydrozirconation products and MAO as catalysts in the polymerisation of ethene, polyethene was obtained. The polyethene product of various catalytic runs with different catalyst precursors appeared to be slightly different. The melting points are almost the same, but the polydispesity of the products appeared to be significantly different.

Chapter 7

Conclusions

The synthesis and chemistry of several carbosilane dendrimers were investigated. These dendrimers were analysed using a variety of techniques. Both a convergent and a divergent methodology were used to build up the carbosilane dendrimers. The carbosilane dendrimers were derived using mainly hydrosilylation reactions. These reactions appeared to be particularly useful as they appeared to go to completion. It was necessary to use quantitative reactions to prevent unreacted functionalities on the dendrimers. A formula was given that calculates the relative amounts of the various products in incomplete reactions.

The simple allyl-terminated dendrimers were functionalised with a variety of silanes. These silanes were then used to further functionalise the dendrimers. A number of derivatives of chloromethylsilyl terminated dendrimers were investigated. The chloromethyl functionality in these dendrimers was reacted with various nucleophiles, such as Fp^-, Rp^-, Mp^-, Wp^- and the cobaloxime anion. These reactions were moderately successful, only giving the desired products after reactions with Fp^- and Rp^-. The chloromethylsilyl terminated dendrimers were also reacted with NaI in acetone to give the iodomethylsilyl terminated dendrimers. These are expected to be more reactive towards nucleophilic substitution than the chloromethylsilyl terminated dendrimers.

The generation of lithiated dendrimers, based on the above mentioned dendrimers, was achieved. Deprotonation of allyl terminated dendrimers appeared to be impossible, probably due to steric constraints in the dendrimer. Reaction of the chlormethylsilyl terminated dendrimers with metallic lithium was also unsuccessful. The lithiomethylsilyl terminated dendrimers were finally obtained via reaction of phenylthiomethyl terminated dendrimers with lithium dihydronaphtalyde in THF. The lithiated dendrimers were generated *in situ*, using this method, and reacted with a variety of silyl and stannyl chlorides. These compounds were air- and moisture-stable, and were fully analysed.

Reaction of the tributyltin terminated dendrimer with *n*-butyllithium also resulted in the formation of the lithiated dendrimers. The side-product of this reaction is tetrabutyltin, an inert, highly soluble liquid. Separation of the side product from the lithiated dendrimer was readily achieved by washing the lithiated dendrimers with pentane. The phenylthiomethyl functionalised dendrimers could not be separated from the side products.

A number of zirconocene complexes was prepared in order to link these to the dendrimers through a σ-bond and a number of model compounds was prepared. Reaction of Schwartz's reagent with the zeroth, first and second generation dendrimer was performed. These compounds were used in polymerisation reactions, described in Chapter 6. These compounds were activated using MAO, but it is not certain that activation using MAO results in selective activation. A number of asymmetric zirconocenes was also prepared. These compounds, with one methyl group and one silylmethyl group, can be activated selectively by using $B(C_6F_5)_3$ as the activating agent.

Reactions of the lithiated dendrimers with $Cp_2ZrMeCl$ were attempted. The anticipated dendrimers were not isolated. Side reactions with small amounts of tetrabutyltin appeared to hamper the isolation of these products. When activation of these dendritic zirconocenes was attempted, a mixture of components was found that could not be separated.

In the final section of this work, several catalytic reactions were described. Of particular interest was the dimerisation of allyltrimethylsilane by Cp_2ZrCl/MAO. An attempt at an explanation is made in this chapter. The unsuccessful co-polymerisations of the dendrimers with ethene are also described in this section.

Although the zirconated dendrimers were not isolated and characterised in this work, a new class of dendrimers, the lithiated dendrimers, was synthesised and characterised. The general methodology of synthesising these dendrimers is flexible towards the type of dendrimer used. In this work, only carbosilane dendrimers were used. The thio-ether functionalisation can readily be applied to other types of dendrimers. Functionalisation using tributyltin is more limited as reagent for the generation of lithium reagents. Because the stannane/lithium exchange reaction is an equilibrium reaction, additional stabilisation of the formed lithium reagent is necessary. This stabilisation is readily provided in the silane dendrimers due to the silicon α to the carbanion functionality.

Chapter 8

Experimental details

8.1 General Procedures

All manipulations of air- and/or moisture sensitive compounds were carried out under an inert atmosphere of argon using standard Schlenk techniques[129] or in an inert atmosphere M Braun Unilab glovebox containing dinitrogen. Inert gases were purified by passage through columns filled with molecular sieves (5Å) and BASF catalyst.[130] Solvents and solutions were transferred through stainless steel canula (volumes > 50 cm^3) using a positive pressure of inert gas or glass syringes equipped with stainless steel needles. Non-volatile materials that were transferred from air were suspended in dry THF followed by removal of the THF *in vacuo* three times, to remove traces of water, prior to use in reactions. Sublimations were performed according to the technique described by Pool and Teuben.[131] Some reactions were performed using a double- or H-type Schlenk vessel.[132] Syringes were stored at 60 °C and all other glassware was thoroughly dried for minimal 4 h at 210 °C before use.

Materials

All solvents were thoroughly deoxygenated before use by repeated evacuation followed by admission of argon. Solvents were pre-dried by passage through a column containing alumina (neutral, Brockmann grade I) followed by distillation from the appropriate drying/deoxygenating agent,[133] transferred into dry vessels equipped with Teflon valve closures, and stored under argon. The drying agent and indicators are given in *Table 7.1.*

Solvent/reagent	Supplier	Drying agent	Distillation	Colour
Acetone		Dryrite	Yes	Blue
Acetonitrile-*d3*	Sigma-Aldrich	3 Å Molecular sieves	No	-
Allyl halide	Sigma-Aldrich	CaH_2	Yes	-
Allyltrimethylsilane	Sigma-Aldrich	4 Å Molecular sieves	No	-
Benzene-*d6*	Sigma-Aldrich	Sodium/potassium aloy	Yes	-
Dichloromethane		CaH_2	Yes	-
Diethyl ether	Merck	Sodium/benzophenone	Yes	Blue/purple
Hexane		-	Yes	-
Pentane		Sodium/benzophenone/tetraglyme	Yes	Blue/purple
Tetraallylsilane	Sigma-Aldrich	4 Å Molecular sieves	No	-
THF	Merck	Sodium/benzophenone	Yes	Blue/purple
Toluene		Sodium	Yes	Melt
Toluene-*d8*	Sigma-Aldrich	Sodium/potassium aloy	Yes	-
Xylene		Sodium	Yes	Melt

Table 8.1 Solvent/reagent and their drying procedure

Chlorotrimethylsilane, chlorodimethylsilane, silicon tetrachloride and trichlorosilane were purchased from Sigma Aldrich, distilled under argon and stored in Teflon valved storage vessels. *n*-Butyllithium (1.6 *M* in hexanes), *t*-butyllithium (1.7 *M* in pentane), chloro(chloromethyl) dimethylsilane, MAO (10 % ww in toluene) methyllithium (1.6 *M* in diethyl ether) and trimethyl-aluminium were purchased from Sigma Aldrich and transferred into Teflon valved storage flasks. All storage vessels were wrapped with aluminium foil.

Cp_2ZrCl_2, $[CpW(CO)_3]_2$, $[CpMo(CO)_3]_2$, $[CpFe(CO)_2]_2$ were purchased from Strem and used as received. Chloroplatinic acid was received as a gift from Johnson-Matthey.

$CDCl_3$, divinyltetramethyl-1,3-disiloxane, tetraallylsilane, was purchased from Sigma Aldrich and used as received.

C_3H_5MgX (X = Cl, Br),[134] $C_6H_5CH_2K$,[111] $[CpRu(CO)_2]_2$[135] and $CpRe(CO)_3$[136] were prepared according to literature methods.

Instrumentation

Melting points were recorded on a Kofler hotstage microscope (Reichert Thermovar). Microanalysis data were obtained from the University of Cape Town Microanalytical Laboratory. Infrared spectra were recorded on a Perkin-Elmar Paragon 1000 FT-IR spectrometer in the range 450 to 4400 cm^{-1}. Samples were either prepared neat between NaCl discs for liquids, as Nujol mulls between NaCl disks (solids) or as dilute solutions in a solution cell with NaCl windows. Solution spectra were referenced to a blank cell containing only the solvent. All data are given in wavenumbers (cm^{-1}).

NMR spectra were recorded on either a Varian Unity-400 (^1H: 400 MHz; ^{13}C: 100.6 MHz; ^{29}Si: 79.5 MHz) spectrometer or a Varian Mercury-300 (^1H: 300 MHz; ^{13}C: 75.5 MHz) spectrometer at ambient temperature. ^1H NMR spectra were referenced internally using the residual protonated impurities in the solvent ($CDCl_3$: δ 7.27; C_6D_6: δ 7.16; CD_3CN: δ 1.95; THF-*d8*: δ 1.73, 3.58) and reported relative to tetramethylsilane (δ 0.00). ^{13}C NMR spectra were internally referenced to solvent resonances ($CDCl_3$: δ 77.0; C_6D_6: δ 128.0; CD_3CN: δ 1.3, 117.7; THF-*d8*: δ 25.5, 67.7) and reported relative to tetramethylsilane (δ = 0.0). ^{29}Si NMR spectra were referenced externally to tetramethylsilane (δ = 0.0). All chemical shifts are quoted in δ and coupling constants are given in Hertz.

Mass spectra were determined by Dr. Boshoff of the mass spectrometry unit at the Cape Technikon. The selected *m/z* values given refer to the isotopes ^1H, ^{12}C, ^{28}Si, ^{32}S and ^{120}Sn. In all cases the isotopic distribution pattern was checked against the theoretical distribution.

8.2 Procedures pertaining to chapter 2

Karstedt catalyst[53]

Chloroplatinic acid (100 mg; 0.244 mmol) was dissolved in ethanol (2.0 cm^3). Divinyltetramethyl-1,3-disiloxane (1.2 cm^3; 5.2 mmol) was added, followed by sodium hydrogencarbonate (120 mg; 1.43 mmol). The mixture was stirred vigorously and heated under reflux for 30 min. The brown colour faded to light yellow. The mixture was stirred for another 14 h. Volatiles were removed *in vacuo*. Toluene (5.0 cm^3) was added and the colourless supernatant solution was transferred to a storage vessel. The catalyst solution (1.1 % Pt, theoretical) was used without identification.

G1(Cl_3)$_4$, Si($CH_2CH_2CH_2SiCl_3$)$_4$

The procedure is based on the method by van der Made and van Leeuwen.[51] A solution of trichlorosilane (15 cm^3, 149 mmol) (*poisonous, reacts with H_2O to form HCl*) in THF (15 cm^3) was condensed unto a mixture of tetraallylsilane (5.0 g, 26.0 mmol) and Karstedt catalyst solution (1 % Pt in toluene, 50 mm^3) in a thick walled reaction vessel. The vessel was allowed to attain room temperature and after several minutes a strong exotherm was observed. The mixture was stirred for 12 h and then heated to 100 °C. When the reaction was complete (IR and ^{1}H NMR), the volatiles were removed *in vacuo* while heating in a boiling water bath to give a waxy white solid **G1(Cl_3)$_4$**, Si($CH_2CH_2CH_2SiCl_3$)$_4$ (7.5 g, 100 %);

$\tilde{\nu}_{max}/cm^{-1}$ 2926 (s, $\nu_{as}(CH_2)$), 2878 (s, $\nu_s(CH_2)$), 2797, 1452 (m, $\delta_{as}(CH_2)$), 1413, 1339, 1239, 1150, 1086, 1020, 979, 944, 911, 798 (s, $\nu(SiCH_2)$), 693, 584 (SiCl) and 562 (neat);

δ_H(C_6D_6, 400 MHz) 1.33 (8 H, m, 4 $CH_2CH_2CH_2$), 1.01 (8 H, m, 4 $SiCH_2$) and 0.28 (8 H, m, 4 CH_2Si);

$\delta_{C\{H\}}$(C_6D_6, 100.6 MHz) 27.8 (4 C, 4 $CH_2CH_2CH_2$), 17.0 (4 C, $SiCH_2$) and 14.60 (4 C, 4 CH_2Si).

G2(allyl)$_{12}$, Si[$CH_2CH_2CH_2Si(CH_2CH{=}CH_2)_3$]$_4$

A solution of the chlorosilane terminated dendrimer **G1(Cl_3)$_4$** (7.5 g, 26.0 mmol) in diethyl ether (20 cm^3) was slowly added to an ice cooled solution of allyl Grignard[134] in diethyl ether (1.3 M, 100 cm^3, 130 mmol). After the addition was complete, the mixture was heated under reflux for 15 h.* The reaction mixture was cooled to 0 °C and the excess Grignard reagent was hydrolised with an aqueous 10 % NH_4Cl solution (100 cm^3). The aqueous layer was separated from the organic layer and extracted with diethyl ether (3 x 50 cm^3). The combined organic phases were washed with water (3 x 50 cm^3) and brine (3 x 50 cm^3), dried over $MgSO_4$, filtered and the diethyl ether was removed *in vacuo*. The residual golden-brown oil was dried under vacuum to give crude Si[$CH_2CH_2CH_2Si(CH_2CH{=}CH_2)_3$]$_4$. The oil was purified by chromatography over silica, eluting with

* The solution was occasionally checked for active Grignard by quenching an aliquot in water and checking with phenolphtalein for base (red colour).

hexane : acetone = 10 : 1. The solvent was evaporated *in vacuo* to give the title compound as a colourless oil. **G2(allyl)$_{12}$**, $Si[CH_2CH_2CH_2Si(CH_2CH{=}CH_2)_3]_4$

(16.99 g, 89 % from $Si(CH_2CH{=}CH_2)_4$),

(Found: C, 72.1; H, 10.85. Calc. for $C_{48}H_{84}Si_5$ (801.6): C, 71.9; H, 10.6 %);

$\tilde{\nu}_{max}$/cm^{-1} 3075 (ν(CH=CH_2)), 2970 (ν(CH=CH_2)), 2913 (s, $\nu_{as}(CH_2)$), 2877 (s, $\nu_s(CH_2)$), 1629 (s, ν(C=C)), 1419 (m, $\delta_{as}(CH_2)$), 1391, 1193, 1156, 1034, 990 (s, γ(HC=CH_2)), 929 (m, γ(HC=CH_2)), 893, 805, 707, 597 and 526 (neat);

δ_H($CDCl_3$, 400 MHz) 0.58 (8 H, m, ^3J(HCCH) 3 Hz, $Si(CH_2CH_2)_4$), 0.67 (8 H, m, ^3J(HCCH) 3 Hz, 4 CH_2CH_2Si), 1.36 (8 H, m, 4 $CH_2CH_2CH_2$), 1.60 (24 H, d, ^3J(HCCH) 8 Hz, 4 $Si(CH_2CH)_3$), 4.89 (24 H, m, 12 CH=CH_2) and 5.80 (12 H, m, $CH{=}CH_2$);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 134.39 (C6), 113.55 (C5), 19.73 (C4), 18.29 (C1), 17.54 (C2) and 16.66 (C3). C-H correlation's were determined by HSQC 2D NMR spectroscopy.

$\delta_{Si\{H\}}$($CDCl_3$, 79.5 MHz) 2 peaks were visible in the spectrum, separated by 1.72 ppm.

m/z (FAB) 761 ($M^+ - CH_2CH{=}CH_2$), 720 ($M^+ - 2\ CH_2CH{=}CH_2$), 679 ($M^+ - 3\ CH_2CH{=}CH_2$) and 638 ($M^+ - 4\ CH_2CH{=}CH_2$). The parent ion (M^+ = 802) was not observed.

Higher generation dendrimers

The higher generation dendrimers were synthesised using the same method as for the second generation dendrimer **G2(allyl)$_{12}$**. The reactions were performed with 5.00 g starting material, and the same amount of trichlorosilane (15 cm^3, 149 mmol) and THF (15 cm^3) were used for every generation.

$G_2(Cl_3)_{12}$, $Si[CH_2CH_2CH_2Si(CH_2CH_2CH_2SiCl_3)_3]_4$

(13.9 g, 94 %);

$\tilde{\nu}_{max}$/cm^{-1} 2926 (s, $\nu_{as}(CH_2)$), 2878 (s, $\nu_s(CH_2)$), 2797, 1452 (s, $\delta_{as}(CH_2)$), 1413, 1339, 1239, 1150, 1087, 1020, 979, 944, 911, 798 (s, ν($Si(CH_2)_4$)), 693, 584 (SiCl, ν), 562 and 470 (neat);

δ_H(C_6D_6, 400 MHz) 1.51 (m, 32 H,), 1.11 (t, 24H,), 0.92 (t, 8H,), 0.79 (t, 8H,) and 0.50 (t, 24H,);

$\delta_{C\{H\}}$(C_6D_6, 100.6 MHz) 28.11, 19.10, 17.93, 17.76, 17.55 and 15.34.

$G_3(Cl_3)_{36}$, $Si[CH_2CH_2CH_2Si[CH_2CH_2CH_2Si(CH_2CH_2CH_2SiCl_3)_3]_3]_4$

Yield not determined, all product used in the synthesis of **G4(allyl)$_{108}$**.

$\tilde{\nu}_{max}$/cm^{-1} 2924 (s, $\nu_{as}(CH_2)$), 2874 (s, $\nu_s(CH_2)$), 2796 (w), 1451 (m, $\delta_{as}(CH_2)$), 1413, 1339, 1240 (s, δ($Si(CH_2)_4$)), 1149, 1114, 1020, 979, 943, 911, 840 (s, ν($Si(CH_2)_4$)), 798, 694, 585, 563 and 470 (neat);

δ_H(C_6D_6, 300 MHz) 1.64 (m), 1.33 (m), 1.0 (m), 0.85 (m) and 0.68 (m). Peaks due to impurities were observed at δ 3.12 (m) and 3.02 (m);

$\delta_{C\{H\}}$(C_6D_6, 75.5 MHz) 28.5. 19.3, 18.2, 17.8 and 15.7. Peaks due to impurities were observed at δ 69.9, 44.8, 29.8 and 27.3.

$G_3(allyl)_{36}$, $Si\{CH_2CH_2CH_2Si[CH_2CH_2CH_2Si(CH_2CH=CH_2)_3]_3\}_4$

(14.05 g, 87 %)

$\tilde{\nu}_{max}/cm^{-1}$ 3075 (w, $\nu(CH=CH_2)$), 2970, 2913 (s, $\nu_{as}(CH_2)$), 2877 (s, $\nu_s(CH_2)$), 1629 (m, $\nu(C=C)$), 1419, 1391, 1193, 1156, 1034, 990 (s, $\gamma(CH=CH_2)$), 929 (s, $\gamma(CH=CH_2)$), 893, 805, 707, 597 and 526 (neat);

$\delta_H(CDCl_3$, 400 MHz) 5.77 (m, H, CH=), 4.88 (m, H, $=CH_2$), 1.59 (d, H), 1.36 (m, H,), 0.67 (m, H,) and 0.57 (m, H,).);

$\delta_{C\{H\}}(CDCl_3$, 100.6 MHz) 134.36 (C6), 113.60 (C5), 19.74 (C4), 18.33 (C1), 17.57 (C2) and 16.72 (C3). C-H correlations were determined by HSQC 2D NMR spectroscopy.

$\delta_{Si\{H\}}(CDCl_3$, 79.5 MHz) 2 peaks were visible in the spectrum, separated by 2.2 ppm.

$G_4(allyl)_{108}$, $Si\{CH_2CH_2CH_2Si[CH_2CH_2CH_2Si(CH_2CH_2CH_2Si(CH_2CH=CH_2)_3)_3]_3\}_4$

$\tilde{\nu}_{max}/cm^{-1}$ 3075 ($CH=CH_2$, ν(M)), 2970, 2913 (CH_2, ν_{as}(S)), 2877 (CH_2, ν_s(S)), 1629 (C=C, ν(S)), 1419 (CH_2, δ_{as}(M)), 1391, 1193, 1156, 1034, 990 ($CH=CH_2$, δ(S)), 929 ($CH=CH_2$, δ(S)), 893, 805, 707, 597 and 526 (neat);

$\delta_H(CDCl_3$, 400 MHz) 5.77 (m, H, CH=), 4.88 (m, H, $=CH_2$), 1.59 (d, H), 1.36 (m, H,), 0.67 (m, H,) and 0.57 (m, H,).);

$\delta_{C\{H\}}(CDCl_3$, 100.6 MHz) 134.36 (C6), 113.60 (C5), 19.74 (C4), 18.33 (C1), 17.57 (C2) and 16.72 (C3). C-H correlations were determined by HSQC 2D NMR spectroscopy.

$\delta_{Si\{H\}}(CDCl_3$, 79.5 MHz) 2 peaks were visible in the spectrum, separated by 2.2 ppm.

2, $ClCH_2CH_2CH_2Si(CH_2CH=CH_2)_3$

Karstedt catalyst solution (1 % Pt in toluene, 10 mm^3) was added to a mixture of allyl chloride (1.5 cm^3, 18.4 mmol) and trichlorosilane (2.0 cm^3, 20 mmol). The mixture was stirred for 72 h after which time the volatiles were removed *in vacuo*. The product, **1**, was dissolved in diethyl ether (20 cm^3) and a solution of allylmagnesium bromide in diethyl ether (26 cm^3, 1.14 M, 30 mmol) was added at –40 °C and stirred for 1 h at –40 °C. The mixture was quenched with saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer extracted with diethyl ether (3 x 20 cm^3). The combined organic layers were washed with water (3 x 20 cm^3), brine (3 x 20 cm^3), dried over $MgSO_4$, filtered and the volatiles were removed *in vacuo*. The product was filtered over a pad of alumina, eluting with hexane. The hexane was removed *in vacuo* to give **2**, $ClCH_2CH_2CH_2Si(CH_2CH=CH_2)_3$ as a colourless oil. (3.49 g, 83 %)

$\delta_H(CDCl_3$, 400 MHz) 5.78 (3 H, m, 3 =C*H*), 4.89 (6 H, m, 3 $=CH_2$), 3.50 (2 H, t, $ClCH_2$), 1.90 (2 H, m, $CH_2CH_2CH_2$), 1.61 (6 H, d, 3 CH_2CH) and 0.88 (2 H, m, CH_2Si);

$\delta_{C\{H\}}(CDCl_3$, 100.6 MHz) 133.93, 113.95, 47.75, 27.19, 19.49 and 9.27.

G1(H$_3$)$_4$, Si(CH$_2$CH$_2$CH$_2$SiH$_3$)$_4$

$LiAlH_4$ (2.0 g, 5.3 mmol) was dissolved in diethyl ether (40 cm^3) and cooled down in an ice/water bath. A solution of $Si(CH_2CH_2CH_2SiCl_3)_4$, **G1(Cl$_3$)$_4$**, (5.7 g, 7.8 mmol), freshly prepared from 1.8 cm^3 tetraallylsilane and trichlorosilane) in diethyl ether (20 cm^3) was slowly added to the $LiAlH_4$ solution. A white solid was seen to form and the reaction was strongly exothermic. The mixture was stirred overnight and filtered. The solution was slowly added to a mixture of 6 M hydrochloric acid (60 cm^3) and ice (200 cm^3). A violent reaction was observed and a heterogeneous mixture was obtained. The mixture was extracted with diethyl ether (3 x 50 cm^3). The combined organic layers were washed with water (3 x 50 cm^3) and brine (3 x 50 cm^3) and subsequently dried over $MgSO_4$. After filtration, the diethyl ether was removed on a rotary-evaporator and the resulting colourless oil dried under vacuum to give $Si(CH_2CH_2CH_2SiH_3)_4$, **G1(H$_3$)$_4$**, as a colourless oil. (2.04 g, 74 %);

$\tilde{\nu}_{max}/cm^{-1}$ 2918 (s, $\nu_{as}(CH_2)$), 2884 (s, $\nu_s(CH_2)$), 2145 (s, ν(SiH)), 1617, 1449 (m, $\delta_{as}(CH_2)$), 1404, 1334, 1236, 1215, 1145, 1084, 1030, 923 (s, $\delta(SiH_3)$), 821 (s, $\nu(Si(CH_2)_4)$), 786, 689, 606 and 522 (neat);

δ_H($CDCl_3$, 400 MHz) 3.48 (12 H, t, ^3J(HCSiH) 4 Hz, ^2J(SiH) 96.0 Hz, 4 Si*H*$_3$), 1.42 (8 H, m, 4 $CH_2CH_2CH_2$), 0.81 (8 H, octet, ^3J(HCSiH) 4 Hz , 4 CH_2SiH_3) and 0.59 (8 H, m, ^3J(HCCH) 9 Hz, 4 $SiCH_2$);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 21.0 (4 C, 4 $CH_2CH_2CH_2$), 15.8 (4 C, $Si(CH_2)_4$) and 10.43 (4 C, 4 CH_2SiH_3). Coupling between CH_2 and SiH_3 was additionally confirmed by COSY 2D NMR spectroscopy. Correlation between H and C was confirmed by HSQC 2D NMR spectroscopy.

G1(Cl)$_4$, Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$Cl]$_4$

Tetraallylsilane, **G1(allyl)$_4$**, (230 mm^3; 1.0 mmol) was mixed with chlorodimethylsilane (1.0 cm^3; 9.0 mmol) in a Schlenk tube. Karstedt catalyst (20 mm^3; 1 % Pt in toluene) was added by syringe and the mixture stirred. After 1 h an exotherm was observed. After 16 h of stirring the volatiles were removed *in vacuo* to leave a colourless oil **G1(Cl)$_4$**, $Si[CH_2CH_2CH_2Si(CH_3)_2Cl]_4$ (0.53 g, 99 %);

δ_H(C_6D_6, 400 MHz) 1.58 (8 H, m, 4 $CH_2CH_2CH_2$), 0.8 (8 H, m, 4 CH_2Si), 0.7 (8 H, m, 4 $SiCH_2$) and 0.3 (24 H, s, 4 $Si(CH_3)_2$);

$\delta_{C\{H\}}$ (C_6D_6, 100.6 MHz) 23.7 (4 C, 4 $CH_2CH_2CH_2$), 18.0 (4 C, 4 CH_2Si), 16.4 (4 C, 4 $SiCH_2$) and 1.8 (8 C, 8 CH_3).

Note: the use of Speier's catalyst did not give any product, even after heating to 110 °C for prolonged periods.

G1(H)$_4$, Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$H]$_4$

Lithium aluminiumhydride (0.131 g, 3.45 mmol) was suspended in diethyl ether (5.0 cm^3). Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$Cl]$_4$, **G1(Cl)$_4$**, (0.53 g, 1.0 mmol) was added as a diethyl ether solution (5.0 cm^3) by syringe. A slight exotherm was observed. The mixture was stirred. After 16 h it was slowly poured into 2.0 M aqueous HCl at 0 °C. The organic product was extracted with diethyl ether and dried over magnesium sulphate. Evaporating the volatiles *in vacuo* gave a viscous oily **G1(H)$_4$**, Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$H]$_4$ (0.29 g, 66 % (from Si(CH$_2$CH=CH$_2$)$_4$);

δ_H(C$_6$D$_6$, 400 MHz) 3.8 (4 H, m, 4 Si*H*), 1.55 (8 H, m, 4 CH$_2$C*H*$_2$CH$_2$), 0.55 (8 H, m, 4 C*H*$_2$Si), 0.35 (8 H, m, 4 SiC*H*$_2$) and –0.5 (24 H, d, 4 Si(C*H*$_3$)$_2$);

$\delta_{C\{H\}}$(C$_6$D$_6$, 100.6 MHz) 19.04 (4 C, 4 CH$_2$*C*H$_2$CH$_2$), 18.99 (4 C, 4 *C*H$_2$Si), 16.8 (4C, 4 *C*H$_2$Si) and –4.37 (8 C, 8 *C*H$_3$).

G1(Cp)$_4$, Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$C$_5$H$_5$]$_4$[59]

Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)Cl]$_4$, **G1(Cl)$_4$**, (0.480 g, 0.84 mmol) was dissolved in THF (5.0 cm^3) and loaded in a dropping funnel. This solution was slowly added to a solution of CpNa, prepared from NaH (0.400 g, 16.7 mmol) and freshly cracked CpH (0.35 cm^3, 4.3 mmol) in THF, at –78 C. The precipitation of a white solid was observed. The mixture was warmed to room temperature and the THF was removed *in vacuo*. Pentane (10 cm^3), followed by concentrated ammonium chloride solution (10 cm^3), was added. The organic layer was separated. The aqueous layer was extracted with hexane (2 x 20 cm^3). The combined organic layers were washed with water (3 x 20 cm^3), brine (2 x 20 cm^3) and dried over MgSO$_4$. Care was taken to do all handling at 0 °C by cooling with ice/water. The volatiles were removed *in vacuo* after filtration to give a golden-yellow oil. **G1(Cp)$_4$**, Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$C$_5$H$_5$]$_4$[59] (0.421 g, 73 %)

δ_H(CDCl$_3$, 400 MHz) 6.55, 6.45 (16 H, br., 4 C$_5$*H*$_4$), 2.96 (4 H, s, 4 SiC*H*(C$_4$H$_4$)), 1.33 (8 H, m, CH$_2$C*H*$_2$CH$_2$), 0.58 (16 H, m, 8 SiC*H*$_2$) and –0.10 (24 H, s, 8 C*H*$_3$);

$\delta_{C\{H\}}$(CDCl$_3$, 100.6 MHz) 133.1, 130 (20 C, 4 *C*$_5$H$_5$), 29.3 (4 *C*H$_2$), 20.0 (4 C, *C*H$_2$), 17.4 (4 C, *C*H$_2$) and –2.1 (8 C, *C*H$_3$)

NMR data were in agreement with literature.[59]

G1(Fp)$_4$, Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$Fe(CO)$_2$C$_5$H$_5$]$_4$[59]

[CpFe(CO)$_2$]$_2$ (0.300 g, mmol) was cracked over NaK-melt[64] (from 0.200 g K and 0.060 g Na) in THF in 2.5 h in a double Schlenk-tube. The mixture was filtered and a solution of Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$Cl]$_4$ in THF (2.5 cm^3, 1.41cm^3, 0.1mmol) was added. The mixture was stirred overnight. The volatiles were removed *in vacuo* and the residue was extracted with pentane (10 + 3 x 5 cm^3). The evaporation of the solvent gave a colourless oil: **G1(Fp)$_4$**, Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$Fe(CO)$_2$C$_5$H$_5$]$_4$ (0.106 g, 52 %) R_f (silica/CH$_2$Cl$_2$:hexane = 1:1) 0.76;

$\tilde{\nu}_{max}$/cm^{-1} 1997 (s, ν(CO)) and 1944 (s, ν(CO)) (hexane);

δ_H($CDCl_3$, 300 MHz): 4.68 (20 H, s, 4 C_5H_5), 1.42 ($CH_2CH_2CH_2$), 0.85 (CH_2), 0.59 (CH_2) and 0.32 (24 H, s, 8 CH_3);

$\delta_{C\{H\}}$($CDCl_3$, 75.5 MHz): 215.5 (8 C, 8 *C*O), 83.3 (20 C, 4 C_5H_5), 20.5, , 17.2 and –4.0 (8 C, 8 CH_3).

NMR data was in agreement with the literature.[59]

4, (Chloromethyl)dimethylsilane[137]

Chloro(chloromethyl)dimethylsilane (20 cm^3, 152 mmol) was added to a stirred suspention of $LiAlH_4$ (2.145 g, 56.5 mmol) in diethyl ether (60 cm^3). An exotherm was observed, causing the diethyl ether to boil. After the exotherm died away, the mixture was heated under reflux overnight. The volatiles were condensed into a trap at –78 °C. Distillation afforded the pure **4**, (chloromethyl)dimethylsilane (8.92 g, 54 %), bp 82 °C;

(Found: C, 33.0; H, 8.6. C_3H_9SiCl (108.6) requires C, 33.2; H, 8.4 %);

$\tilde{\nu}_{max}$/cm^{-1} 2964 (s, $\nu_{as}(CH_3)$), 2930 (s), 2138 (s, ν(Si-H)), 1397 (s), 1253 (s, $\delta(Si(CH_3)_2)$), 1177 (m), 1104 (m), 1070 (m), 885 (s, δ_s(Si-H)) and 806 (s, $\nu(Si(CH_3)_2)$) (neat);

δ_H($CDCl_3$, 400 MHz): 4.05 (1 H, m, Si*H*), 2.85 (2 H, d, CH_2Cl) and 0.21 (6 H, d, 2 CH_3);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz): 29.00 (1 C, CH_2Cl) and –5.79 (2 C, 2 CH_3).

G0(CH_2Cl)$_1$, (Chloromethyl)dimethyl(3-(trimethylsilyl)propyl)silane

A solution of (chloromethyl)dimethylsilane, **4**, (2.0 g, 18.4 mmol) in THF (5.0 cm^3) was slowly added to a cooled (ice/water) solution of allyltrimethylsilane, **G0(allyl)$_1$**, (2.0 g, 17.5 mmol) and Karstedt catalyst solution (1 % Pt in toluene, 100 mm^3) in tetrahydrofuran (5.0 cm^3). After the addition was complete, the mixture was stirred at room temperature for 1h and heated with reflux for 3 days. The volatiles were removed *in vacuo* to give a colourless oil mixed with a black precipitate. The solids were removed by filtration over a pad of silica, eluting with hexane. Evaporation of the hexane gave $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_2CH_2Cl$, **G0($CH_2Cl$)$_1$**, as a colourless oil (3.41 g; 87 %)

(Found: C, 48.4; H, 10.6. $C_9H_{23}Si_2Cl$ (222.9) requires C, 48.5; H, 10.4 %);

$\tilde{\nu}_{max}$/cm^{-1} 2955 (s, $\nu_{as}(CH_3)$), 2914 (s, $\nu_{as}(CH_2)$), 2875 (s, $\nu_s(CH_3)$), 2792, 1450 (s, $\delta_{as}(CH_3)$), 1396 (m, $\delta_{as}(CH_2)$), 1337, 1249 (m, $\delta_s(CH_3)$), 1217, 1175, 1143, 1079, 1024, 944, 909, 836 (s, $\nu(Si(CH_2)_4)$), 747, 692 and 643 (neat);

δ_H($CDCl_3$, 400 MHz) 1.39 (2 H, m, $CH_2CH_2CH_2$), 0.71 (2H, m, ^3J(HCCH) 8 Hz, CH_2Si), 0.58 (2 H, m, ^3J(HCCH) 8 Hz, CH_2Si), 0.11 (6 H, s, $Si(CH_3)_2$) and 0.01 (9 H, s, $Si(CH_3)_3$);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 30.52, 21.19, 18.18, 18.14, –1.61 (2 C, $Si(CH_3)_2$) and –4.53 (3 C, $Si(CH_3)_3$);

m/z (EI) 209 (97), 208 (28), 207 (31) and 181 (25 %) (M^+ 222 was not observed).

G1(CH$_2$Cl)$_4$, Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$Cl]$_4$

Chloromethyldimethylsilane, **4**, (1.500 g, 13.8 mmol) was loaded into a roundbottom flask in air. The silane was mixed with tetraallylsilane, **G1(allyl)$_4$**, (700 mm^3, 3.0 mmol) and THF (7.0 cm^3). The mixture was degassed through three pump/refill cycles. Karstedt catalyst solution (1 % Pt in toluene, 100 mm^3) was added and the mixture stirred. After an induction period of about 10 min a strong exotherm was observed, and the colour changed to yellow/orange. When the exotherm died away, the mixture was heated under reflux. The reaction was monitored by observing the decrease of the C=C stretch frequency at 1618 cm^{-1} (removal of volatiles *in vacuo*, IR: neat). After heating to reflux overnight, the signal was reduced to negligible. The volatiles were removed *in vacuo*, and the dendrimer dissolved in pentane. The pentane solution was filtered over Celite to remove the platinum catalyst. Evaporation of the solvent *in vacuo* afforded the dendrimer **G1(CH$_2$Cl)$_4$**, Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$Cl]$_4$

(1.79 g, 95 %); R_f(silica/hexane) 0.55

(Found: C, 45.8; H, 9.3. $C_{24}H_{56}Cl_4Si_5$ (626.95) requires C, 46.0; H, 9.0 %);

$\tilde{\nu}_{max}$/cm^{-1} 2957 (s, $\nu_{as}(CH_3)$), 2915 (s, $\nu_{as}(CH_2)$), 2875 (s, $\nu_s(CH_3)$), 2793 (w), 1448 (m, $\delta_{as}(CH_3)$), 1396 (s, $\delta_s(CH_3)$), 1335 (m), 1250 (s, $\delta_s(Si(CH_3)_2)$), 1176 (m), 1144 (m), 1076 (m, br), 944 (m), 910 (m), 846 (s, $\nu(Si(CH_2)_4)$) and 810 (s, $\nu(Si(CH_3)_2)$) (neat);

δ_H($CDCl_3$, 400 MHz) 2.76 (8 H, s, 4 C*H*$_2$Cl), 1.35 (8 H, m, 4 CH$_2$C*H*$_2$CH$_2$), 0.70 (8 H, m, 4 C*H*$_2$Si), 0.59 (8 H, m, 4 Si[C*H*$_2$) and 0.095 (24 H, s, 8 C*H*$_3$);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 30.46 (4 C, 4 *C*H$_2$Cl), 18.62 (4 C,), 18.33 (4 C,), 17.32 (4 C,) and –4.49 (8 C, 8 *C*H$_3$);

$\delta_{Si\{H\}}$($CDCl_3$, 74.5 MHz) 3.94 (1 Si, *Si*(CH$_2$)$_4$) and 1.02 (4 Si, 4 *Si*CH$_2$Cl);

m/z (FAB) 477 (M$^+$ – .CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$Cl). The parent ion (M$^+$ = 627) was not observed.

G2(CH$_2$Cl)$_{12}$, Si{CH$_2$CH$_2$CH$_2$Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$Cl]$_3$}$_4$

Chloromethyldimethylsilane, **4**, (1.500 g, 13.8 mmol) was loaded in a round bottomed flask in air. The silane was mixed with second generation dendrimer **G2(allyl)$_{12}$** (0.809 g, 1.0 mmol) and THF (7.0 cm^3). The mixture was degassed through three pump/refill cycles. Karstedt catalyst solution (1 % Pt in toluene, 100 mm^3) was added and the mixture stirred. After an induction period of about 10 min a strong exotherm was observed, and the colour changed to yellow/orange. After the exotherm died away, the mixture was heated under reflux. The reaction was monitored by observing the decrease of the C=C stretch frequency at 1618 cm^{-1}. After heating to reflux overnight, the signal was reduced to negligible. The volatiles were removed *in vacuo*, and the dendrimer dissolved in pentane. The pentane solution was filtered over Celite. Evaporation of the solvent *in vacuo* afforded the dendrimer **G2(CH$_2$Cl)$_{12}$**, Si{CH$_2$CH$_2$CH$_2$Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)CH$_2$Cl]$_3$}$_4$ (2.0 g, 95 %); R_f(silica/hexane) 0.40,

(Found: C, 49.0; H, 10.0. $C_{84}H_{192}Cl_{12}Si_{17}$ (2105.3) requires C, 47.9; H, 9.2 %);

$\tilde{\nu}_{max}/cm^{-1}$ 2957 (s, $\nu_{as}(CH_3)$), 2915 (s, $\nu_{as}(CH_2)$), 2875 (s, $\nu_s(CH_3)$), 2793 (m, $\nu_s(CH_2)$), 1448 (m, $\delta_{as}(CH_2)$), 1396 (m), 1335 (m), 1250 (s, $\delta_s(CH_3)$), 1176 (m), 1144 (m), 1076 (m, br), 944 (m), 910 (m), 846 (s, $\nu(Si(CH_2)_4)$) and 810 (s, $\nu_s(Si(CH_3)_2)$);

$\delta_H(CDCl_3, 400\ MHz)$ 2.76 (24 H, s 12 CH_2Cl), 1.38 (24 H, m, 12 $CH_2CH_2CH_2$; branches), 1.28 (8 H, m, 4 $CH_2CH_2CH_2$; core propyl), 0.70 (24 H, m, 12 CH_2Si; branches), 0.59 (40 H, m, 20 $SiCH_2$) and 0.095 (72 H, s, 24 CH_3).

$\delta_{C\{H\}}(CDCl_3, 100.6\ MHz)$ 30.43 (12 C, 12 CH_2Cl), 18.66 (12 C, 12 $SiCH_2$), 18.36 (16 C, 16 $CH_2CH_2CH_2$), 17.83 (4 C, 4 $SiCH_2$), 17.67 (4 C, 4 $SiCH_2$), 17.36 (12 C, $SiCH_2$) and –4.43 (24 C, 24 CH_3);

$\delta_{Si\{H\}}(CDCl_3, 74.9\ MHz)$

m/z (FAB) Compound decomposed in the spectrometer; only low *m/z* were observed.

G3$(CH_2Cl)_{36}$, Si{$CH_2CH_2CH_2Si[CH_2CH_2CH_2Si(CH_2CH_2CH_2Si(CH_3)_2CH_2Cl)_3]_3$}$_4$

To a mixture of **G3(allyl)$_{36}$** (1.00 g, 0.38 mmol) and Karstedt catalyst solution (1 % Pt in toluene, 100 mm^3) in THF (5.0 cm^3) was slowly added at 0 °C, a solution of (chloromethyl)dimethylsilane, **4**, (2.0 g, 18.4 mmol) in THF (5.0 cm^3). The mixture was allowed to attain room temperature and was stirred for 2 h. The mixture was then heated under reflux for 14 days, the progress of the reaction was followed by IR spectroscopy (ν(C=C) frequency). The volatiles were removed *in vacuo* and the product filtered over a pad of Celite, eluting with hexane. The hexane was removed *in vacuo*, heating to 100 °C, to give colourless oily **G3$(CH_2Cl)_{36}$**, Si{$CH_2CH_2CH_2Si[CH_2CH_2CH_2Si(CH_2CH_2CH_2Si(CH_3)_2CH_2Cl)_3]_3$}$_4$ (2.28 g, 92 %)

$\delta_H(CDCl_3, 400\ MHz)$ 2.77 (72 H, s, 36 CH_2Cl), 1.4–1.2 (104 H, m, 52 $CH_2CH_2CH_2$), 0.72 (72 H, m, ^3J(HCCH) 8 Hz, 36 CH_2SiCH_2Cl), 0.7–0.4 (136 H, m, 68 $SiCH_2$) and 0.11 (216 H, s, 72 CH_3);

$\delta_{C\{H\}}(CDCl_3, 75.45\ MHz)$ 30.36 (36 C, 36 CH_2Cl), 18.72 (36 C, 36 $SiCH_2$), 18.43 (36 C, 36 $CH_2CH_2CH_2$), 17.38 (36 C, 36 $SiCH_2$) and –4.31 (72 C, 72 CH_3). Resonances due to the 'core' Si{$CH_2CH_2CH_2Si[CH_2CH_2CH_2Si]_3$}$_4$ were not visible due to difference in intensities and overlap (signals are visible between δ 18.5 and 17.5). Correlation between H and C was confirmed by HSQC 2D NMR spectroscopy.

G0$(CH_2I)_1$, $ICH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3$

Sodium iodide (2.0 g, 13.3 mmol) and $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_2CH_2Cl$, **G0$(CH_2Cl)_1$**, (1.500 g, 6.7 mmol) were dissolved in acetone (20 cm^3). The mixture was heated under reflux for 2 h, during which time a white solid precipitated. The volatiles were removed *in vacuo*. The remaining solids were partitioned between hexane (25 cm^3) and water (25 cm^3). The aqueous layer was extracted with hexane (3 x 25 cm^3). The combined organic layers were washed with water (3 x 25

cm^3) and brine (3 x 25 cm^3), dried over $MgSO_4$ and filtered. Removal of the volatiles *in vacuo* gave **G0(CH$_2$I)$_1$**, $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_2CH_2I$ (1.8 g, 78 %);

δ_H($CDCl_3$, 400 MHz) 1.99 (2 H, s, CH_2I), 1.35 (2 H, m, $CH_2CH_2CH_2$), 0.70 (2 H, m, ^3J(HCCH) 8 Hz, $SiCH_2$), 0.55 (2 H, m, ^3J(HCCH) 8 Hz, $SiCH_2$), 0.10 (6 H, s, $Si(CH_3)_2$) and –0.03 (9 H, s, $Si(CH_3)_3$);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 21.2 (1 C, $CH_2CH_2CH_2$), 19.3 (1 C, $SiCH_2$), 18.3 (1 C, $SiCH_2$), –1.6 (3 C, $Si(CH_3)_3$), –3.0 (2 C, $Si(CH_3)_2$) and –13.1 (1 C, CH_2I)

G1(CH$_2$Fp)$_4$, Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$Fe(CO)$_2$C$_5$H$_5$]$_4$

$[CpFe(CO)_2]_2$ (0.300 g, 0.85 mmol) was cracked over NaK-melt[64] (from 0.200 g K and 0.060 g Na) in THF in 2.5 h in a double Schlenk-tube. The mixture was filtered and a solution of **G1(CH$_2$Cl)$_4$**, $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Cl]_4$ (0.100 g, 0.16 mmol) in THF (2.0 cm^3) was added *via* syringe. The mixture was stirred overnight and the solvent distilled off *in vacuo*. Extraction with pentane gave a yellow solution. The product was purified through column chromatography (silica/CH_2Cl_2:hexane = 1:1) and the first yellow band was collected. Evaporation of the solvent gave a yellow oil: **G1(CH$_2$Fp)$_4$**, $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Fe(CO)_2C_5H_5]_4$

(0.169 g, 89 %), R_f(silica/CH_2Cl_2:hexane = 1:1) 0.79;

$\tilde{\nu}_{max}$/cm^{-1} 2011 (s, ν(CO)) and 1959 (s, ν(CO)) (hexane);

δ_H($CDCl_3$, 400 MHz) 4.79 (20 H, s, 4 C_5H_5), 1.36 (8 H, m, 4 $CH_2CH_2CH_2$), 0.59 (16 H, m, ^3J(HCCH) 8 Hz, 8 $SiCH_2$), 0.01 (24 H, s, 8 CH_3) and –0.32 (8 H, s, 4 CH_2Fe);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 217.45 (8 C, 8 CO), 84.84 (20 C, 4 C_5H_5), 24.04 (4 C), 19.02 (4 C), 17.95 (4 C), 0.24 (8 C, 8 CH_3) and –24.99 (4 C, 4 CH_2Fe).

G1(CH$_2$Rp)$_4$, Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$Ru(CO)$_2$C$_5$H$_5$]$_4$

$[CpRu(CO)_2]_2$ (0.300 g, 0.68 mmol) was cracked over NaK-melt[64] (from 0.200 g K and 0.060 g Na) in THF in 2.5 h in a double Schlenk-tube. The mixture was filtered and a solution of **G1(CH$_2$Cl)$_4$**, $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Cl]_4$ (0.100 g, 0.16 mmol) in THF (2.0 cm^3) was added *via* syringe. The mixture was stirred overnight and the solvent distilled off *in vacuo*. Extraction with pentane gave a colourless solution. The product was purified through column chromatography (silica/CH_2Cl_2:hexane = 1:1) and the first band was collected. Evaporation of the solvent gave a colourless oil: **G1(CH$_2$Rp)$_4$**, $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Ru(CO)_2C_5H_5]_4$

(0.169 g, 84 %), R_f(silica/CH_2Cl_2:hexane = 1:1) 0.81;

$\tilde{\nu}_{max}$/cm^{-1} 2011 (s, ν(CO)) and 1959 (s, ν(CO)) (hexane);

δ_H($CDCl_3$, 400 MHz) 4.81 (20 H, s, 4 C_5H_5), 1.36 (8 H, m, 4 $CH_2CH_2CH_2$), 0.59 (16 H, m, ^3J(HCCH) 8 Hz, 8 $SiCH_2$), 0.01 (24 H, s, 8 CH_3) and –0.22 (8 H, s, 4 CH_2Ru);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 217. 5 (8 C, 8 CO), 84.8 (20 C, 4 C_5H_5), 24.0 (4 C), 19.02 (4 C), 18.0 (4 C), 0.2 (8 C, 8 CH_3) and –23.8 (4 C, 4 CH_2Ru).

Allyl(chloromethyl)dimethylsilane

A solution of allylmagnesium bromide in diethyl ether (1.0 M, 20 cm^3, 20 mmol) was slowly added to chloro(chloromethyl)dimethylsilane (2.6 cm^3, 2.8 g, 19.7 mmol) in diethyl ether (10 cm^3) at –80 °C. The immediate precipitation of a white solid was observed. The mixture was stirred and heated to –40 °C over 1 h. The reaction was quenched with concentrated NH_4Cl solution at –40 °C. The organic layer was separated and the aqueous layer washed with diethyl ether (3 x 10 cm^3). The combined organic layers were washed with saturated KF-solution (3 x 10 cm^3), water (3 x 10 cm^3) and brine (3 x 10 cm^3), dried over $MgSO_4$, filtered and the diethyl ether was distilled off at atmospheric pressure to leave a colourless oily $ClCH_2Si(CH_3)_2CH_2CH{=}CH_2$. (1.93 g, 65 %).

δ_H($CDCl_3$, 400 MHz) 5.78 (1 H, m, C*H*), 4.90 (2 H, m, =CH_2), 2.79 (2 H, s, CH_2Cl), 1.66 (2 H, d, ^3J(HCCH) 8 Hz, CH_2CH) and 0.13 (6 H, s, 2 CH_3);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 133.67 (1 C, *C*H), 113.87 (1 C, =CH_2), 29.62 (1 C, CH_2Cl), 21.32 (1 C, CH_2CH) and –5.03 (2 C, 2 CH_3);

m/z (EI) 149 (M^+) and 109 ($M^+ - C_3H_5$).

8.3 Procedures pertaining to chapter 3

$(CH_3)_3SiCH=CHCH_2Si(CH_3)_3$

A solution of *n*-butyllithium in hexane (8.0 cm^3, 1.6 M, 12.8 mmol) was added to a solution of potassium *tert*-butoxide (1.5 g, 12.3 mmol) in pentane (10 cm^3) at –78 °C. The mixture was warmed to room-temperature and stirred for 0.5 h. The mixture was cooled to –20 °C, diethyl ether (10 cm^3) was added followed by allyltrimethylsilane (1.0 cm^3, 6.3 mmol). The mixture was slowly warmed to room temperature and stirred for 3 h. Chlorotrimethylsilane (5.0 cm^3, mmol) was added at –20 °C and the mixture was warmed to room-temperature. The colour of the mixture changed to faint yellow and a white precipitate formed. The volatiles were removed in vacuo and the products partitioned between hexane (10 cm^3) and water (10 cm^3). The aqueous layer was extracted with hexane (3 x 10 cm^3). The combined organic layers were washed with water (3 x 10 cm^3) and brine (3 x 10 cm^3), dried over $MgSO_4$ and filtered. Removal of the volatiles *in vacuo* left *trans*-$(CH_3)_3SiCH=CHCH_2Si(CH_3)_3$ (1.05 g, 100 %)

(Found: C, 54.4; H, 11.4. $C_9H_{22}Si_2$ (186.45) requires C, 58.0; H, 11.9 %)

$\tilde{\nu}_{max}/cm^{-1}$ 2955 (s, $\nu_s(CH_3)$), 2896 (s, $\nu(CH)$), 1606 (s, $\nu(C=C)$), 1400(m, $\delta_{as}(CH_2)$), 1249 (s, $\delta_s(Si(CH_3)_3)$), 1142, 1057, 1015, 986 (*s*, γ(*trans*-HC=CH)), 844 (s, $\nu(Si(CH_3)_3)$), 756 (s, $\nu(Si(CH_3)_3)$), 720 (s, $\delta(CH_2)$) and 669 (neat);

δ_H($CDCl_3$, 400 MHz) 6.04 (1 H, dt, ^3J(HCCH) 18 Hz, ^3J(HCCH) 8 Hz, =C*H*CH_2), 5.46 (1 H, d, ^3J(HCCH) 18 Hz, SiC*H*=), 1.64 (2 H, d, ^3J(HCCH) 8 Hz, CH_2), 0.05 (9 H, s, 3 CH_3) and 0.02 (9 H, s, 3 CH_3);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 143.76 (1 C, =$CHCH_2$), 128.27 (1 C, =*C*HSi), 28.54 (1 C, CH_2), -0.83 (3 C, 3 CH_3) and -1.87 (3 C, 3 CH_3). Correlation between H and C was confirmed by HSQC 2D NMR spectroscopy.

$\delta_{Si\{H\}}$($CDCl_3$, 79.5 MHz) 0.23 (1 Si, *Si*$(CH_3)_3$) and –11.55 (1 Si, =CH*Si*$(CH_3)_3$).

m/z (FAB) only low *m/z* peaks were observed.

Attempted synthesis of $Si(CH=CHCH_2D)_4$

A solution of *n*-butyllithium in hexane (6.0 cm^3, 1.6 M, 9.6 mmol) was added to a solution of potassium *tert*-butoxide (1.2 g, 10.6 mmol) in pentane (10 cm^3) at –78 °C. The mixture was stirred for 30 min and tetraallylsilane (0.5 cm^3, 2.2 mmol) was added by syringe. The dark red-brown solution immediately turned yellow. Diethyl ether (10 cm^3) was added to dissolve any polymetallic species. The solution was heated, in subsequent experiments, to 0 °C, room temperature or reflux for 3 h. The mixture was cooled down to –20 °C and D_2O (3.0 cm^3, 166 mmol) was added. The volatiles were removed *in vacuo*. The resulting products were suspended between water (10 cm^3) and hexane (10 cm^3). The aqueous layer was extracted with hexane (3 x 10 cm^3) and the

combined organic layers were washed with water (3 x 10 cm^3) and brine (3 x 10 cm^3) and dried over $MgSO_4$. Filtration followed by evaporation of the volatiles *in vacuo* afforded a mixture of products as a colourless oil. ^1H and ^{13}C NMR revealed that a maximum of 81 % of the branches were converted to the internal, deuterated alkene. The product composition is therefore (theoretical): $Si(CH=CHCH_2D)_4$: 43 %; $(CH_2=CHCH_2)Si((CH=CHCH_2D)_3$: 40 %; $(CH_2=CHCH_2)_2Si((CH=CHCH_2D)_2$: 14 %; $(CH_2=CHCH_2)_3Si((CH=CHCH_2D)$: 2 % and $(CH_2=CHCH_2)_4Si$: 0.1 %

Attempted synthesis of $Si[CH=CHCH_2Si(CH_3)_3]_4$

i) A solution of *n*-butyllithium in hexane (12 cm^3, 1.6 M, 19.2 mmol) was added to a solution of potassium *tert*-butoxide (2.2 g, 19.6 mmol) in hexane (10 cm^3) at –78 °C. The mixture was warmed to room-temperature and stirred for 30 min. The mixture was cooled down to –78 °C and tetraallylsilane (0.5 cm^3, 2.2 mmol) and diethyl ether (2.0 cm^3) were added. The solution was heated to reflux for 3 h. The brown/yellow suspention was cooled down to –20 °C and chlorotrimethylsilane (5.0 cm^3, 39.4 mmol) was added. The volatiles were removed in vacuo. The resulting products were suspended between water (10 cm^3) and hexane (10 cm^3). The aqueous layer was extracted with hexane (3 x 10 cm^3) and the combined organic layers were washed with water (3 x 10 cm^3) and brine (3 x 10 cm^3) and dried over $MgSO_4$. Filtration followed by evaporation of the volatiles *in vacuo* afforded a mixture of products as a colourless oil. ^1H and ^{13}C NMR revealed that a maximum of 80 % of the branches were converted to the internal, silylated alkene.

ii) To a solution of tetraallylsilane (100 mm^3, 0.43 mmol) and TMEDA (280 mm^3, 1.85 mmol) in pentane (3.0 cm^3) at –78 °C was added a solution of *n*-butyllithium in hexane (1.3 cm^3, 1.6 M, 2.1 mmol). The mixture was allowed to attain room temperature. After stirring for 16 h and heatng under reflux for 10 min the mixture was cooled down and chlorotrimethylsilane (5.0 cm^3, mmol) was added. A white solid formed immediately. The volatiles were removed in vacuo. The resulting products were suspended between water (10 cm^3) and hexane (10 cm^3). The aqueous layer was extracted with hexane (3 x 10 cm^3) and the combined organic layers were washed with water (3 x 10 cm^3) and brine (3 x 10 cm^3) and dried over $MgSO_4$. Filtration followed by evaporation of the volatiles *in vacuo* afforded a mixture of products as a colourless oil. ^1H and ^{13}C NMR revealed that maximum 80 % of the branches were converted to the internal, silylated alkene.

Attempted synthesis of $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Li]_4$ through halogen/metal exchange

A solution of $Si[CH_2CH_2CH_2Si(CH_3)_2Cl]_4$, **G1($CH_2Cl$)$_4$**, (0.10 g, 0.16 mmol) in diethyl ether (8 cm^3) was slowly added to a suspention of lithium pieces (0.30 g, 43 mmol) in diethyl ether (8 cm^3) at 0 °C. A white precipitate formed. After all of the dendrimer, **G1(CH_2Cl)$_4$**, was added, the mixture

was stirred for 16 h and then quenched with CH_3OD (1 cm^3, mmol). The salts were dissolved in water (10 cm^3) and the organic layer separated. The aqueous layer was extracted with diethyl ether (3 x 10 cm^3). The combined organic layers were washed with water (3 x 10 cm^3) and brine (3 x 10 cm^3), dried over $MgSO_4$ and filtered. The volatiles were removed *in vacuo* to give $Si[CH_2CH_2CH_2Si(CH_3)_3]_4$, **G1(CH$_3$)$_4$**, (0.03 g, 43 %)

δ_H($CDCl_3$, 400 MHz) 1.34 (8 H, m, $CH_2CH_2CH_2$), 0.57 (16 H, m, 8 $SiCH_2$) and –0.01 (36 H, s, 4 $Si(CH_3)_3$);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 21.68 (4 C, 4 $SiCH_2$), 18.55 (4 C, 4 $CH_2CH_2CH_2$), 17.52 (4 C, 4 $SiCH_2$) and –1.54 (12 C, 4 $Si(CH_3)_3$).

No trace of deuteration was observed in either the ^1H or the ^{13}C NMR spectrum.

7, $HSi(CH_3)_2CH_2SC_6H_5$[83]

A modified literature method was used to synthesise this compound.[83] ^{n}BuLi (58 cm^3, 1.6 M, 92.8 mmol) was added to a solution of thioanisole (10.0 cm^3; 85.18 mmol) in diethyl ether (10 cm^3). The mixture was heated under reflux for 18 h during which time a white solid precipitated. The mixture was cooled to –78 °C and chlorodimethylsilane (12 cm^3; 85 mmol) was added by syringe. The mixture was warmed to room temperature for 30 min and then heated under reflux for 1h. The volatiles were removed *in vacuo* and the mixture taken up in hexane. The resulting hexane solution was filtered to remove LiCl and the volatiles removed *in vacuo*. The resulting pale yellow oil was distilled at 109 °C, 1 mm Hg to give **7**, $HSi(CH_3)_2CH_2SC_6H_5$ (11.8 g, 76 %) bp. 109 °C (1 mm Hg)

(Found: C, 59.1; H, 7.6; S, 16.0. $C_9H_{14}SSi$ (182.4) requires C, 59.3; H, 7.7; S, 17.6 %);

$\tilde{\nu}_{max}/cm^{-1}$ 3074 (s, ν(C-H_{ar})), 3058 (s, ν(C-H_{ar})), 3018, 2959 (s, $\nu_{as}(CH_3)$), 2921 (s, $\nu_{as}(CH_2)$), 2890, 2129 (s, ν(Si-H)), 1579 (m, ν(C=C)), 1479 (m, ν(C=C)), 1438 (s, $\delta_{as}(CH_3)$), 1424, 1388, 1298, 1251 (s, $\delta_s(CH_3)$), 1183, 1130, 1087, 1069, 1025, 883, 841 (s, $\nu_s(Si(CH_2)_3)$), 807 (s, $\nu(Si(CH_3)_2)$), 780, 737 (s, $\gamma(CH_{ar})$), 689 (s, $\gamma(CH_{ar})$), 626 and 473 (neat);

δ_H($CDCl_3$, 300 MHz) 7.40–7.33 (4 H, m, H-1, -5, -2, -4 of C_6H_5), 7.31 (1H, m, H-3 of C_6H_5), 4.10 (1 H, m, Si*H*), 2.27 (2 H, d, ^3J(HSiCH) 3 Hz, CH_2) and 0.24 (6 H, d, ^3J(HSiCH) 4 Hz, 2 CH_3);

$\delta_{C\{H\}}$($CDCl_3$, 75.5 MHz) 139.8 (1 C, C-1 of SC_6H_5), 128.7 (2 C), 126.5 (2 C)(C-2, -5 and C-3, -4 of SC_6H_5), 124.9 (1 C, C-4 of SC_6H_5), 16.0 (1 C, SCH_2) and –4.5 (2 C, 2 CH_3);

$\delta_{Si\{H\}}$($CDCl_3$, 79.5 MHz) –14.4;

m/z (FAB) 182.05806 (M^+, 33 %) ($C_9H_{14}SSi$ requires 182.05855), 167 ($M^+ - CH_3$, 59), 166 ($M^+ - CH_3 - H$, 15), 123 ($C_6H_5SCH_2^+$, 29), 109 ($C_6H_5S^+$, 12) and 77 ($C_6H_5^+$, 39).

The ^1H NMR, IR and MS data were in agreement with the literature values.[83] The ^{13}C and ^{29}Si NMR data was not reported previously.

G0(CH_2SPh)$_1$, $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5$

(Phenylthiomethyl)dimethylsilane, **7**, (0.705 g, 0.39 mmol), allyltrimethylsilane, **G0(allyl)$_1$**, (1.0 cm^3, 0.6 mmol) and Karstedt catalyst solution (1 % Pt in toluene, 100 mm^3) were heated to 100 °C for 3 h. The initially yellow solution slowly turned black. The volatiles were removed *in vacuo*, leaving a colourless oil and a black precipitate. The oil was filtered over a pad of silica gel, eluting with hexane. Removal of the volatiles left a colourless oil, **G0(CH_2SPh)$_1$**, $(CH_3)_3SiCH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5$ (1.11 g, 96 %)

(Found: C, 61.4; H, 9.9; S, 10.5. $C_{15}H_{28}SSi_2$ (296.6) requires C, 60.7; H, 9.5; S, 10.8 %);

$\tilde{\nu}_{max}/cm^{-1}$ 3073 (w, $\nu(CH_{ar})$), 3058 (w, $\nu(CH_{ar})$), 3016, 2952 (s, $\nu_{as}(CH_3)$), 2910 (s, $\nu_{as}(CH_2)$), 1933 (w), 1851 (w), 1784 (w) and 1695 (w) (monosubstituted benzene), 1584 (m, ν(C=C)), 1479 (m, ν(C=C)), 1437 (s, $\delta_{as}(CH_2)$), 1390, 1335, 1248 (s, $\delta_s(CH_3)$), 1215, 1085, 1025, 979, 943, 908, 864, 836 (s, $\nu(Si(CH_3)_2)$), 736 (s, γ(CH)), 689 (s, γ(CH)) and 472;

δ_H($CDCl_3$, 300 MHz) 7.40–7.33 (4 H, m, H-1, -5, -2, -4 of C_6H_5), 7.31 (1H, m, H-3 of C_6H_5), 2.22 (2H, s, CH_2S), 1.46 (2H, m, $CH_2CH_2CH_2$), 0.77 (2H, m, ^3J(HCCH) 9 Hz, $SiCH_2$), 0.63 (2H, m, ^3J(HCCH) 8 Hz, $SiCH_2$), 0.19 (6H, s, $Si(CH_3)_2$) and 0.03 (9H, s, $Si(CH_3)_3$);

δ_C($CDCl_3$, 75.5 MHz) 140.5 (1 C, C-1 of SC_6H_5), 128.6 (2 C), 126.1 (2 C)(C-2, -5 and C-3, -4 of SC_6H_5), 124.6 (1 C, C-4 of SC_6H_5), 21.2 (1 C, $SiCH_2$), 19.5 (1 C, $SiCH_2$), 18.3 (1 C, $CH_2CH_2CH_2$), 17.2 (1 C, SCH_2), –1.5 (3 C, $Si(CH_3)_3$) and –3.2 (2 C, $Si(CH_3)_2$); Correlation between H and C was confirmed by HSQC 2D NMR spectroscopy.

$\delta_{Si\{H\}}$($CDCl_3$, 79.5 MHz) 2.89 (1 Si, $SiCH_2S$), 0.95 (1 Si, $Si(CH_3)_3$);

m/z (FAB) 296 (M^+, 27 %), 281 ($M^+ - CH_3$, 58), 209 ($M^+ - CH_2Si(CH_3)_3$, 4), 181 ($Si(CH_3)_2CH_2SPh^+$, 100), 165 ($Si(CH_2)CH_2SPh^+$, 65), 151 ($SiCH_2SPh^+$, 14), 135 (25), 99 (43) and 91 (15).

G1(CH_2SPh)$_4$, $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5]_4$

(Phenylthiomethyl)dimethylsilane, **7** (4.92 g, 27 mmol), tetraallylsilane, **G1(allyl)$_4$**, (1.5 cm^3, 6.48 mmol) and Karstedt catalyst solution (200 mm^3) were heated to 120 °C for 18 h. The reaction was followed by monitoring the peak at 1610 cm^{-1} in the IR spectrum of the mixture (associated with the C=C stretch resonance). The volatiles were removed *in vacuo* at 140 °C, leaving a colourless oil and a black precipitate. The oil was filtered over a pad of silica gel, eluting with hexane. Removal of the volatiles *in vacuo* left colourless **G1(CH_2SPh)$_4$**, $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5]_4$ (5.79 g, 97 %)

(Found: C, 62.1; H, 8.4; S, 13.5. $C_{48}H_{76}S_4Si_5$ (921.8) requires C, 62.5; H, 8.3; S, 13.9 %);

$\tilde{\nu}_{max}/cm^{-1}$ 3072 (w, $\nu(CH_{ar})$), 3057 (w, $\nu(CH_{ar})$), 3016, 2952 (s, $\nu_{as}(CH_3)$), 2911 (s, $\nu_{as}(CH_2)$), 1934 (w), 1851 (w), 1784 (w) and 1717 (w) (monosubstituted benzene), 1581 (m, ν(C=C)), 1479 (m, ν(C=C)), 1438 (s, $\delta_{as}(CH_2)$), 1390, 1333, 1249 (s, $\delta_s(CH_3)$), 1138, 1085, 1067, 1025, 982, 943, 909, 844 (s, $\nu(Si(CH_3)_2)$), 736 (s, γ(CH)), 697, 689 (s, γ(CH)), 668 (S-C ?) and 472;

δ_H($CDCl_3$, 400 MHz) 7.3–6.9 (20 H, m, 4 C_6H_5), 2.09 (8 H, s, 4 CH_2S), 1.30 (8 H, m, 4 $CH_2CH_2CH_2$), 0.70 (8 H, m, ^3J(HCCH) x Hz, 4 $SiCH_2$), 0.55 (8 H, m, ^3J(HCCH) x Hz, 4 CH_2Si) and 0.06 (24 H, s, 8 CH_3);

$\delta_{C\{H\}}$($CDCl_3$, 75.5 MHz) 140.4 (4 C, C-1 of SC_6H_5), 128.6 (8 C), 126.1 (8 C)(C-2, -6 and C-3, -5 of SC_6H_5), 124.6 (4 C, C-4 of SC_6H_5), 19.9 (4 C, 4 $CH_2CH_2CH_2$), 18.5 (4 C, 4 $SiCH_2$), 17.4 (4 C, 4 CH_2Si), 17.2 (4 C, 4 CH_2S) and –3.2 (8 C, 8 CH_3);

$\delta_{Si\{H\}}$($CDCl_3$, 79.45 MHz) 2.04 (4Si, $Si(CH_3)_2$) and 0.95 (1Si, $SiCH_2$);

m/z (FAB) 919 (M^+ – H, 0.5 %), 905 (M^+ – CH_3, 2), 811 (M^+ – SC_6H_5, 3), 797 (M^+ – $CH_2SC_6H_5$, 100), 697 (M^+ – $C_3H_6Si(CH_3)_2CH_2SC_6H_5$, 30), 589 ($M^+$ – $CH_2SC_6H_5$ – $C_2H_4Si(CH_3)_2CH_2SC_6H_5$, 2), 575 ($M^+$ – $CH_2SC_6H_5$ – $C_3H_6Si(CH_3)_2CH_2SC_6H_5$, 2), 475 ($M^+$ – 2 $C_3H_6Si(CH_3)_2CH_2SC_6H_5$, 4) and 181 ($Si(CH_3)_2CH_2SC_6H_5^+$, 80).

G2(CH_2SPh)$_{12}$, Si{$CH_2CH_2CH_2Si[CH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5]_3$}$_4$

$Si[CH_2CH_2CH_2Si(CH_2CH{=}CH_2)_3]_4$, **G2(allyl)$_{12}$**, (0.50 g, 0.62 mmol), $HSi(CH_3)_2CH_2SC_6H_5$ (1.5 g, 8.24 mmol) were mixed and degassed. Karstedt catalyst solution (1 % Pt in toluene, 100 mm^3) was added and the mixture was heated to 130 °C for 16 h. The excess silane was distilled off *in vacuo* at 130 °C and the catalyst was removed by filtration over a pad of silica, eluting with dichloromethane. The solvent was removed in vacuo to give **G2(CH_2SPh)$_{12}$**, Si{$CH_2CH_2CH_2Si[CH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5]_3$}$_4$ as a colourless oil. (1.79 g, 96 %)

δ_H($CDCl_3$, 300 MHz) 7.3-7.0 (60 H, m, 12 SC_6H_5), 2.13 (24 H, s, 12 SCH_2), 1.45-1.20 (32 H, m, 16 $CH_2CH_2CH_2$), 0.75 (24 H, m, 12 $CH_2Si(CH_3)_2$), 0.59 (40 H, m, 20 CH_2Si) and 0.11 (72 H, s, 24 CH_3);

$\delta_{C\{H\}}$($CDCl_3$, 75.5 MHz) 140.4 (12 C, C-1 of SC_6H_5), 128.6 (24 C), 126.1 (24 C)(C-2, -6 and C-3, -5 of SC_6H_5), 124.6 (12 C, C-4 of SC_6H_5), 19.9 (12 C, 4 $CH_2CH_2CH_2$), 18.5 (12 C, 4 $SiCH_2$), 17.4 (12 C, 4 CH_2Si), 17.2 (12 C, 4 CH_2S) and –3.1 (24 C, 8 CH_3); The 'core' propyl chain was not visible due to low intensity of the signal.

$\delta_{Si\{H\}}$($CDCl_3$, 79.45 MHz) 1.99 (12 Si, $Si(CH_3)_2$), 0.76 (4 Si, $SiCH_2$) and 0.50 (1 Si, $Si(CH_2)_4$).

G1(CH_2D)$_4$, Si[$CH_2CH_2CH_2Si(CH_3)_2CH_2D$]$_4$

Lithium metal chunks (0.090 g, mmol) were added to a solution of naphthalene (0.090 g, 0.70 mmol) in THF (5 cm^3) at 0 °C and stirred for 30 min. A dark green solution of lithium naphthalenide developed seconds after adding the metal. A solution of **G1(CH_2SPh)$_4$**, $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5]_4$ (0.600 g, 0.65 mmol) in THF (4 cm^3) was added at such a rate that the green colour of lithium naphthalenide did *not* disappear (± 1 h). The mixture was cooled to –40 °C and D_2O (2.0 cm^3) in THF (2.0 cm^3) was added. The colour of the lithium naphthalenide disappeared completely within seconds to leave a colourless/grey solution. The volatiles were removed *in vacuo* and the products were partitioned between hexane (10 cm^3) and

water (10 cm^3). The aqueous layer was extracted with hexane (3 x 10 cm^3) and the organic phases combined. The organic phase was washed with water (3 x 10 cm^3), dilute aqueous NaOH (3 x 10 cm^3), water (3 x 10 cm^3) and brine (3 x 10 cm^3), dried over $MgSO_4$, filtered and the volatiles were evaporated *in vacuo*. The bulk of the naphthalene was sublimed out of the product at 150 °C, 10^{-3} mm Hg. Chromatography over silica gel, eluting with hexane gave **G1(CH_2D)$_4$**, $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2D]_4$ as a colourless oil (0.265 g, 83 %)

(Found: C, 59.1; H, 11.7 %. $C_{24}H_{56}D_4Si_5$ (493.1) requires C, 58.5; H, 12.2 %);

δ_H($CDCl_3$, 400 MHz) 1.27 (8 H, m, 4 $CH_2CH_2CH_2$), 0.49 (16 H, m, ^3J(HCCH) 8 Hz, 4 CH_2Si), –0.10 (24 H, s, 8 CH_3) and –0.12 (8 H, t, ^2J(DCH) 2 Hz, 4 CH_2D);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 21.6 (4 C, 4 $CH_2CH_2CH_2$), 18.6 (4 C, 4 CH_2Si), 17.5 (4 C, 4 CH_2Si), –1.6 (8 C, 8 CH_3) and –1.9 (4 C, t, ^1J(CD) 18 Hz, 4 CH_2D);

$\delta_{Si\{H\}}$($CDCl_3$, 79.45 MHz) 0.74 (4 Si, $Si(CH_3)_3$) and 0.50 (1 Si, $SiCH_2$);

m/z (FAB) 492.37854 (M^+) ($C_{24}H_{56}D_4Si_5$ requires 492.37925), 462 (M^+ – 2 CH_3), 376 (M^+ – $C_3H_6Si(CH_3)_2CH_2D$), 361 (M^+ – $C_3H_6Si(CH_3)_2CH_2D$ – CH_3), 260 (M^+ – 2 $C_3H_6Si(CH_3)_2CH_2D$), 186 ($C_3H_6SiC_3H_6Si(CH_3)_2CH_2D^+$), 144 ($SiC_3H_6Si(CH_3)_2CH_2D^+$), 100 ($SiC_3H_6Si(CH_3)_2^+$) and 74 ($Si(CH_3)_2CH_2D^+$).

G1(CH_2SiMe_3)$_4$, Si[$CH_2CH_2CH_2Si(CH_3)_2CH_2Si(CH_3)_3$]$_4$

Lithium metal chunks (0.100 g, 14.4 mmol) were added to a solution of naphthalene (0.100 g, 0.78 mmol) in THF (5 cm^3) at 0 °C and stirred for 30 min. A dark green solution of lithium naphthalenide developed seconds after adding the metal. A solution of **G1(CH_2SPh)$_4$**, $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5]_4$ (0.630 g, 0.68 mmol) in THF (3 cm^3) was added at such a rate that the green colour of lithium naphthalenide did *not* disappear (± 1 h). The resulting solution was cooled down to –40 °C and chlorotrimethylsilane (2.0 cm^3, 15.8 mmol) was added quickly. The colour disappeared completely within seconds to leave a colourless/grey solution. The volatiles were removed *in vacuo* and the products were partitioned between hexane (10 cm^3) and water (10 cm^3). The aqueous layer was extracted with hexane (3 x 10 cm^3) and the organic phases combined. The organic phase was washed with water (3 x 10 cm^3), dilute aqueous NaOH (0.1 M; 3 x 10 cm^3), water (3 x 10 cm^3) and brine (3 x 10 cm^3), dried over $MgSO_4$, filtered and the volatiles were evaporated *in vacuo*. The bulk of the naphthalene was sublimed out of the product at 150 °C, 10^{-3} mm Hg. Chromatography over silica gel, eluting with hexane gave $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Si(CH_3)_3]_4$, **G1($CH_2SiMe_3$)$_4$** as a colourless oil (0.461 g, 87 %)

(Found: C, 56.8; H, 12.2. $C_{36}H_{92}Si_9$ (777.9) requires C, 55.5; H, 11.9 %);

$\tilde{\nu}_{max}/cm^{-1}$ 2952 (s, $\nu_{as}(CH_3)$), 2911 (s, $\nu_{as}(CH_2)$), 1448 (m, $\delta_{as}(CH_2)$), 1412 (m), 1353 (m), 1333 (m), 1250 (s, $\delta_s(CH_3)$), 1141 (m), 1051 (s), 983 (w), 943 (w), 909 (s), 837 (vs br, $\nu(Si(CH_3)_3)$), 789 (s), 762 (s, $\nu(Si(CH_3)_3)$), 687 (s), 614 (w), 589 (w) and 553 (w);

δ_H($CDCl_3$, 400 MHz) 1.35 (8 H, m, 4 $CH_2CH_2CH_2$), 0.57 (16 H, m, ^3J(HCCH) 8 Hz, 8 CH_2Si), 0.03 (36 H, s, 4 $Si(CH_3)_3$), 0.00 (24 H, s, 4 $Si(CH_3)_2$) and –0.29 (8 H, s, 4 $SiCH_2Si$);

δ_c($CDCl_3$, 100.6 MHz) 23.0 (4 C, 4 $CH_2CH_2CH_2$), 18.7 (4 C, 4 CH_2Si), 17.7 (4 C, 4 CH_2Si), 2.8 (4 C, 4 $SiCH_2Si$), 1.4 (12 C, 4 $Si(CH_3)_3$) and –0.5 (8 C, 4 $Si(CH_3)_2$);

$\delta_{Si\{H\}}$($CDCl_3$, 79.45 MHz) 1.0 (4 Si, 4 $Si(CH_3)_2$), 0.82 (4 Si, 4 $Si(CH_3)_3$) and 0.5 (1 Si, $Si(CH_2)_4$);

m/z (EI) 776 (M^+, 0.8), 705 (7), 643 (13), 566 ($C_{28}H_{62}Si_6$, 60), 493 ($C_{25}H_{53}Si_5$, 100), 442 ($C_{21}H_{50}Si_5$, 59) and 331 ($C_{18}H_{31}Si_3$, 93 %).

G1(CH_2SnMe_3)$_4$, Si[$CH_2CH_2CH_2Si(CH_3)_2CH_2Sn(CH_3)_3$]$_4$

Lithium metal chunks (0.100 g, 14.4 mmol) were added to a solution of naphthalene (0.100 g, 0.78 mmol) in THF (5 cm^3) at 0 °C and stirred for 30 min. A dark green solution of lithium naphthalenide developed seconds after adding the metal. A solution of **G1(CH_2SPh)$_4$**, Si[$CH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5$]$_4$ (0.630 g, 0.68 mmol) in THF (3 cm^3) was added at such a rate that the green colour of lithium naphthalenide did *not* disappear (± 1 h). The resulting solution was cooled down to –40 °C and a solution of chlorotrimethyltin in THF (5.0 cm^3, 1.0 M, 5.0 mmol) was added quickly. The colour disappeared completely within seconds to leave a colourless/grey solution. The volatiles were removed *in vacuo* and the products were partitioned between hexane (10 cm^3) and water (10 cm^3). The aqueous layer was extracted with hexane (3 x 10 cm^3) and the organic phases combined. The organic phase was washed with water (3 x 10 cm^3), dilute aqueous NaOH (0.1 M; 3 x 10 cm^3), water (3 x 10 cm^3) and brine (3 x 10 cm^3), dried over $MgSO_4$, filtered and the volatiles were evaporated *in vacuo*. The bulk of the naphthalene was sublimed out of the product at 150 °C, 10^{-3} mm Hg. Chromatography over silica gel, eluting with hexane gave Si[$CH_2CH_2CH_2Si(CH_3)_2CH_2Si(CH_3)_3$]$_4$, **G1($CH_2SnMe_3$)$_4$** as a colourless oil (0.74 g, 80 %)

(Found: C, 40.1; H, 8.4 %. $C_{36}H_{92}Si_5Sn_4$ (1140.4) requires C, 37.9; H, 8.1 %);

(Found: C, 40.1; H, 8.4 %. $C_{36}H_{92}Si_5Sn_4.C_6H_{14}$ (1226.5) requires C, 41.1; H, 8.6 %);

$\tilde{\nu}_{max}$/cm^{-1} 2951 (s, $\nu_{as}(CH_3)$), 2911 (s, $\nu_{as}(CH_2)$), 2875 (s, $\nu_s(CH_3)$), 1448 (m, $\delta_s(CH_3)$), 1412, 1357, 1333, 1246 (s, $\delta_s(SiCH_3)$), 1215, 1188 (m, $\delta_s(SnCH_3)$), 1141, 1079, 998, 941, 906, 833 (s, $\nu_{as}(SiC)$), 772, 720, 581 and 524 (s, $\nu_{as}(SnC)$);

δ_H($CDCl_3$, 400 MHz) 1.34 (8 H, m, 4 $CH_2CH_2CH_2$), 0.58 (16 H, t, 8 $SiCH_2$), 0.10 (36 H, s, 2J(HCSn) Hz, 4 $Sn(CH_3)_3$), –0.02 (24 H, s, 4 $Si(CH_3)_2$) and –0.26 (8 H, s, 2J(HCSn) Hz, 4 $SiCH_2Sn$);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 22.24 (4 C,), 18.75 (4 C,), 17.65 (4C,), –0.22 (8 C, 4 $Si(CH_3)_2$), –5.65 (12 C, ^1J(CSn) Hz, 4 $Sn(CH_3)_3$) and –8.00 (4 C, ^1J(CSn) Hz, $SiCH_2Sn$);

$\delta_{Si\{H\}}$($CDCl_3$, 79.45 MHz) 4.07 (4 Si, 4 $Si(CH_3)_2$) and 0.82 (1 Si, $Si(CH_2)_4$);

m/z (FAB) (M^+ = 1144) Compound decomposed in the spectrometer; only low *m/z* were observed.

G1(CH_2SnBu_3)$_4$, Si[$CH_2CH_2CH_2Si(CH_3)_2CH_2Sn(CH_2CH_2CH_2CH_3)_3$]$_4$

Lithium metal chunks (0.100 g, 14.5 mmol) were added to a solution of naphthalene (0.100 g, 0.78 mmol) in THF (5 cm^3) at 0 °C and stirred for 30 min. A dark green solution of lithium naphthalenide developed seconds after adding the metal. A solution of **G1(CH_2SPh)$_4$**, Si[$CH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5$]$_4$ (0.600 g, 0.65 mmol) in THF (3 cm^3) was added at such a rate that the green colour of lithium naphthalenide did *not* disappear (± 1 h). The resulting solution was cooled to –40 °C and tributyltin chloride (1.0 cm^3, 3.7 mmol) was added quickly. The colour disappeared completely within seconds to leave a colourless/grey solution. The volatiles were removed *in vacuo* and the products were suspended in hexane (5 cm^3). The solution was filtered over a pad of silica, eluting with hexane. The volatiles were evaporated *in vacuo* and the residual tributyltin chloride was distilled off at 230 °C/0.01 mm Hg. Chromatography over silica gel, eluting with hexane gave Si[$CH_2CH_2CH_2Si(CH_3)_2CH_2Sn(CH_2CH_2CH_2CH_3)_3$]$_4$, **G1($CH_2SnBu_3$)$_4$**, as a colourless oil (0.992 g, 92 %).

An alternative work-up is the following: After adding the tributyltin chloride, the volatiles were removed *in vacuo*. The oily residue was partitioned between hexane (20 cm^3) and water (20 cm^3). To this mixture, KF (0.5 g) and KOH (0.2 g) were added and the mixture was vigorously stirred. The precipitation of tributyltintrifluoride was observed as a white solid. The aqueous phase was extracted with hexane (3 x 10 cm^3) and the combined organic layers were washed with water (3 x 10 cm^3) and brine (3 x 10 cm^3); dried over $MgSO_4$, filtered and concentrated *in vacuo*. The bulk of the naphthalene was sublimed out of the mixture at 150 °C/0.01 mm Hg. Chromatography over silica gel, eluting with hexane gave the product in comparable yield and purity. The aqueous work-up is preferred because the toxic tributyltin chloride is reacted immediately to form the non-toxic fluoride.

R_f(silica/hexane) 0.95;

(Found: C, 53.0; H, 9.4 %. $C_{72}H_{164}Si_5Sn_4$ (1645.4) requires C, 52.6; H, 10.05 %);

$\tilde{\nu}_{max}/cm^{-1}$ 2954 (s, $\nu_{as}(CH_3)$), 2921 (s, $\nu_{as}(CH_2)$), 2871 (s, $\nu_s(CH_3)$), 2853 (s, $\nu_s(CH_2)$), 1464 (s, $\delta_{as}(CH_2)$), 1416, 1376 (s, $\delta_s(CH_3)$), 1356, 1339, 1291, 1246 (s, $\delta_s(Si(CH_3)_3)$), 1214, 1180, 1142, 1070, 1043, 992. 960, 906, 861, 831 (s, $\nu(Si(CH_3)_2)$), 770, 723 (s, $\delta((CH_2)_x)$), 689, 668, 592 (s, ν(SnC)) and 506 (s, ν_{as}(SnC));

δ_H($CDCl_3$, 400 MHz) 1.5–1.2, 0.95-0.68 (116 H, m, $SnCH_2C$, CCH_2C, CCH_2CH_3, CCH_3, $SiCCH_2$), 0.50 (16 H, m, 8 $SiCH_2C$), –0.09 (24 H, s, 4 $Si(CH_3)_2$) and –0.40 (8 H, s, 4 $SiCH_2Sn$);

$\delta_{C\{H\}}$($CDCl_3$, 100 MHz) 29.2 (12 C, $^3J(CCC^{119/117}Sn)$ 10.0/9.2 Hz, 12 CH_2CH_3), 27.5 (12 C, $^2J(CC^{119/117}Sn)$ 29.1/27.5 Hz, 4 $Sn(CH_2CH_2)_3$), 23.5 (4 C, 4 $SiCH_2CH_2CH_2$), 18.8 (4 C, 4 $SiCH_2C$), 17.7 (4 C, 4 $SiCH_2C$), 13.7 (12 C, 12 CCH_3), 10.4 (12 C, $^1J(C^{119/117}Sn)$ 161.8/154.9 Hz, 4 $Sn(CH_2C)_3$), –0.1 (8 C, $^3J(CSiC^{119/117}Sn)$ 6.0/5.3 Hz, 4 $Si(CH_3)_2$) and –8.8 (4 C, $^1J(C^{117/119}Sn)$ Hz, 4 $SiCH_2Sn$);

$\delta_{Si\{H\}}$($CDCl_3$, 79.45 MHz) 3.10 (4 Si, ^2J(SiCSn) Hz, 4 $SiCH_2Sn$) and 0.59 (1 Si, $SiCH_2$);
m/z (FAB) fragments only ($C_{72}H_{164}Si_5Sn_4$ requires 1648) 291 ($Sn((CH_2)_3CH_3)_3^+$).

G2(CH_2SnBu_3)$_{12}$, Si{$CH_2CH_2CH_2Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Sn(CH_2CH_2CH_2CH_3)_3]_3$}$_4$

Lithium metal chunks (0.100 g, 14.5 mmol) were added to a solution of naphthalene (0.100 g, 0.78 mmol) in THF (5 cm^3) at 0 °C and stirred for 30 min. A dark green solution of lithium naphthalenide developed seconds after adding the metal. A solution of **G2(CH_2SPh)$_{12}$**, Si{$CH_2CH_2CH_2[CH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5]_3$}$_4$ (0.600 g, 0. mmol) in THF (3 cm^3) was added at such a rate that the green colour of lithium naphthalenide did *not* disappear (± 1 h). The resulting solution was cooled to –40 °C and tributyltin chloride (1.0 cm^3, 3.7 mmol) was added quickly. The colour disappeared completely within seconds to leave a colourless/grey solution. The volatiles were removed *in vacuo* and the products were suspended in hexane (5 cm^3). The solution was filtered over a pad of alumina, eluting with hexane. The volatiles were evaporated *in vacuo* and the residual tributyltin chloride was distilled off at 230 °C/0.01 mm Hg. Chromatography over silica gel, eluting with hexane gave **G2(CH_2SnBu_3)$_{12}$**, Si{$CH_2CH_2CH_2Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Sn(CH_2CH_2CH_2CH_3)_3]_3$}$_4$ as a colourless oil (0.992 g, 92 %)

δ_H($CDCl_3$, 400 MHz) 1.5–1.2, 0.95-0.68 (116 H, m, $SnCH_2C$, CCH_2C, CCH_2CH_3, CCH_3, $SiCCH_2$), 0.55 (64 H, m, 32 $SiCH_2C$), –0.02 (72 H, s, 24 CH_3) and –0.34 (24 H, s, ^2J(SnCH) 28 Hz, 12 $SiCH_2Sn$);

$\delta_{C\{H\}}$($CDCl_3$, 100.6 MHz) 29.2 (12 C, $^3J(CCC^{119/117}Sn)$ 10.0/9.2 Hz, 12 CH_2CH_3), 27.5 (12 C, $^2J(CC^{119/117}Sn)$ 29.1/27.5 Hz, 4 $Sn(CH_2CH_2)_3$), 23.5 (4 C, 4 $SiCH_2CH_2CH_2$), 18.8 (4 C, 4 $SiCH_2C$), 17.7 (4 C, 4 $SiCH_2C$), 13.7 (12 C, 12 CCH_3), 10.4 (12 C, $^1J(C^{119/117}Sn)$ 161.8/154.9 Hz, 4 $Sn(CH_2C)_3$), –0.1 (8 C, $^3J(CSiC^{119/117}Sn)$ 6.0/5.3 Hz, 4 $Si(CH_3)_2$) and –8.7 (4 C, $^1J(C^{117/119}Sn)$ Hz, 4 $SiCH_2Sn$);

G1(CH_2Li)$_4$, Si[$CH_2CH_2CH_2Si(CH_3)_2CH_2Li$]$_4$

A solution of *n*-butyllithium in hexane (450 mm^3, 2.2 M, 0.99 mmol) was added to a solution of Si[$CH_2CH_2CH_2Si(CH_3)_2CH_2Sn(CH_2CH_2CH_2CH_3)_3$]$_4$, **G1($CH_2SnBu_3$)$_4$** (0.360 g, 0.224 mmol) in THF (1.0 cm^3) at 0 °C in a double Schlenk-tube. The mixture was stirred for 30 min at 0 °C, during which time the initially yellow solution faded to colourless. Several drops of *n*-butyllithium in hexane were added to the other leg of the double Schlenk-tube for solvent drying during purification. The volatiles were evaporated *in vacuo* to leave a white solid and a colourless oil. Pentane (2.0 cm^3) was brought into the vessel on the *n*-butyllithium and distilled unto the solid. Through this extra drying procedure, pure solvents were guaranteed. The mixture was stripped with pentane once. Pentane (10 cm^3) was added and the mixture was washed 3 times through filtering to the 'butyllithium' leg and distilling the solvent unto the lithiated dendrimer. The volatiles

were removed *in vacuo* to leave a white solid ($Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Li]_4$, **$G1(CH_2Li)_4$**) in the one leg and a yellow oil ($SnBu_4$ + BuLi) in the other. The yield was not determined.

δ_H(C_6D_6/THF-*d8*, 300 MHz) 1.60 (8 H, m, 4 $CH_2CH_2CH_2$), 0.75 (8 H, t, 4 CH_2Si), 0.60 (8 H, t, 4 CH_2Si), 0.02 (24 H, s, 8 CH_3) and –2.2 (8 H, s, 4 CH_2Li);

$\delta_{C\{H\}}$(C_6D_6/THF-*d8*, 75 MHz) 28.1 (4 C, 4 $CH_2CH_2CH_2$), 21.4 (4 C, 4 CH_2Si), 20.3 (4 C, 4 CH_2Si), 4.7 (8 C, 8 CH_3) and –7.9 (4 C, 4 CH_2Li).

One drop of D_2O was added to an NMR sample of $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Li]_4$, the ^1H spectrum of the resulting product was identical to the spectrum of $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2D]_4$ prepared from $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5]_4$. To an other sample, an excess of chlorotrimethylsilane was added, resulting in a ^1H-NMR spectrum identical to the one of $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2Si(CH_3)_3]_4$ prepared from $Si[CH_2CH_2CH_2Si(CH_3)_2CH_2SC_6H_5]_4$.

Dimethylbis(phenylthiomethyl)silane[81]

A modified literature method was used to synthesise this compound.[81] A solution of *n*-butyllithium in hexane (20 cm^3, 1.6 M, 32 mmol) was added to a solution of thioanisole (3.5 cm^3, 29.8 mmol) in diethyl ether (5 cm^3). The mixture was heated to reflux for 5 h. A white precipitate was observed to form. A solution of dichlorodimethylsilane (1.8 cm^3, mmol) in diethyl ether (5 cm^3) was added slowly at 0 C. The mixture was allowed to attain room temperature and the solvent was removed *in vacuo*. The mixture was taken up in hexane and the white solid was filtered off. The volatiles were removed *in vacuo* and residual thioanisole was distilled off by heating to 100 °C under vacuum. The product was further purified by column chromatography over silica, eluting with hexane to give dimethylbis(phenylthiomethyl)silane (g, %)

δ_H($CDCl_3$, 300 MHz) 7.10-7.40 (10 H, m, 2 C_6H_5), 2.35 (4 H, s, 2 $SiCH_2S$) and 0.34 (6 H, s, 2 CH_3);

$\delta_{C\{H\}}$($CDCl_3$, 75.5 MHz) 139.5 (2 C, C1- of SC_6H_5), 128.7 (4 C), 126.3 (4 C)(C-2, C-6 and C-3, C-5 of SC_6H_5), 124.9 (2 C, C-4 of SC_6H_5), 16.7 (2 C, 2 $SiCH_2S$) and –3.3 (2 C, 2 CH_3);

$\delta_{Si\{H\}}$($CDCl_3$, 79.5 MHz) 2.6;

All data was in agreement with the reported data.[81]

8.4 Procedures pertaining to Chapter 4

9, $[Cp_2Zr(H)Cl]_n$[97] (Schwartz's reagent)

Lithium aluminiumhydride (0.176 g, 18.55 mmol) was dissolved in diethyl ether (5.0 cm^3). This solution was added, after filtration, to a solution of zirconocene dichloride, **8** (4.904 g, 16.77 mmol) in THF. Immediately a white precipitate formed. The mixture was stirred for 16 h, after which time the solids were allowed to settle and the supernatant liquid was decanted off. The THF/diethyl ether mixture was distilled back onto the solids and, after stirring and settling of the solid, decanted again. This procedure was repeated 4 times. Dichloromethane (1.0 cm^3) was added to the white precipitate. After stirring for 20 min, the volatiles were removed *in vacuo*. Dichloromethane (5.0 cm^3) was added again, and evaporated after 20 minutes. The white solid was subsequently washed with diethyl ether (4 x 15 cm^3) and dried *in vacuo* to give Schwartz's reagent (2.43 g, 56 %). The insoluble product cannot be identified directly, therefore it has to be converted to zirconocene isopropoxychloride. After this conversion, no resonances due to the insertion product of the dihydride were observed in the ^1H and ^{13}C NMR spectra.

$Cp_2Zr[O\text{-}CH(CH_3)_2]Cl$

Schwartz's reagent, **9** (see synthesis above) (0.0205 g, 0.08 mmol) was loaded into a Teflon valved NMR tube inside the glovebox. Acetone (7.0 mm^3, 0.10 mmol) followed by C_6D_6 (0.4 cm^3) were added and the tube sealed. Regular shaking of the NMR tube resulted in the reaction of all solids to give a clear solution. This was shown to be $Cp_2Zr[O\text{-}CH(CH_3)_2]Cl$ by ^1H and ^{13}C NMR spectroscopy.

$\delta_H(C_6D_6$, 400 MHz) 5.92 (10 H, s, 2 C_5H_5), 4.03 (1H, septet, ^3J(HCCH) 6 Hz, OC*H*), 1.53 (s, acetone) and 0.95 (6 H, d, ^3J(HCCH) 6 Hz, 2 CH_3). No signals due to the di-*iso*propoxy group were observed ($\delta_H(C_6D_6$, 400 MHz) 3.95 (2 H, septet, ^3J(HCCH) 6 Hz, 2 OCH) and 1.05 (12 H, d, ^3J(HCCH) 6 Hz, 4 CH_3));

$\delta_{C\{H\}}(C_6D_6$, 100.6 MHz) 113.83 (acetone, C=O), 112.98 (10 C, 2 C_5H_5), 76.01 (1 C, OCH), 29.75 (2 C, 2 CH_3) and 25.44 (acetone, 2 CH_3).

10, $[Cp_2Hf(H)Cl]_n$

A solution of hafnocene dichloride (2.40 g, 6.32 mmol) in THF (10 cm^3) was added to a filtered solution of $LiAlH_4$ (0.07 g, 1.8 mmol) in diethyl ether (2.0 cm^3). The formation of a white precipitate was observed. The mixture was stirred for 24 h. The white solid was allowed to precipitate and the supernatant liquid was decanted off. The solid was washed with THF (3 x 10 cm^3) and dried *in vacuo* to give $[Cp_2Hf(H)Cl]_n$, **10** (0.85 g, 39 %) The insoluble product cannot be identified directly, therefore it has to be converted to hafnocene isopropoxychloride. After this

conversion, no resonances due to the insertion product of the dihydride were observed in the ^{1}H and ^{13}C NMR spectrum.

$Cp_2Hf[O\text{-}CH(CH_3)_2]Cl$

The hydrohafnation reagent **10** (see synthesis above) (0.0108 g, mmol) was loaded into a Teflon valved NMR tube inside the glovebox. Acetone (5.0 mm^3, 0.07 mmol) followed by deuterated benzene (0.4 cm^3) were added and the tube sealed. Regular shaking of the NMR tube resulted in the reaction of all solids to give a clear solution.

$\delta_H(C_6D_6$, 400 MHz) 5.97 (10 H, s, 2 C_5H_5), 4.15 (1 H, septet, ^3J(HCCH) 6 Hz, OC*H*) and 1.11 (6 H, d, ^3J(HCCH) 6 Hz, 2 CH_3). No signals due to the di-*iso*propoxy group were observed

$\delta_{C\{H\}}(C_6D_6$, 100.6 MHz) 110.53 (10 C, 2 C_5H_5), 72.96 (1 C, OCH) and 26.82 (2 C, 2 CH_3).

G0(ZrCl)$_1$, $Cp_2ZrClCH_2CH_2CH_2Si(CH_3)_3$

Schwartz's reagent (0.158 g, 0.61 mmol) and allyltrimethylsilane, **G0(allyl)$_1$**, (198 mm^3, 1.25 mmol) were mixed in THF (1.6 cm^3) at room temperature and stirred for 1 h. A clear yellow solution was obtained. The volatiles were removed *in vacuo* and the yellow oil was stripped with pentane (2 x 1.0 cm^3). The product was extracted into pentane (3 x 2.0 cm^3) and the volatiles were removed *in vacuo* to give a yellow oil $Cp_2ZrClCH_2CH_2CH_2Si(CH_3)_3$, **G0(ZrCl)$_1$** (0.23 g, 68 %)

$\delta_H(C_6D_6$, 400 MHz) 5.78 (10 H, 2 C_5H_5), 1.70 (2 H, m, $CH_2CH_2CH_2$), 1.17 (2 H, m, ^3J(HCCH) 8 Hz, $ZrCH_2$), 0.62 (2 H, m, ^3J(HCCH) 8 Hz, $SiCH_2$) and 0.09 (9 H, s, 3 CH_3);

$\delta_{C\{H\}}(C_6D_6$, 50.3 MHz) 112.20 (10 C, 2 C_5H_5), 60.16 (1 C, $ZrCH_2$), 28.79 (1 C, $CH_2CH_2CH_2$), 24.18 (1 C, CH_2Si) and –1.04 (3 C, 3 CH_3).

13, $Ag[B(C_6H_5)_4]$

This activating agent was obtained by mixing aqeous solutions of equimolar amounts of $AgNO_3$ and $Na[B(C_6H_5)_4]$. The silver tetraphenylborate, **13**, immediately precipitated as a white solid and was isolated through suction filtration. The solid was washed with hot deionized water (4 x) followed by a minimum amount of ethanol. Drying under vacuum for several hours gave the required activating agent. *Note: silver tetraphenylborate is light sensitive. Slow decomposition in the dark at room temperature (in about two weeks) was observed.*

14, $Cp_2Zr(CH_3)_2$[10]

Zirconocene dichloride, **8** (1.50 g, 5.0 mmol) was suspended in diethyl ether (20 cm^3) at –30 °C. Slowly, a solution of methyllithium in diethyl ether (6.8 cm^3, 1.6 M, 10.9 mmol) was added. The mixture was allowed to warm to 0 °C. After mixture was stirred at 0 °C for 1 h, the volatiles were removed *in vacuo* to give a white solid. The solid was powdered and transferred to a sublimation flask. Sublimation at 110 °C/0.015 mm Hg gave white crystalline $Cp_2Zr(CH_3)_2$ (0.96 g, 76 %);

$\delta_H(C_6D_6$, 400 MHz) 5.68 (10 H, s, 2 C_5H_5) and –0.16 (6 H, s, 2 CH_3);

$\delta_{C\{H\}}(C_6D_6$, 100.6 MHz) 110.21 (10 C, 2 C_5H_5) and 30.10 (2 C, 2 CH_3).

$[Cp_2ZrCH_3(NCCH_3)_2][B(C_6H_5)_4]$[138]

Dimethylzirconocene, **14**, (0.080 g, 0.32 mmol) was added as an acetonitrile solution (5.0 cm^3) to a suspention of silver tetraphenylborate in acetonitrile (5.0 cm^3) at 0 °C. A black precipitate formed immediately. After stirring for an hour at room temperature, the suspention was filtered through a pad of Celite and the volatiles removed *in vacuo* to give a white solid. Analysis through NMR spectroscopy showed that the solid was $[Cp_2ZrCH_3(NCCH_3)_2][B(C_6H_5)_4]$, the spectrum being identical to the one for the $[Cp_2ZrMe][B(C_6H_5)_4]$ obtained through protonolysis (except for the two THF signals).

G0(ZrBz)$_1$, $Cp_2Zr(CH_2C_6H_5)CH_2CH_2CH_2Si(CH_3)_3$

Schwartz's reagent (0.0268 g, 0.10 mmol) and allyltrimethylsilane, **G1(allyl)$_1$**, (16.5 mm^3, 0.10 mmol) were dissolved in toluene-*d8* in a Teflon valved NMR-tube. The tube was shaken until a clear yellow solution was obtained. ^1H and ^{13}C NMR spectroscopy revealed that **G0(ZrBz)$_1$**, $Cp_2ZrClCH_2CH_2CH_2Si(CH_3)_3$ had formed. The solution was added to $KCH_2C_6H_5$ (0.015 g, 0.12 mmol) at –40 °C and immediately a ^1H NMR spectrum was run. The ^1H NMR spectrum showed that the solution contained the title compound.

$\delta_H(C_7D_8$, 400 MHz) 7.3-6.6 (5 H, multiple signals overlapping with solvent signal, C_6H_5), 5.61 (10 H, 2 C_5H_5), 1.60 (2 H, s, $CH_2C_6H_5$), 1.55 (2 H, m, $CH_2CH_2CH_2$), 0.78 (4 H, m, $SiCH_2$, $ZrCH_2$), 0.12 (9 H, 3 CH_3). The product decomposed before a ^{13}C NMR spectrum could be obtained. Upon decomposition a purple/brown solid formed.

12, $[Cp'_2Fe][B(C_6H_5)_4]$[139]

1,1'-Dimethylferrocene (1.070 g, 5.0 mmol) was dissolved in concentrated sulphuric acid (6.0 cm^3) and stirred for one hour. The resulting dark blue solution was poured into an ice/water mixture and filtered to remove some brown solids. The resulting blue solution was slowly added to a concentrated solution of sodium tetraphenylborate (1.72 g, 5.0 mmol) to give a light blue precipitate. The solid was isolated through suction filtration and washed with de-ionized water (4 x 20 cm^3). The solid was dried in air for one night followed by drying *in vacuo*. Analysis of this solid was not possible, however the literature[139] states that it can be used as is.

19, $Cp_2Zr(C_3H_5)_2$[140]

The literature method was adapted. Zirconocene dichloride, **8**, (0.751 g, 2.56 mmol) was suspended in diethyl ether (15 cm^3) and cooled down to –41 °C by means of an acetonitrile slush bath. Allylmagnesiumbromide solution in diethyl ether (1.0 M, 5.4 cm^3, 5.4 mmol) was added by

syringe. Immediately the formation of a white precipitate was observed, as well as a slight colour change to yellow. After 10 minutes voluminous amounts of a cream-coloured solid precipitated. Care was taken that the temperature did not rise above 0 °C during the work-up. The solvent was removed *in vacuo* to leave a waxy off-white solid. This solid was stripped twice with pentane (2.0 cm^3). The remaining solids were extracted twice with toluene (5.0 cm^3) to give a dark-brown, clear solution. Concentration, followed by layering with pentane (5.0 cm^3) and cooling to –30 °C resulted in yellow crystals. Filtration followed by washing with pentane (2.0 cm^3) and evaporation of the volatiles *in vacuo* resulted in cream coloured crystalline **19**, $Cp_2Zr(C_3H_5)_2$ (g, %);

$\delta_H(C_6D_6$, 400 MHz) 5.65 (2 H, q, ^3J(HCCH) 11.5 Hz, 2 CH), 5.11 (10 H, s, 2 C_5H_5) and 2.90 (8 H, d, ^3J(HCCH) 11.5 Hz, 4 CH_2);

$\delta_{C\{H\}}(C_6D_6$, 100.6 MHz)

16, $Cp_2ZrClMe$[141]

Dimethyl zirconocene, **14**, (0.700 g, 2.78 mmol) was loaded into a solid addition tube. Lead dichloride (0.390 g, mmol) and toluene (10 cm^3) were loaded in a double Schlenk-tube and stirred. Upon adding the dimethyl zirconocene, **14**, at room temperature, the colour immediately darkened and the insoluble lead salts were seen to disappear. After stirring for 1 h, just metallic lead was observed in the otherwise clear colourless solution. Filtration, followed by concentration to approximate 4 cm^3 gave a viscous solution. The solution was layered with pentane (10 cm^3) and stirred at –78 °C. The precipitated white solid was isolated through filtration and dried. Analysis revealed pure $Cp_2ZrClCH_3$ (0.584 g; 77.3 %) (M_{av}=271.897)

21, $Cp_2Zr(CH_3)[CH_2Si(CH_3)_3]$[142]

Chloromethyl zirconocene, **16**, (0.584 g, 2.15 mmol) was dissolved in diethyl ether (10 cm^3) in a centrifuge tube and cooled down to –78 °C by means of an alcohol/CO_2 bath. A solution of trimethylsilylmethyllithium, **6** (2.2 cm^3, 1.0 M, 2.2 mmol) was added by syringe. The mixture was stirred and allowed to warm to room temperature. A white solid was seen to precipitate. The solvent was removed *in vacuo*. The resulting white solid was suspended in toluene (5.0 cm^3) and the precipitates were centrifuged off. The clear supernatant liquid was transferred to a Schlenk tube. The extraction was repeated two times. As crystallization from toluene/pentane was not successful, the toluene was removed *in vacuo*. The (brownish) oil was stripped with pentane (3 x 2.0 cm^3) to give an off white solid. Washing with pentane at –78 °C (3 x 5.0 cm^3) gave a white solid. This was shown to be **21**, $Cp_2Zr(CH_3)[CH_2Si(CH_3)_3]$ from the ^1H and ^{13}C NMR data.

$\delta_H(C_6D_6$, 400 MHz) 5.72 (10 H, s, 2 C_5H_5), 0.09 (2 H, s, CH_2), 0.07 (9 H, s, $Si(CH_3)_3$) and –0.18 (3 H, s, CH_3);

$\delta_{C\{H\}}(C_6D_6$, 100.6 MHz) 110.09 (10 C, 2 C_5H_5), 48.09 (1 C, CH_2), 28.30 (1 C, CH_3) and 3.47 (3 C, $Si(CH_3)_3$).

All data was in agreement with the literature.[142]

G0(CH_2Li)$_1$, $LiCH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3$

A solution of (chloromethyl)dimethyl(3-(trimethylsilyl)propyl)silane, **G0(CH_2Cl)$_1$**, (0.409 g, 1.8 mmol) in diethyl ether (3 cm^3) was slowly added to a vigorously stirred suspention of lithium pieces (0.450 g, 65 mmol) in diethyl ether (10 cm^3). The formation of a white solid was observed and the surface of the lithium pieces started shining. The mixture was stirred for an additional 2 h. and filtered over Celite to give a clear colorless solution. The concentration was determined using the Gilman 'double titration' to be 0.26 M. Yield: 6 cm^3, 1.56 mmol, 87 %

G0(CH_2ZrMe)$_1$, $Cp_2Zr(CH_3)[CH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3]$

Chloromethyl zirconocene, **16**, (0.178 g, 0.65 mmol) was dissolved in diethyl ether (2.0 cm^3) in a centrifuge tube and cooled to –78 °C by means of an alcohol/CO_2 bath. A solution of $LiCH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3$, **G0($CH_2Li$)$_1$**, in diethyl ether (2.5 cm^3, 0.26 M, 0.65 mmol) was added *via* syringe. Upon stirring the mixture a white precipitate formed. The mixture was heated to 0 °C by removing the alcohol/CO_2 bath. The volatiles were removed *in vacuo* to leave a white liquid. The liquid was stripped with pentane (2 x 0.5 cm^3) before it was extracted into pentane (10 cm^3). The solids were centrifuged off and the supernatant colourless liquid was transferred to a Schlenk-tube. The extraction was repeated (2 x 5 cm^3). The volatiles were removed *in vacuo* to give a slightly yellow liquid. The liquid was dissolved in pentane and cooled to –78 °C, at which temperature a white solid separated. The supernatant liquid was syringed off at –78 °C and the product dried under vacuum. The product was identified as **G0(CH_2ZrMe)$_1$**, $Cp_2Zr(CH_3)[CH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3]$ by ^1H and ^{13}C NMR.

δ_H(C_6D_6, 400 MHz) 5.75 (10 H, s, 2 C_5H_5), 1.25 (2 H, m, $CH_2CH_2CH_2$), 0.87 (4 H, m, 2 $SiCH_2$), 0.12 (2 H, s, $ZrCH_2$), 0.09 (6 H, s, $Si(CH_3)_2$), 0.04 (9 H, s, $Si(CH_3)_3$) and –0.15 (3 H, $ZrCH_3$);

$\delta_{C\{H\}}$(C_6D_6, 100.6 MHz) 110.10 (10 C, 2 C_5H_5), 46.73 (1 C, $ZrCH_2$), 28.28 (1 C, $ZrCH_3$), 25.05, 21.73, 19.29, 1.55 (3 C, $Si(CH_3)_3$) and –1.45 (2 C, $Si(CH_3)_2$).

G0(CH_2Zr^+)$_1$, $[Cp_2ZrCH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3]^+[H_3CB(C_6F_5)_3]^-$

Solid $B(C_6F_5)_3$ was added to a solution of $Cp_2Zr(CH_3)[CH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3]$, **G0($CH_2ZrMe$)$_1$**, in C_6D_6 in an NMR tube. The tube was shaken to dissolve all of the borane and the solution turned yellow. The only compound in solution was shown to be $[Cp_2ZrCH_2Si(CH_3)_2CH_2CH_2CH_2Si(CH_3)_3]^+[H_3CB(C_6F_5)_3]^-$

δ_H(C_6D_6, 400 MHz) 5.58 (10 H, s, 2 C_5H_5), 1.36 (), 0.7-0.4 three overlapping triplets, 0.05 (9 H, s), –001 (2 H, s) and –0.17 (2 H, s);

$\delta_{C\{H\}}$(C_6D_6, 100.6 MHz) 113.62 (10 C, 2 C_5H_5), 70.85, 24.21, 21.53, 18.87, 0.86 and –1.68.

15, $[Cp_2ZrCH_3]^+[H_3CB(C_6F_5)_3]^-$

Dimethylzirconocene, **14**, was dissolved in C_6D_6 in a NMR-tube. $B(C_6F_5)_3$ was added as a solid and the tube was shaken to dissolve the borane. The colour changed immediately from colourless to yellow.

$\delta_H(C_6D_6$, 400 MHz) 5.43 (10 H, s, 2 C_5H_5), 0.27 (3 H, s, $ZrCH_3$) and 0.11 (3 H, br s, BCH_3);

$\delta_{C\{H\}}(C_6D_6$, 100.6 MHz) 113.96 (10 C, 2 C_5H_5) and 40.94 (1 C, Zr-CH_3). The ^{13}C NMR resonances for BCH_3 was not observed due to coupling with ^{11}B. The C_6F_5 resonances were broad due to coupling with ^{19}F.

23, $Cp_2Zr[CH_2Si(CH_3)_3]_2$

Zirconocene dichloride, **8**, (0.720 g, 2.45 mmol) was dissolved in diethyl ether (5.0 cm^3) and cooled down to –42 °C. A solution of $LiCH_2Si(CH_3)_3$, **6**, in diethyl ether (5.0 cm^3; 1.0 M; 5.0 mmol) was added via syringe. The mixture was stirred and allowed to warm to room temperature. The precipitation of a white solid was observed. The solvent was evaporated *in vacuo* and the product was extracted into pentane (2 x 10 cm^3). The resulting slightly yellow solution was concentrated and stored at –30 °C to give colourless crystals of **23**, $Cp_2Zr[CH_2Si(CH_3)_3]_2$ (0.448 g, %);

$\delta_H(C_6D_6$, 400 MHz) 5.77 (10 H, 2 C_5H_5), 0.08 (18 H, s, 6 CH_3) and 0.03 (4 H, s, 2 CH_2);

$\delta_{C\{H\}}(C_6D_6$, 100.6 MHz) 109.85 (10 C, 2 C_5H_5), 45.50 (2 C, 2 CH_2) and 3.51 (6 C, 6 CH_3).

Attempted synthesis of $[Cp_2ZrCH_2Si(CH_3)_3]^+[(CH_3)_3SiCH_2B(C_6F_5)_3]^-$

To a solution of $Cp_2Zr[CH_2Si(CH_3)_3]_2$ in C_6D_6 in a NMR-tube was added solid $B(C_6F_5)_3$. The tube was shaken to dissolve the borane and immediately an orange oil separated. No signals were found in the ^1H and ^{13}C NMR spectrum, indicating that the product is insoluble in C_6D_6. Addition of the more polar C_6D_5Br did not result in the observation of any signals.

$[Cp_2ZrCH_3(THF)][B(C_6H_5)_4]$[143]

Dimethylzirconocene (0.076 g, 0.30 mmol) was combined with $[HNCH_2CH_2CH_2CH_3][B(C_6H_5)_4]$ (0.176 g, 0.33 mmol) in an H-type Schlenk tube. At –78 °C THF was syringed (3.0 cm^3) to this mixture, and a clear colourless solution was obtained. Upon warming to roomtemperature this mixture turned faintly yellow. Large amounts of white insoluble material precipitated in a few seconds. The solid was isolated by decanting the supernatant liquid at -78 °C. Back-distillation of the solvent, stirring and decanting at –78 °C was repeated twice to wash the solid. Drying *in vacuo* gave an off white solid, which appeared to be the crude product. Crystallisation from THF with diffusion of pentane gave $[Cp_2ZrCH_3(THF)][B(C_6H_5)_4]$

$\delta_H(CD_3CN$, 400 MHz): 0.27 (s, 3H, CH_3), 1.83 (m, 4H, $O(CH_2CH_2)_2$), 3.64 (m, 4H, $O(CH_2CH_2)_2$), 6.07 (s, 10H, Cp), 6.91 (t, 4H, *para*-$B(C_6H_5)_4$), 7.06 (t, 8H, *meta*-$B(C_6H_5)_4$), 7.43–7.35 (m, 8H, *ortho*-$B(C_6H_5)_4$);

$\delta_{C\{H\}}$(CD_3CN, 100.6 MHz) 112 (Cp), 122.66 (*para*-$B(C_6H_5)_4$), 126.48 (*ortho*-$B(C_6H_5)_4$), 136.65 *meta*-$B(C_6H_5)_4$).

Due to insertion of CD_3CN in the Zr-CH_3 bond, the compound $[Cp_2Zr(NC(CH_3)(CD_3)(NCCD_3)][B(C_6H_5)_4]$ was obtained. The resonances at 0.27 and 6.07 ppm in the ^1H NMR spectrum disappeared and the resonance at 1.95 (overlapping with the CD_2HCN resonance) increased in intensity, as well as the growth of a resonance at 6.45 ppm. This observation is also reported in literature.[ref]

18, $[HN(CH_2CH_2CH_2CH_3)_3][B(C_6H_5)_4]$

Tri-*n*-butylamine (6.0 cm^3, 25.2 mmol) was mixed with an equal amount of water to give a biphasic system. Slowly, while stirring, concentrated hydrochloric acid was added until a monophasic system was obtained. The pH was at that moment ~1.5. A concentrated sodium tetraphenylborate solution (5.841 g, 17 mmol) was added. Large amounts of a white precipitate were formed. The precipitate was isolated by suction filtration and dried in the air for one night. The drying process was continued under vacuum over a boiling water bath and finally the solid was stripped with dry THF to remove the last traces of water. (g, %);

δ_H(CD_3CN, 400 MHz) 7.31 (8 H, m, C-2, -6 of C_6H_5), 7.02 (8 H, t, *J* 8 Hz, C-3, -5 of C_6H_5), 6.87 (4H, t, *J* 7 Hz, C-4 of C_6H_5), 3.03 (6 H, t, ^3J(HCCH) 8 Hz, NCH_2), 1.63 (6 H, m, NCH_2CH_2), 1.38 (6 H, sextet, ^3J(HCCH) 8 Hz, CH_2CH_3) and 0.97 (9H, t, ^3J(HCCH) 7 Hz, CH_3);

$\delta_{C\{H\}}$(CD_3CN, 100.6 MHz) 136.7, 126.5, 122.7, 53.9, 26.2, 20.3 and 13.70.

8.5 Procedures pertaining to Chapter 5

G1(ZrCl)$_4$, Si[CH$_2$CH$_2$CH$_2$(Cp$_2$ZrCl)]$_4$

(Cp$_2$ZrHCl)$_n$, **9** (0.197 g, 0.764 mmol) was loaded in a reaction vessel. Toluene, 5 cm^3 and tetraallylsilane (40 mm^3, 0.174 mmol) were added by syringe. Stirring overnight gave a yellow suspention, which gave a clear yellow solution after filtration through a pad of Celite. Evaporation of the volatiles yielded the pure product. Yellow crystals were obtained by slow diffusion of pentane into a toluene solution of the compound in a vacuum-sealed ampoule.

δ_H(C$_6$D$_6$, 400 MHz) 5.95 (40 H, s, 8 C$_5$*H*$_5$), 2.00 (8 H, m, 4 CH$_2$C*H*$_2$CH$_2$), 1.41 (8 H, m, ^3J(HCCH) 8 Hz, ZrC*H*$_2$) and 0.98 (8 H, m, ^3J(HCCH) 8 Hz, SiC*H*$_2$).

8.6 Procedures pertaining to Chapter 6

Polymerisation reactions

A literature procedure[144] is adapted to fit our needs. All polymerisation reactions were run using the same system. Variations were made in the temperature, catalyst type and volume. However the same concentrations (for the catalysts: the concentration of active metal centres) were used, irrespective of the several variables. In some polymerisations, the MAO solution is replaced by a mixture of $Al(CH_3)_3$/MAO (4/1), amounting to the same concentration of aluminium without any loss of activity. The polymerisation at a volume of 30 cm^3 is described as an example.

A Schlenk tube was loaded with MAO (10 wt% in toluene, 5.0 cm^3) and toluene (24 cm^3). The Schlenk tube was placed in a water/ice bath, magnetically stirred and ethene was bubbled through. The ethene was bubbled through for the duration of the polymerisation. After allowing 30 min. to equilibrate, a solution (1.0 cm^3, 20 mM, 20 μmol) of the catalyst in toluene was injected quickly to give an orange solution. The precipitation of PE was observed within seconds after adding the catalyst solution. The polymerisation was terminated after 1 h. by the addition of *iso*-propanol (5.0 cm^3), resulting in a colourless mixture. The mixture was poured into 100 cm^3 0.1 M HCl solution and stirred. The mixture was filtered and the solids washed with 0.1 M HCl (3 x 20 cm^3) and water (3 x 50 cm^3) and dried at 70 °C *in vacuo* to constant weight.

Dimerisation of allyltrimethylsilane

A Schlenk tube was loaded with toluene (18 cm^3), MAO (10 wt% in toluene; 6.0 cm^3) and allyltrimethylsilane (5.0 cm^3, 31.5 mmol) and placed in an ice/water bath. After 30 min. a solution of Cp_2ZrCl_2 in toluene (1.0 cm^3, 20 mM, 20 μmol) was added to produce an orange solution. The reaction was terminated by the addition of *iso*-propanol (5 cm^3) after 1 h. resulting in a colourless solution. The mixture was partitioned between hexane (20 cm^3) and 0.1 M aqueous HCl (50 cm^3). The organic layer was washed with 0.1 M aqueous HCL (3 x 50 cm^3), water (3 x 50 cm^3) and brine (3 x 50 cm^3); dried over $MgSO_4$, filtered and the volatiles were removed *in vacuo* to give 2.87 g (79 %) of a colourless oil.

δ_H($CDCl_3$, 400 MHz) 4.75 (2H, s, $=CH_2$), 1.90 (2H, t, ^3J(HCCH) 8Hz CH_2CH_2C), 1.64 (2H, s, $SiCH_2C$), 1.39 (2H, m, $CH_2CH_2CH_2$), 0.58 (2H, m, ^3J(HCCH) 8 Hz, $SiCH_2CH_2$), 0.11 (9H, s, $Si(CH_3)_3$) and 0.02 (9H, s, $Si(CH_3)_3$).

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