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Synthesis, Characterization and Group Modification of

Carbosilane Based Dendrimers

by

Richard Hooper
B.Sc., University of Dundee, 1992

A Dissertation Submitted in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

in the Department of Chemistry

We accept this dissertation as conforming
to the required standard

Dr. S. R. Stobart, Supervisor (Department of Chemistry)

Dr. D. J. Berg, Departmental Member (Department of Chemistry)

Dr. T. M. Fyles, Department Member (Department of Chemistry)

Dr. C. E. Picciotto, Outside Member (Department of Physics and Astronomy)

Dr. W. R. Cullen, External Examiner (Department of Chemistry, University of British Columbia)

Supervisor: Dr. Stephen R. Stobart

ABSTRACT

Carbosilane dendrimers have been prepared *via* iterative hydrosilylation/alkenylation reactions using a variety of chlorosilanes ($HSiMe_{3-n}Cl_n$) and alkenyl nucleophiles (CH_2=$CHCH_2MgBr$ and CH_2=$CHMgBr$). Characterization by multinuclear NMR spectroscopy of the stepwise trifurctate dendrimers $RE\mathit{D}_3$ (E = Si; R = Ph; *D* = Dendritic carbosilane fragment) assists end-group counting (NMR, R *vs D*) and can be related to analogous spheroidal $E\mathit{D}_4$ and hexafunctional $E_2\mathit{D}_6$ systems (E = Si or Ge). Typical *D* units contain $(pr_nSiMe_{3-n})^N{}_{Nb}$ linkers; where pr = $(CH_2)_3$, N = generation number, N_b = branch multiplicity at silicon. For higher symmetry $E\mathit{D}_4$ and $E_2\mathit{D}_6$ systems (and also trifurcate) the N_b = 1 (1B series) or N_b = 2 (2B series) also allows for end-group counting by proton NMR spectroscopy (Ph:D:Me). ^{29}Si NMR chemical shifts have been developed for topographical mapping of dendritic structure.

Peripheral and core substitution reactions have been examined for a series of trifurcate and related $Ge_2\mathit{D}_6$ 'masked trifurcate' dendrimers. Replacement of end groups with a range of substrates is facilitated by the reactivity of the intermediate silicon chlorine bonds formed by hydrosilylation reactions. Selective removal of the core phenyl group (*via* triflic acid), or alternatively oxidative Ge-Ge cleavage, allows for unprecedented 'bifunctionalization'; offering routes into dendrimer periphery:core electron transfer ('photon-harvesting') processes.

Methodology for a 'rapid-synthesis' of hyperbranched structures has been developed and examined on a range of initial core molecules. Use of multinuclear NMR spectroscopy *via* comparison with step-wise products, as well as GPC chromatography, gives some insight into the overall architectures produced. Alteration of Si branch point from N_b = 2 to N_b = 3, using presynthesised 'hypercores' facilitates an alternate method of end group counting for higher symmetry cores. This methodology allows for population counting at large N in dendrimer generation G(N) ($\mathit{D}_{interior}$ *vs* $\mathit{D}_{periphery}$).

Examiners:

Dr. S. R. Stobart, Supervisor (Department of Chemistry)

Dr. D. J. Berg, Departmental Member (Department of Chemistry)

Dr. T. M. Fyles, Department Member (Department of Chemistry)

Dr. C. E. Picciotto, Outside Member (Department of Physics and Astronomy)

Dr. W. R. Cullen, External Examiner (Department of Chemistry, University of British Columbia)

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LIST OF ABBREVIATIONS

Å	Angstroms (10^{-10} m)
bp	boiling point
calcd	calculated
$CDCl_3$	deuterochloroform
CH_2Cl_2	dichloromethane
d	doublet
DEPT	Distortionless Enhancement by Polarization Transfer
equivs.	equivalents
Et	ethyl
et	CH_2CH_2
Hz	Hertz
INEPT	Insensitive Nucleus Enhancement by Polarization Transfer
IR	InfraRed
$^nJ_{AB}$	coupling constant
m	multiplet
M^+	molecular ion
Me	methyl
mol	mole(s)
MS	Mass spectroscopy
MW	molecular weight
nm	nanometres (10^{-9} m)
NMR	Nuclear Magnetic Resonance
p-	para
Ph	phenyl
ppm	parts per million
^iPr	isopropyl
pr	$CH_2CH_2CH_2$

r^2	linear regression best fit value
R or R'	alkyl or aryl
s	Singlet
THF	tetrahydrofuran
TfO	trifluoromethane sulphonate
TLC	thin layer chromatography
TMEDA	N, N, N', N'-tetramethylethylenediamine
TMS	tetramethylSilane
UV	UltraViolet
δ	chemical shift
ε	molar extinction coefficient

ACKNOWLEDGEMENTS

I would like to thank Dr. Stephen R. Stobart for his continued contribution to this research and for financial support throughout these studies at the University of Victoria.

I would also like to acknowledge Dr. Jacques Roovers (NRC, Ottawa) for allowing the use of their GPC apparatus and his helpful discussions for some of the more ambiguous results found.

I am forever indebted to my colleagues and friends whose support over these years has kept me going through the best and worst of times. There are too many to name individually, they know who they are, but without them this may never have happened.

Most of all, I thank my parents for their continuous support and encouragement during my stay in Canada.

For My Family

non illigitimi carborundum

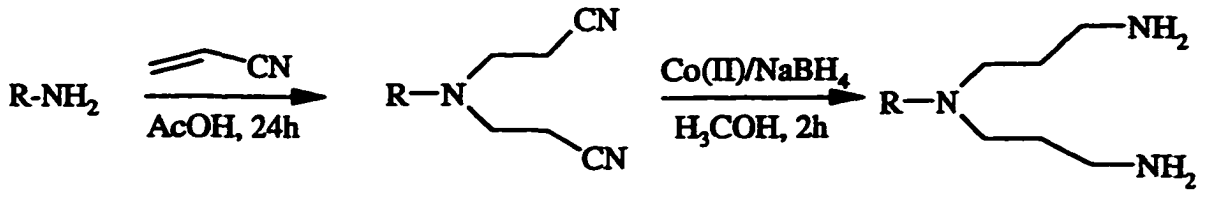
CHAPTER ONE

INTRODUCTION

1.1 Historical Perspective

The term dendrimer was introduced by Tomalia[1] to describe the regular architecture that highly branched "mesomolecular" assemblies may exhibit; it is a combination of two Greek words: 'Dendron' (tree) and 'Meros' (many). Other labels that have appeared over the years include 'Arborol'[2] and 'Cascade molecules',[2] but materials of this type are currently referred to as dendrimers. The inherent interest in such systems, attributable to the iterative synthetic logic, is complemented by the anticipation of novel polymer properties. This new area of supramolecular chemistry has been expanding rapidly for about a decade and considerable literature already exists.[3] The purpose of this introduction is to convey the main synthetic approaches that have been employed, methods for characterization and future directions envisioned.

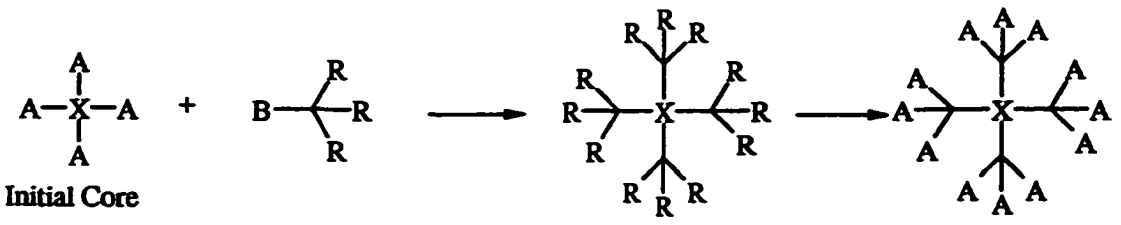
In 1978, Vögtle *et al*[4] prepared the first dendritic compound using a synthetic methodology that is still commonly employed. Classified as a cascade synthesis, it applies two iterative reaction steps of alkylation and reduction, Scheme 1.1, in which 'generational' compounds were formed and characterised at each stage. This methodology, used subsequently by many workers, develops polyfunctional mesomolecules by extension from a central core, and is more commonly referred to now as the "Divergent approach".



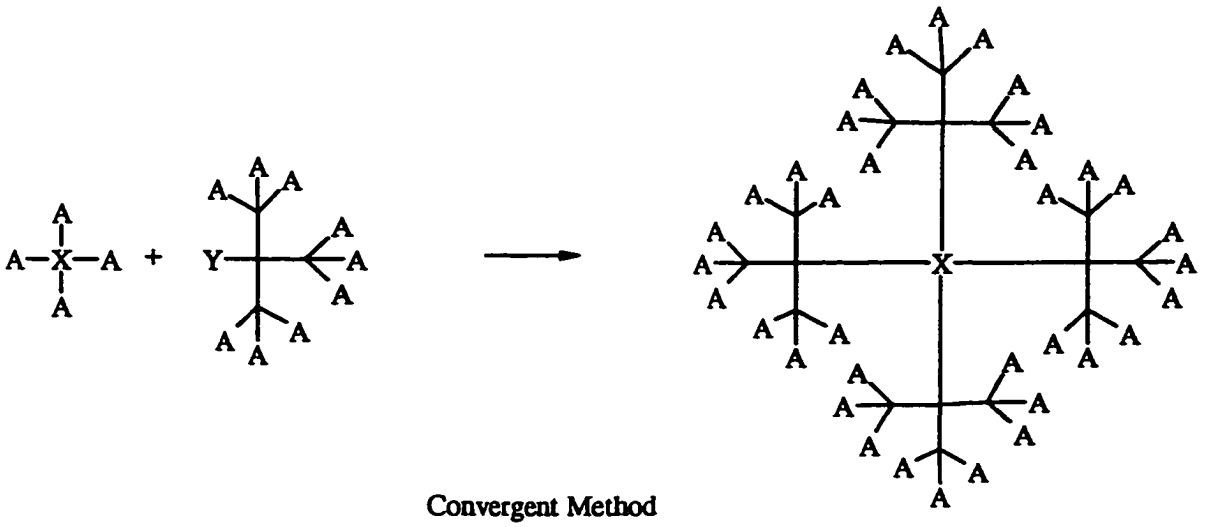
Scheme 1.1 Vögtle's cascade synthesis[4]

Until about 1990, most dendrimer compounds were synthesised by the divergent technique, which usually requires protection-deprotection steps. It was in 1990 that Fréchet and Hawker[5] reported a new procedure described as the "Convergent approach", in which sections of the dendrimer were pre-formed and then attached to a polyfunctional core molecule. Scheme 1.2 compares the divergent and convergent strategies. In the divergent case, a polyfunctional template XA_4 is substituted with a reagent that contains further functional groups, R. These peripheral moieties may be reconverted to the original group A. This process is continued iteratively, so leading to the construction of successive generations. For the alternate convergent methodology, peripheral 'wedges' (monodendrons) are built first, *via* the divergent strategy, then reacted with a polyfunctional core to form the dendrimer. The convergent plan may be seen as more versatile, because larger pre-assembled 'monodendron' segments may be pieced together in a number of different ways.[6]

In both methods the growth of the macromolecule is highly controlled, and after each successive step the intermediate product is isolated and characterised, eventually yielding a monodisperse, highly branched macromolecule. Thus, after completion of each stage, the molecule has a well defined internal connectivity with a specific number of reactive end groups.



Divergent Method



Convergent Method

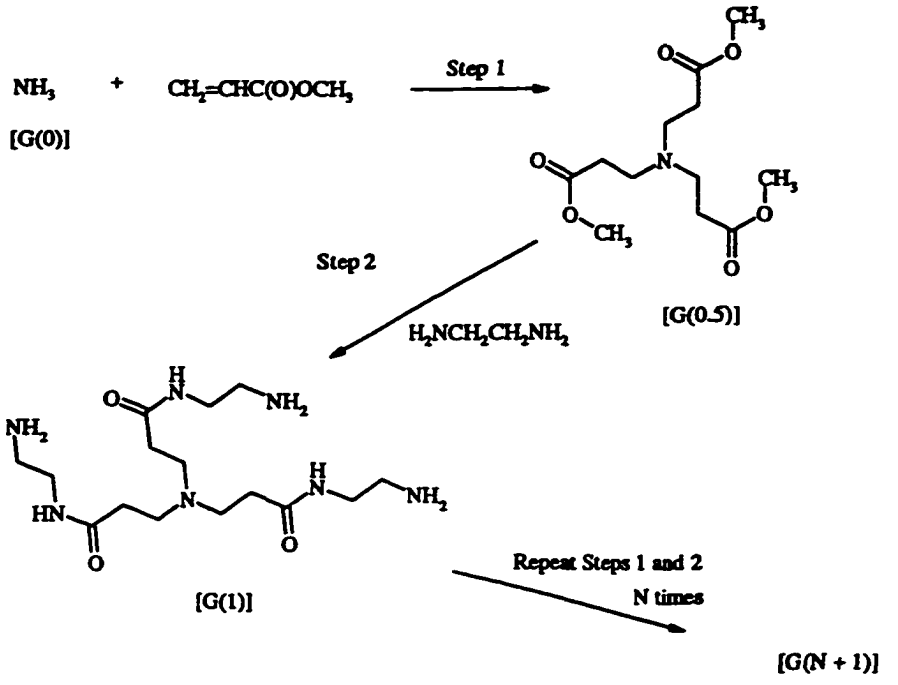
Scheme 1.2 Comparison of Divergent and Convergent strategies

There have also been various attempts to develop a 'one-pot' assembly of dendrimers, but to date there is little evidence for any useful level of control over the internal substructure.[7] The products obtained are, in most instances, poorly characterised polymers which are highly branched ("hyperbranched"). For example, in 1988 Kim and Webster[8] reported the first synthesis of "hyperbranched" polyphenylenes by a more convenient 'one-pot' method. Comparisons between dendrimers and hyperbranched polymers have been made because many of the latter (in attempts to mimic dendrimer connectivity) have now been synthesised.[9]

1.2 Divergent Synthesis

In 1985, the first series of fully characterised dendrimers that were extensively studied (up to a seventh generation) was reported by Tomalia *et al.*[1] The synthesis starts with ammonia as a core molecule. Michael addition of methyl acrylate to the ammonia, followed by amination with ethylene diamine yields the first generation, G(1). Repetition of these two steps results in larger generation [G(N)] poly(amidoamine) dendrimers (PAMAM Starbursts™) as shown in Scheme 1.3.[10] Each new generation results in two more reactive chain ends, doubling the molecular weight at each stage. The final structure may be viewed as a spherical, totally symmetrical molecule where the dendrimer molecule is built from the inside to the outside using a divergent reaction sequence. This is analogous to work by both Vögtle *et al*[4] and Meijer *et al*[11] who used a similar reaction sequence, synthesising secondary

amines as a peripheral functionality to give each new layer two more branch points for further growth.



Scheme 1.3 Divergent synthesis of PAMAM dendrimer[1]

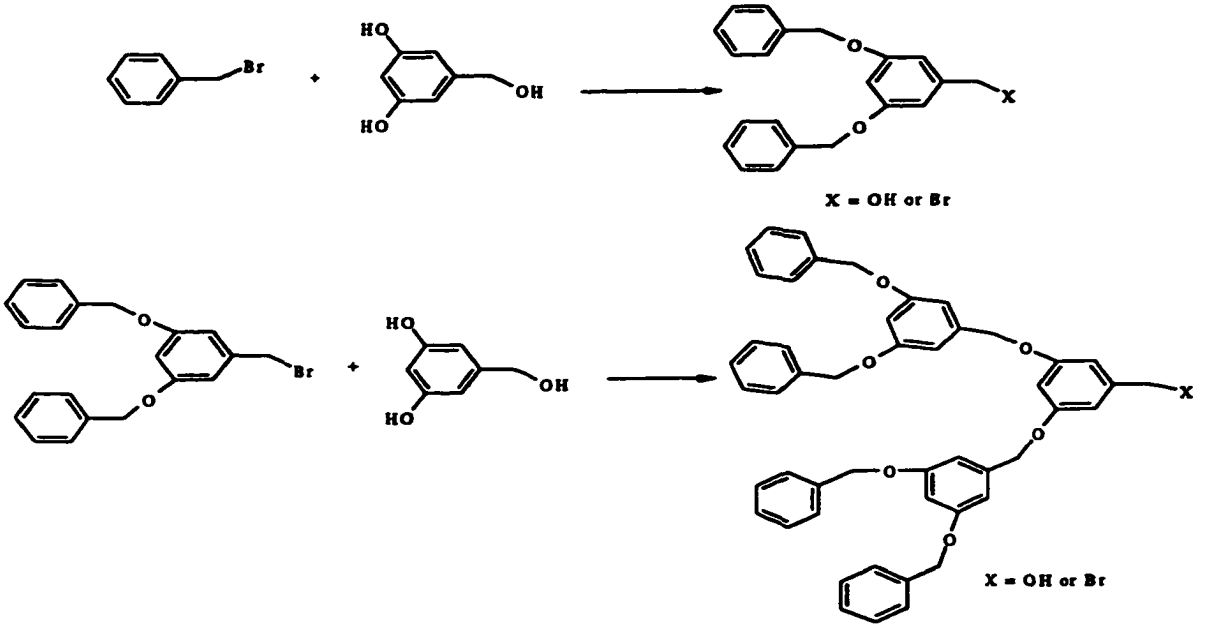
In 1981, Denkewalter *et al*[12] also studied synthesis of dendrimers by the divergent approach; this was the first reported synthesis of a dendritic polypeptide centred on a lysine building block where branching at the chain end was from nitrogen groups (a tenth generation was reached).

Initially all these syntheses were based on organic molecules. It was only in 1989 that Rebrov *et al*[13] published the first series of heteroatom dendrimers based on polycarbosilanes. Since this time many reports about inorganic dendrimers[14] have appeared, such as those containing phosphorus,[14f] gold,[14i] platinum,[14h] and ruthenium[14a,b]. Many syntheses based on divergent technology now exist in the literature and they are far too extensive in number to

elaborate on each individual system; however, they are elegantly summarised in reviews articles and books on this subject.[3]

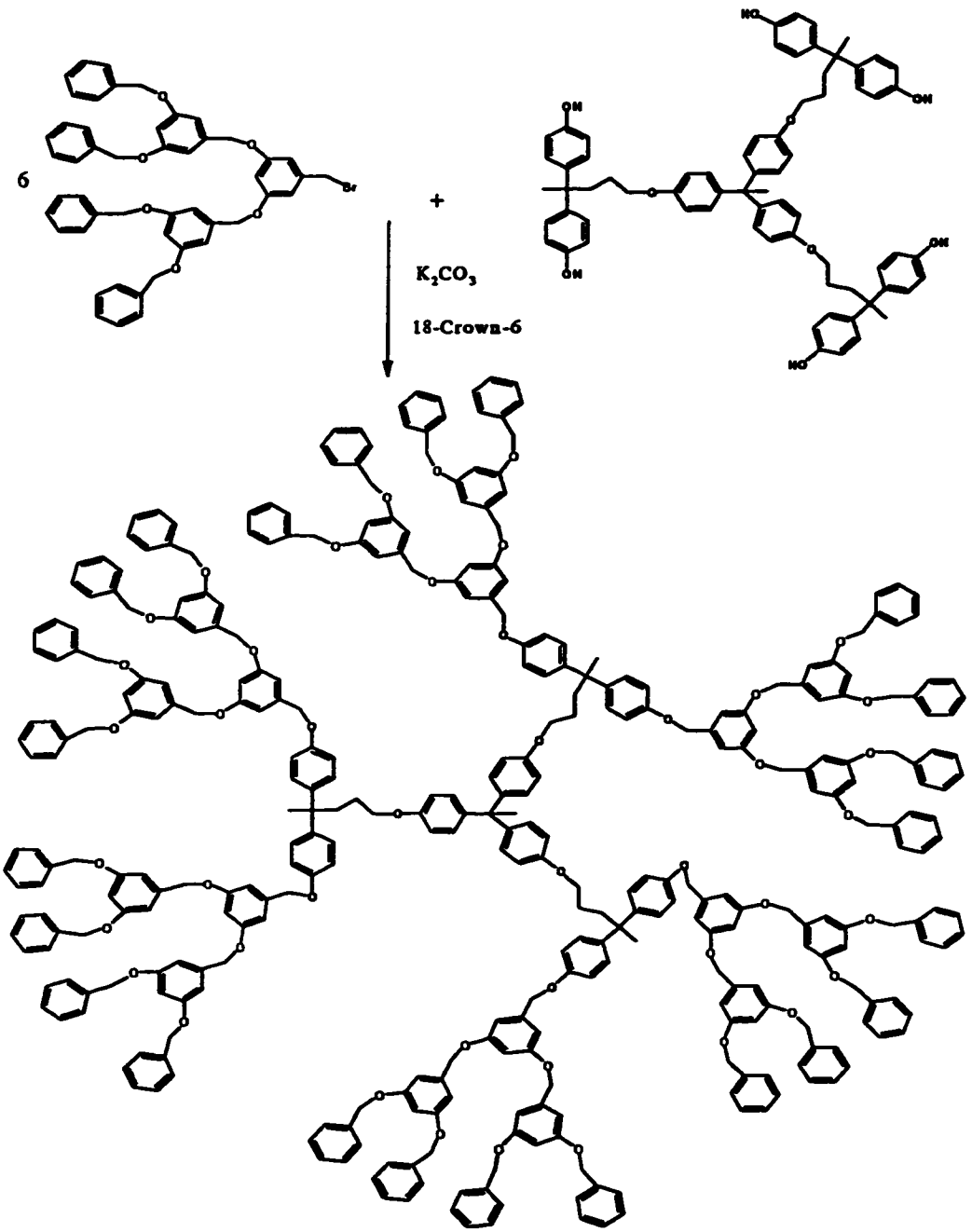
1.3 Convergent Synthesis

In 1990, Fréchet and Hawker[5,6] pioneered the convergent approach to dendrimer synthesis, building dendrimers from the outside-in, where the focal core molecule is reacted with a pre-formed 'monodendron' unit. The dendritic wedges are synthesised using divergent steps from benzyl bromide, which is reacted with two equivalents of 3,5-dihydroxybenzyl alcohol and subsequent conversion back to the benzylic bromide function.[5,6] Repetition of this divergent procedure, with more benzyl bromide, results in the desired 'monodendron' wedge after further activation of the benzylic site, Scheme 1.4.



Scheme 1.4 Synthesis of 'monodendron' wedges[5,6]

Typically, several generations of growth of the monodendron is followed by attachment to the core molecule. This minimises the number of transformations necessary to produce very large molecules as in Scheme 1.5; this illustrates the attachment of six monodendron units to a polyphenol "hypercore" molecule.

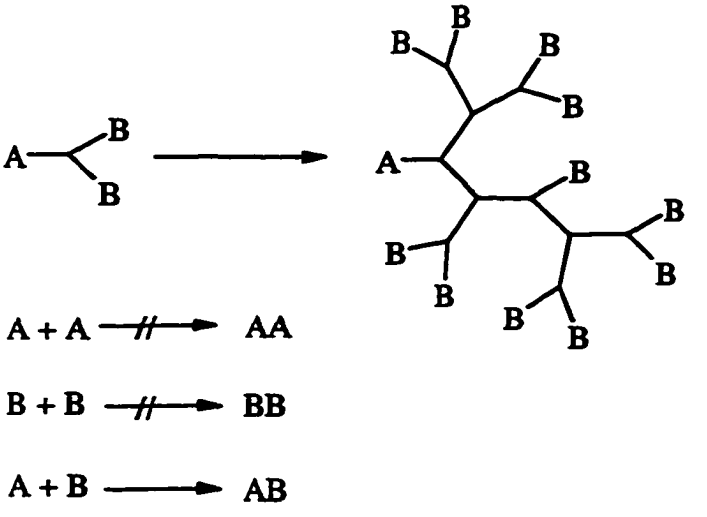


Scheme 1.5 Convergent synthesis of Fréchet and Hawkers polyphenol dendrimer[5,6]

The convergent method is advantageous because it can allow for addition of two completely different substructures to a focal core molecule, as in the case of amphiphilic micellar dendrimers.[15] Moore *et al*[16] were able to apply a convergent procedure for the synthesis of large phenyl acetylene dendrimers in a much greater yield than *via* a divergent approach. Since each 'shell' is isolated and purified, convergent methodology allows for the formation of large, monodisperse materials that may not have been realised by a divergent strategy. As with the divergent method, it was much later that inorganic dendrimers were attempted; probably the work by Imai *et al*[17] based on polysiloxane dendrimers are the best inorganic convergent examples to date.

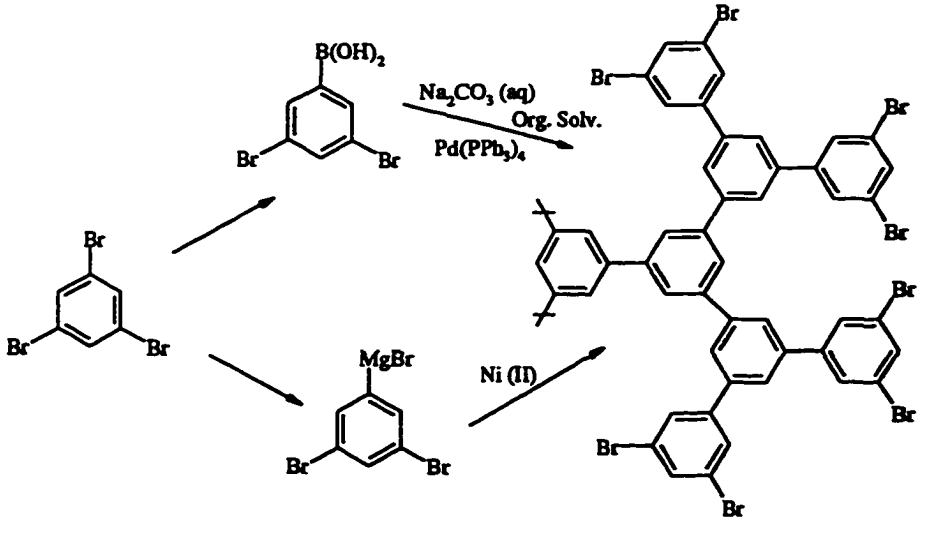
1.4 Hyperbranched Materials

The synthesis of perfectly symmetrical 'idealised' dendrimers, constructed in a well defined manner to control topology has been addressed above. More recently there has been a renewed interest in hyperbranched polymers which can be synthesised in a 'one-pot' procedure by polycondensation of AB_x monomer units, where $x \geq 2$, Scheme 1.6. This concept is not new. Work by Flory[18] in the 1950's, which subsequently earned him the Nobel Prize (1974), was based on this type of monomer polycondensation. This led to the prediction that highly branched polymers could be formed from such reactions.

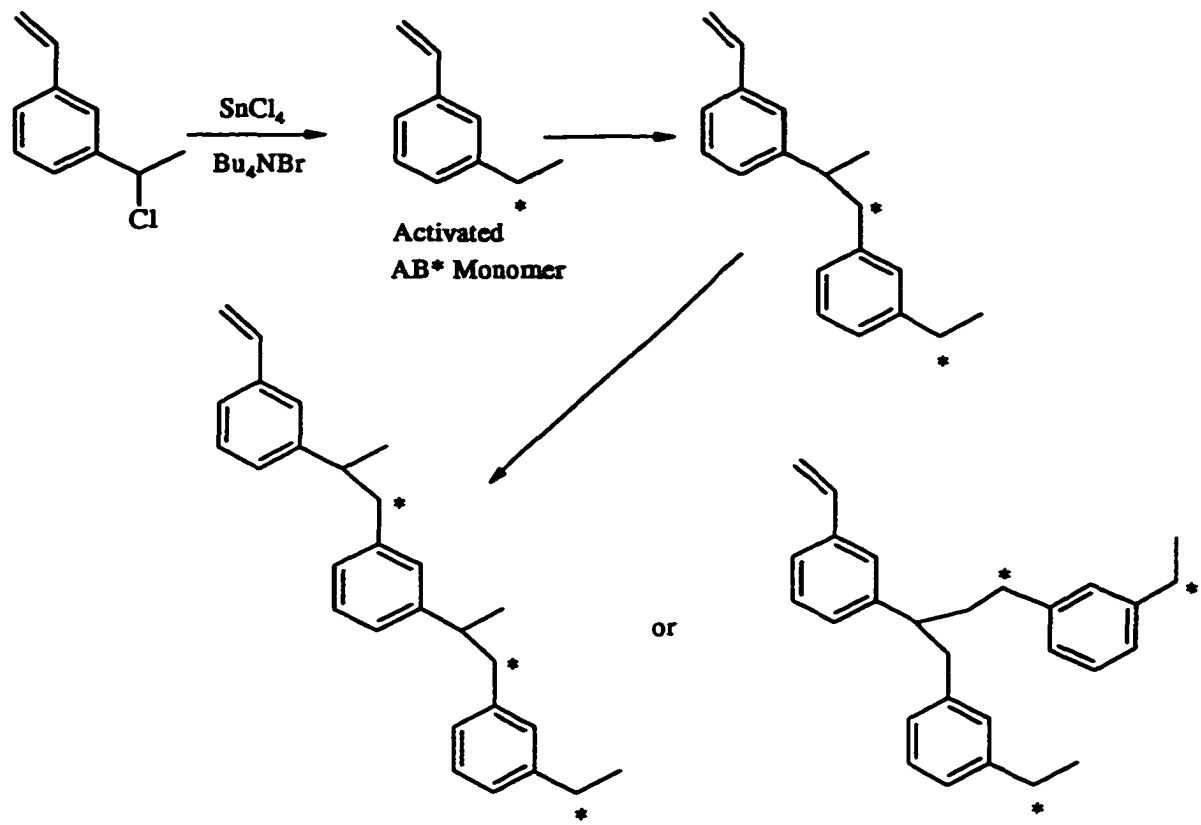


Scheme 1.6 AB_2 polymerisation

Many authors have since synthesised hyperbranched polymers,[19] comparing the properties exhibited to those of the more regularly defined dendrimers with similar connectivities. Kim and Webster[20] showed some of the first examples of hyperbranched polymers, synthesising polyphenylenes *via* Pd or Ni catalysed condensation routes (Scheme 1.7).



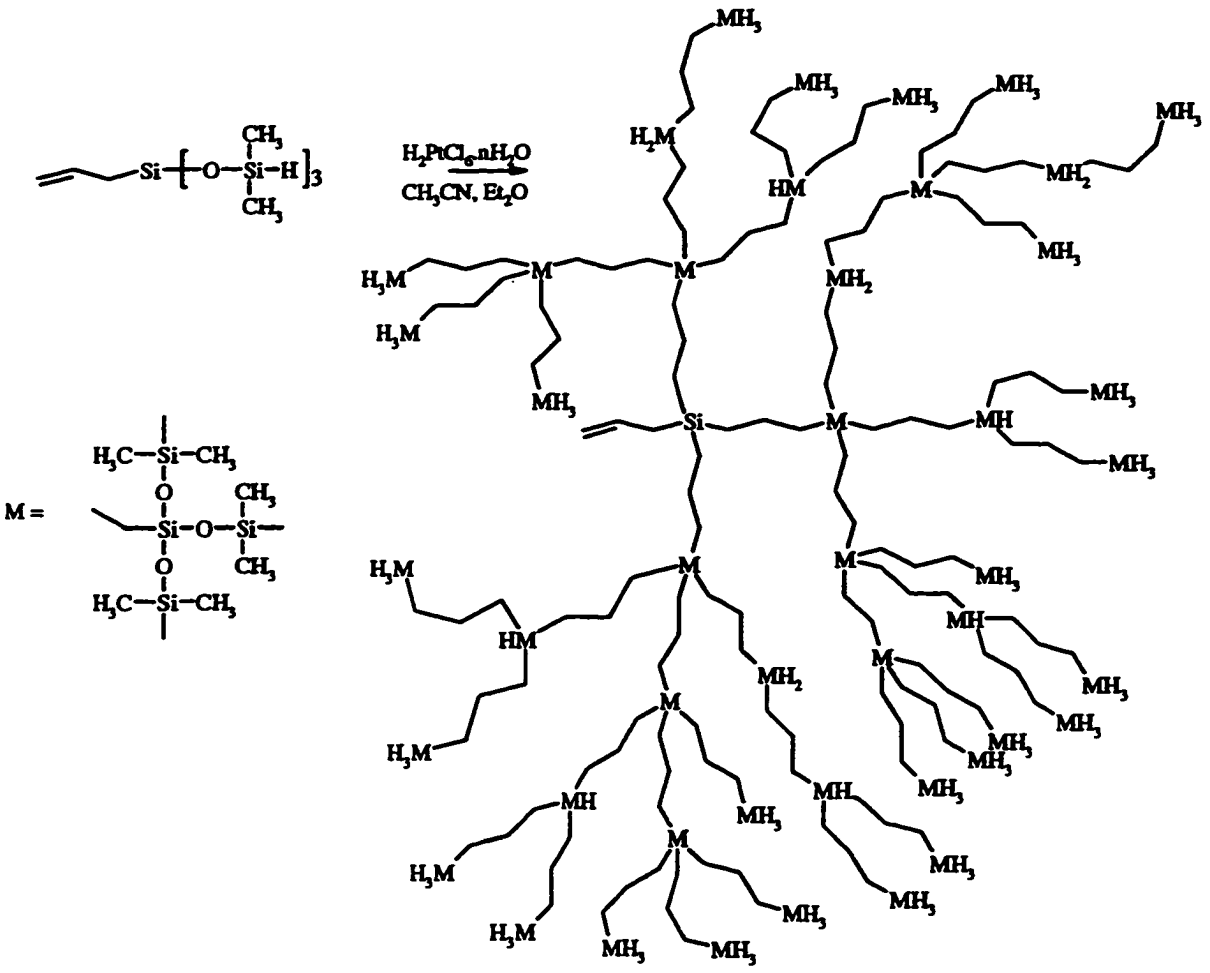
Scheme 1.7 Hyperbranched polyphenylenes by Kim and Webster[20]



Scheme 1.8 'Living' vinyl polymerization by Fréchet *et al*[19b]

Fréchet and Hawker[19b] reported a 'living' vinyl polymerization of 3-(1-chloroethyl)ethenylbenzene to molecular weights of greater than 100 000 amu (Scheme 1.8). Mathias *et al*[21] showed self-condensation to occur with poly(siloxysilanes); ^{1}H NMR integration suggested that growth to a third or fourth generation was achieved (Scheme 1.9) but no definitive structure could be assigned. This synthesis involves a Pt-catalysed hydrosilylation reaction using an AB_3 monomer as shown; the molecular weight was found not to increase greater than 19,000 amu even after addition of more catalyst. In this system any unreacted Si-H functions are unfortunately capable of further reaction *via* cross linking with the siloxane groups. To avoid these unwanted coupling reactions between molecules,

any remaining Si-H groups are capped with allyl phenyl ether at the end of the synthesis.



Scheme 1.9 Hyperbranched poly(siloxysilane) from ref. 21

1.5 Transition Metal Based Dendrimers

In 1992, Constable *et al*[22] synthesised the first series of metal containing dendrimer compounds, using a succession of molecules that incorporated Ru chelates into the backbone of the dendrimer (Figure 1.1). Balzani *et al*[23] further modified this strategy to incorporate the metal atom within the bridging links, while Newkome *et al*[24] melded other building blocks to a polyfunctionalised terpyridine moiety that contains the metal atoms within the lattice of the structure. Since this breakthrough in 1992, many transition metal atoms (and other metals) have been either incorporated into the backbone of the dendrimer or attached to the periphery.[14, 22-24]

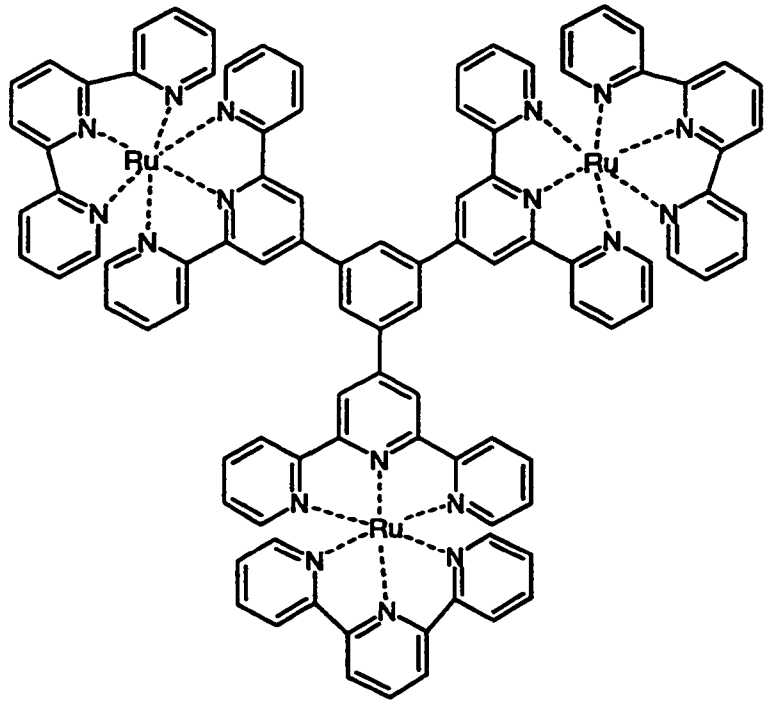


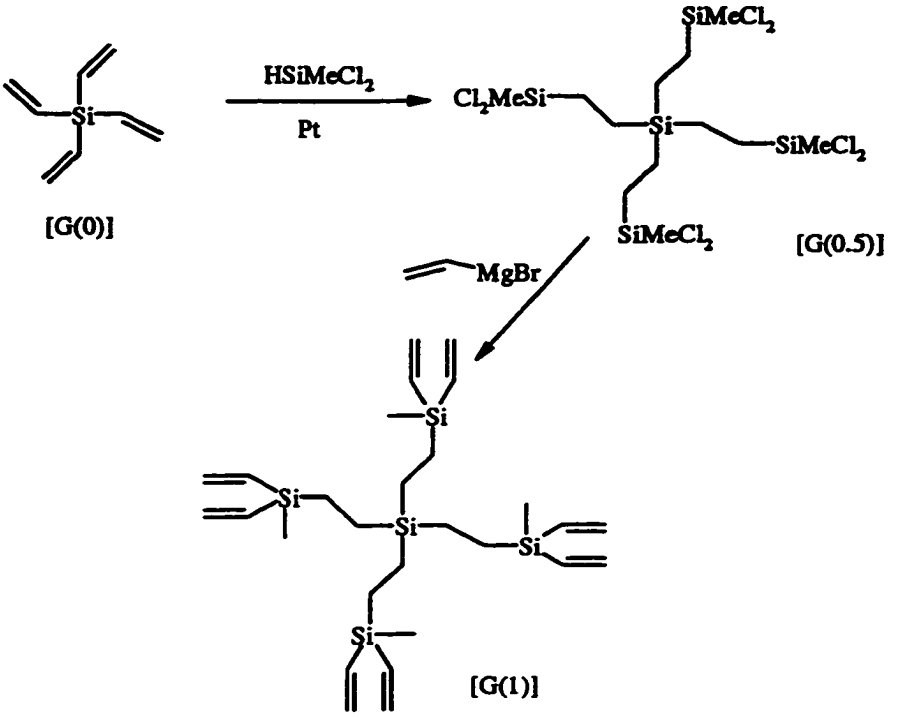
Figure 1.1 Ru-terpyridine dendrimer[22]

1.6 Silicon Based Dendrimers

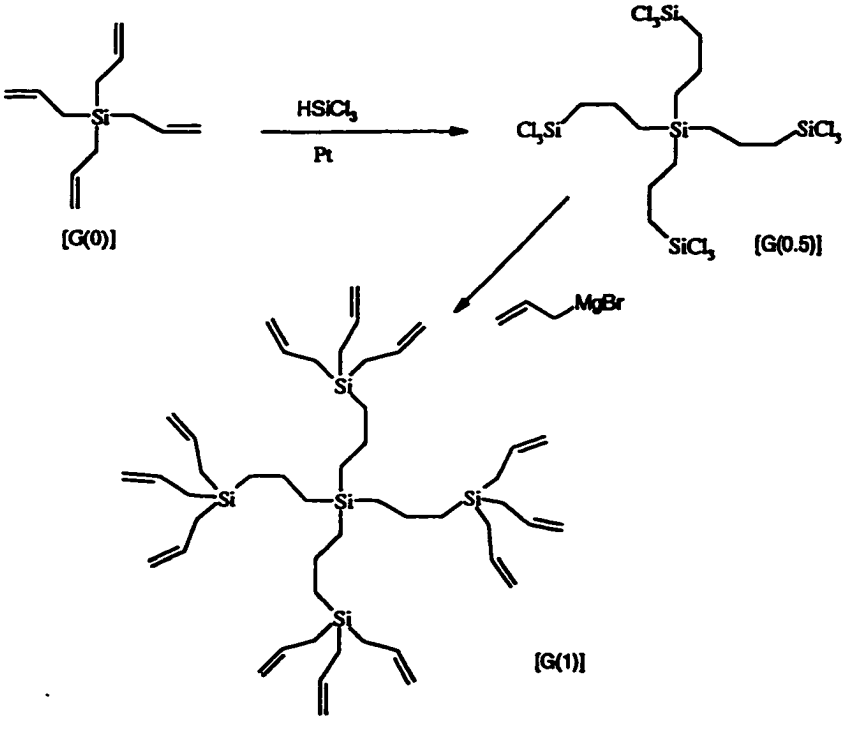
The incorporation of silicon into the dendrimer architecture was first attempted in 1989 by Rebrov *et al*,[13] followed shortly thereafter by Masamune[25] and Imai;[17] all three independently introduced siloxane units into the structure. The best studied of these poly(siloxysilanes) are the previously mentioned examples by Mathias and Carothers (Scheme 1.9).[21] Use of silicon as a branch point allows for the next shell to have a maximum of three further points for expansion at each layer.

However, one problem that may be encountered is that of surface saturation where dense packing of the atoms prevents further peripheral reactions. With the maximum of three branch points per silicon, this surface saturation may be seen at an earlier stage than with amine systems such as Tomalia's.[3] Analysis of dense packing has been explored theoretically by de Gennes (Nobel Prize, Physics 1991) and Hervet[26] on Tomalia's PAMAM Starbursts™. They concluded that the limit of growth, in a Starburst™ dendrimer, is only dictated by the length of the spacer used in the synthesis, *i.e.* between the branching points. Thus, longer spacer units may help to overcome surface saturation problems.

Work on carbosilane dendrimers was initially studied by Roovers *et al*[27] where a divergent pathway was used. Beginning from tetravinylsilane as a core molecule, an iterative procedure of hydrosilylation and alkenylation reactions built successive generations (Scheme 1.10). Soon after, work appeared by van Leeuwen *et al*[28] using tetraallylsilane as the initiator core, Scheme 1.11. In both instances a fifth generation molecule was the largest prepared; after this point it was noted that the hydrosilylation reaction did not go to completion.



Scheme 1.10 Carbosilane dendrimer synthesis from tetravinylsilane by Roovers *et al*[27]



Scheme 1.11 Carbosilane dendrimer from tetraallylsilane by van Leeuwen *et al*[28]

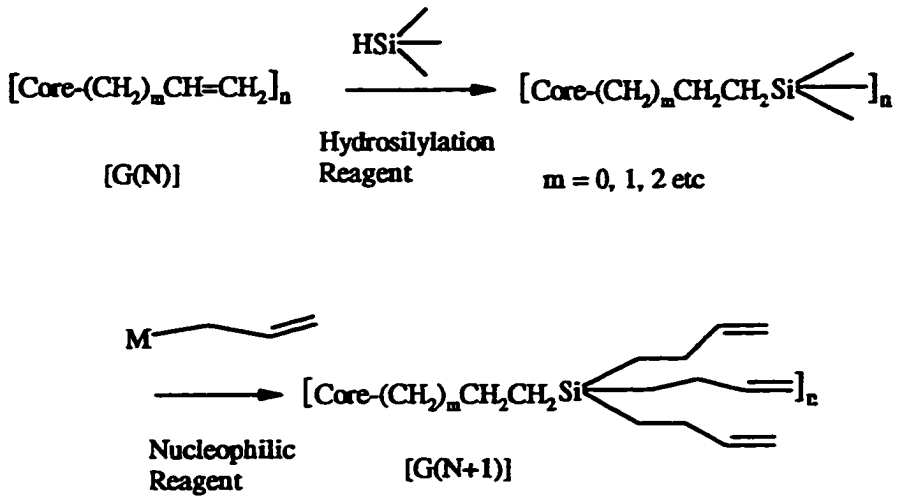
Various carbosilane dendrimers have been documented by other workers, Table 1.1. The general scheme consists of two reactions, each directly forming a Si-C bond, which when iterated allow for the growth of distinct generations ("shells") that can be isolated and characterised (Scheme 1.12, following page). This isolation of individual materials verifies that the reactions have been completed and that gross structural defects may also be distinguished by use of gel permeation chromatography (GPC); an alternating set of reactions is a common method used in all dendrimer systems published to date.[3]

Table 1.1 Carbosilane based dendrimers synthesised according to Scheme 1.12

Author	Core	Hydrosilylation reagent	Nucleophilic reagent	Reference
Roovers	$SiVi_4$	$HSiMeCl_2$	VinylMgBr	27
Seyferth	$SiVi_4$	$HSiCl_3$	VinylMgBr	29
van der Made	$SiAll_4$	$HSiCl_3$	AllylMgBr	28
Morán	$SiAll_4$	$HSiMeCl_2$	AllylMgBr	30
Kim	$MeSiAll_3$	$HSiMeCl_2$	AllylMgBr	31
	$MePhSiAll_2$	$HSiMeCl_2$	AllylMgBr	
Frey	$SiAll_4$	$HSiCl_3$	AllylMgBr	32

All = Allyl; Vi = Vinyl

1.6.1 Synthetic Route

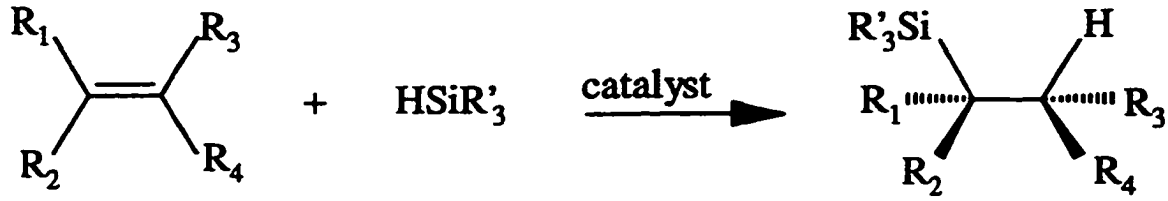


Scheme 1.12 General reaction sequence for preparation of carbosilane dendrimers

The formation of carbosilane dendrimers relies upon the iterative reactions (generically depicted in Scheme 1.12) being quantitative and regioselective. This avoids the possibility of side reactions occurring which would lead to either incomplete or structurally imperfect shells. For this reason a divergent scheme consisting of electrophilic addition followed by nucleophilic substitution (centred on silicon) has been adopted.[27,28] Hydrosilylation has been used for the electrophilic reaction, whilst the nucleophilic substitution generally occurs *via* the use of organomagnesium reagents. A brief overview of each Si-C bond forming reaction will be presented.

1.6.2 Hydrosilylation

The addition of R_3'Si-H (Scheme 1.13) to an unsaturated bond has been comprehensively studied.[33] Many transition metal catalysts have been employed for this conversion, most notably those of Pt and of Pd.



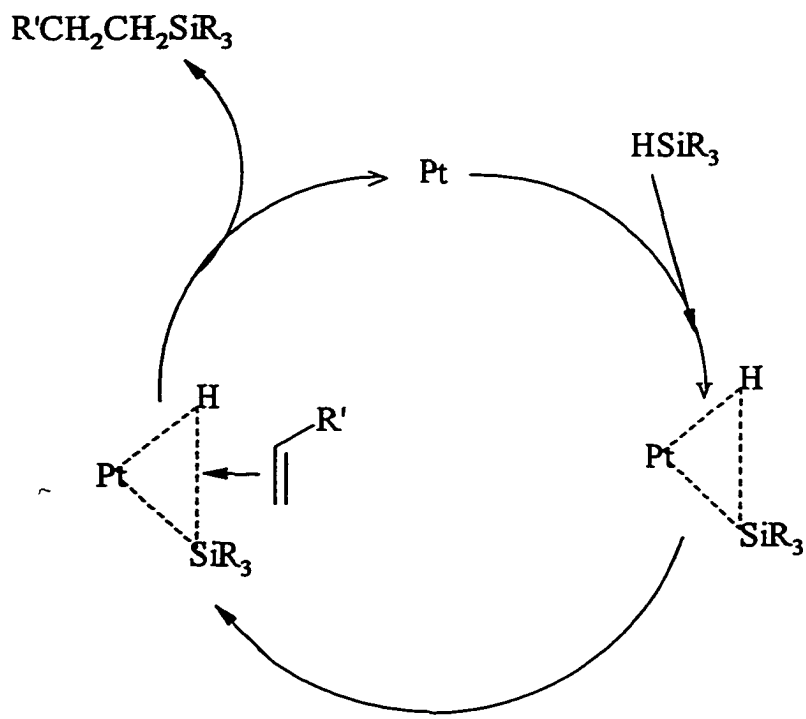
Scheme 1.13 General hydrosilylation reaction[33]

Various commercial Pt catalyst sources exist in which the metal centre can either be Pt(IV), Pt(II) or Pt(0); some of these examples as well as some other transition metals which can perform the desired transformation are highlighted in Table 1.2. This list is by no means exhaustive but shows the variety in reactivity and selectivity between different metals and their various oxidation states.

Table 1.2 Selected hydrosilylation catalysts from ref. 33

Catalyst	Ox. State	Reactivity and Selectivity
Pt/C	Pt (0)	Low temperature needed.
$Pt(COD)_2$	Pt (0)	No induction period, most active catalyst, 100 000 catalyst turnovers.
Karstedt's Pt -$[(CH_3)_2(CH{=}CH_2)Si]_2O$	Pt (0)	Very reactive, low temperatures, no induction period, problems with some functional groups.
$PtCl_2(COD)_2$	Pt (II)	Short induction period, highly active.
Speier's $[H_2PtCl_6{\cdot}6H_2O]$	Pt (IV)	Induction period required, highly selective, low concentrations needed, little interference from functional groups.
Wilkinsons's $[RhCl(Pph_3)_3]$	Rh (I)	Less active than Pt complexes, little selectivity.
$Co_2(CO)_8$	Co (0)	Isomerisation faster than hydrosilylation, decomposes above 60°C.

A representation of the classical Chalk-Harrod[34] mechanism for the metal mediated addition reaction, which has been accepted as a rational explanation of the catalytic cycle, is shown in Scheme 1.14. The mechanism proceeds by formation of an η^2-SiH bond, direct attack of the alkene onto this weakened Si-H bond, followed by elimination of the hydrosilylated product.



Catalytic Cycle

Scheme 1.14 Chalk-Harrod hydrosilylation mechanism from reference 33.

The catalyst employed in all the hydrosilylation reactions described within this thesis is chloroplatinic acid hexahydrate (CPA), more commonly referred to as Speier's catalyst.[34]

This homogeneous catalyst is commonly prepared as a dilute solution in isopropanol (~10^{-4} M) and is believed to be reduced by addition of the silane from a Pt(IV) to Pt(0) oxidation state during an induction period (Equation 1.1).[33] This is not seen for catalysts that are already in a Pt(0) oxidation state where an induction period is not necessary.[33] More accurately the description of Speier's catalyst is one of small Pt (0) crystallites (~ 5 μm), not visible to the naked eye, and so the catalyst is not truly homogeneous.[35]

$$H_2PtCl_6{\cdot}6H_2O{\cdot}10iPrOH + 4\,R_3SiH \longrightarrow Pt(0)\downarrow + 2HCl + H_2\,(g) + 4\,R_3SiCl$$

Equation 1.1

This particular metal catalyst (CPA) has been extensively studied and in general it has been shown to be both highly active and regioselective.[34] When forming a carbosilane based dendrimer, the hydrosilylation step must be quantitative and regioselective in order to minimise defects in the desired structure; addition to the double bond occurs in an anti-Markovnikov manner such that the periphery of the molecule contains the new reactive group.

To generate a dendritic structure, at least two Si-Cl bonds are needed at the peripheral group. Many chlorosilanes are available commercially, the ones studied in this thesis are chlorodimethylsilane ($HSiMe_2Cl$), dichloromethylsilane ($HSiMeCl_2$) and trichlorosilane ($HSiCl_3$). These give branch points in one direction (1B), two directions (2B) and three directions (3B) respectively, where 1B represents one new branching point per silicon atom.

The addition products are air-sensitive intermediates, due to the inherent reactivity of the Si-Cl bond with moisture and oxygen, but will be shown to have been isolated and characterized. They are designated as G(0.5), (1.5) etc. depending on the extent of iteration achieved.

1.6.3 Nucleophilic Substitution: Alkenylation

The second reaction in this dendrimer synthesis will directly form a Si-C bond by nucleophilic displacement of a highly reactive Si-Cl group. Nucleophiles such as Grignard[36] reagents are often used for this purpose since Grignard compounds can support other functional groups in the same molecule.[37]

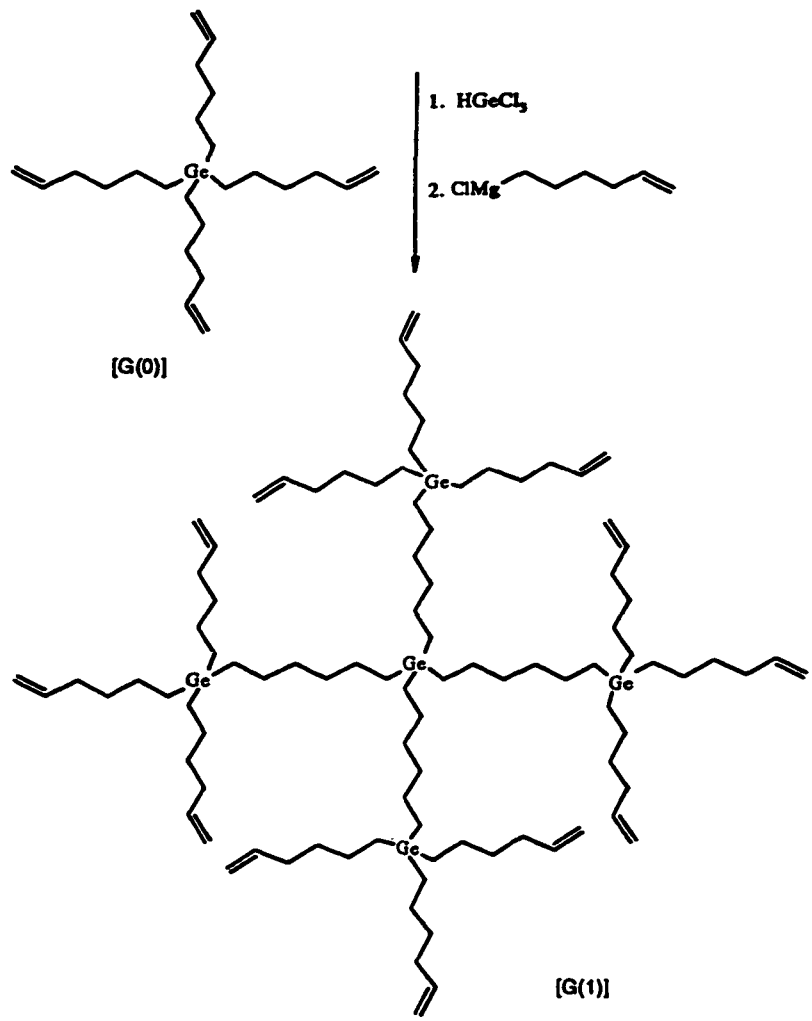
The proposed iterative process requires that the exterior of the compound has an unsaturated group present; this allows for further reactions at the periphery and the choice of Grignard reagent is important. In this thesis allyl bromide was chosen as the halide to form the Grignard reagent; in some instances vinyl bromide was also used. Both of these organomagnesium nucleophiles, when reacted with a Si-Cl bond, terminate the peripheral shell with an unsaturated hydrocarbon group which then allows for further hydrosilylation. Once this reaction has been completed air-stable products are formed which are classed as G(1), (2) etc. depending on how many iterative alkenylations have been performed.

A benefit possessed by these initiator cores is the onset of branching in four directions from tetrahedral silicon centres, whereas work by both Tomalia[3] and Meijer[11] the initial branching could only occur in three directions (from nitrogen). To date the largest core

multiplicities used have been a 'hexapus' molecule by Majoral *et al*[14] and the silsesquioxane cubes by Bassingdale *et al.*[38] These have a practical disadvantage during synthesis; end-group counting (*i.e.* the number of terminal groups relative to internal moieties) relies upon complete, regioselective addition with no branch defects. This becomes very hard to determine at higher generations when a proliferation of overlapped saturated resonances dominates the proton NMR spectra.

1.6.4 Other Group 14 Based Dendrimers

Organogermanium dendrimers first appeared in 1996 by Mazerolles *et al*[39], where the synthesis was attempted by both a divergent and convergent strategy. A mixture of the two procedures were used since forming the second generation failed *via* a convergent route, possibly due to steric constraints (Scheme 1.15).[39] In 1988, Bocharev *et al*[40] reported a synthesis of poly(fluorophenylenegermane) which was achieved by anionic polymerisation to give a hyperbranched structure. No Sn or Pb centred dendrimers have been reported to date.



Scheme 1.15 Synthesis of germanium based dendrimers[39]

1.6.5 Hyperbranched Carbosilanes

The search for a 'one-pot' procedure that could potentially give a dendritic structure of a polycarbosilane has not yet been found; so far, as with all other attempts, only hyperbranched polymers have been produced. The 'rapid-assembly' of carbosilane materials was initially studied by Muzafarov *et al*[41] but characterization of these systems was not complete, *i.e.* no ^{29}Si NMR data was reported.

Recently Frey *et al*[42] published an article on the Pt catalyzed self-condensation of triallylsilane, $HSiAll_3$, anchoring the macromonomer onto an oxazoline termination group. Work of this nature was first studied in the 1950's when Curry[43] polymerized compounds that contained a hydrogen and a vinyl group joined to the same silicon atom; analysis of the products by NMR showed polymeric compounds and unexpectedly a 1,4 disilacyclohexane ring system.[44] In a similar approach to the one reported by Frey *et al*, [42]anchoring the monomer substrate will be examined as a potential route towards forming a more 'perfect' set of branching sites, *i.e.* similar to a dendritic compound.

1.7 Dendrimer Characterization

Dendrimers are large molecules whose backbone is made of identical repeating units that may appear indistinguishable from each other. Proton NMR spectroscopy may not detect one missing group in 100 or more repeating branches since all these internal subunits are

identical. The masses of the molecules themselves are very large yielding low volatility materials. This renders the most conventional mass spectroscopic techniques (chemical ionisation and electron impact) no longer appropriate. There also comes a point where the percentage of each element present reaches a plateau for these materials and so elemental analysis can not distinguish one generation from its predecessor in large N of G(N).

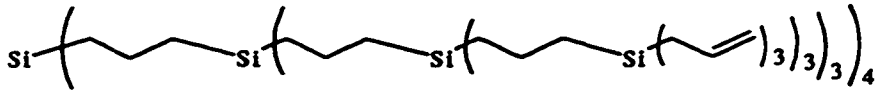
Researchers have looked towards more classical polymer characterization methods; these include amongst others: gel permeation chromatography (GPC),[45] viscosity,[45] laser light scattering (LLS)[46] and vapour pressure osmometry (VPO).[45] Recently a more elaborate mass spectroscopy technique has been used, matrix assisted laser desorption ionisation-time of flight (MALDI-TOF).[32]

1.7.1 Mass Spectroscopy

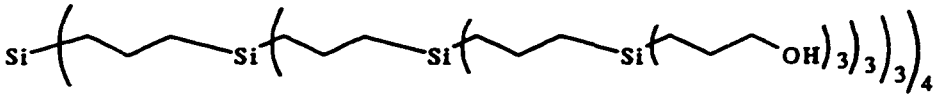
The development of desorption methods for mass spectroscopy, such as field desorption,[47] plasma desorption,[48] fast atom bombardment (FAB),[49] electrospray,[50, 52] and MALDI,[51] has revolutionized the analysis of large, involatile and/or thermally labile high molecular weight compounds. Most recently the MALDI technique has been used for the characterization of carbosilane poly-ol dendrimers by Frey[32] which showed that the structure was not perfect. One of the carbosilane dendrimers analysed (108-en, with 108 terminal allyl groups) is shown below and would have an expected molecular mass of 8 096 amu. The other spectrum, 108-ol with saturated end groups, has a calculated molecular mass of 10 040 amu. Neither of these spectra show peaks at the calculated values; instead they show peaks

at lower or higher masses which implies structurally imperfect shells (8 069.1 for 108-en) or shells that have extra units added (10 085.9 for 108-ol). Also observed are many peaks that correspond to fragmentation of the compound: loss of 152 amu ($SiAll_3$) for 108-en and loss of 188 amu ($Si(CH_2CH_2CH_2OH)_2CH_2CH_2CH_2$).

108-en: 108 allyl-end groups



108-ol: 108 alcohol-end groups



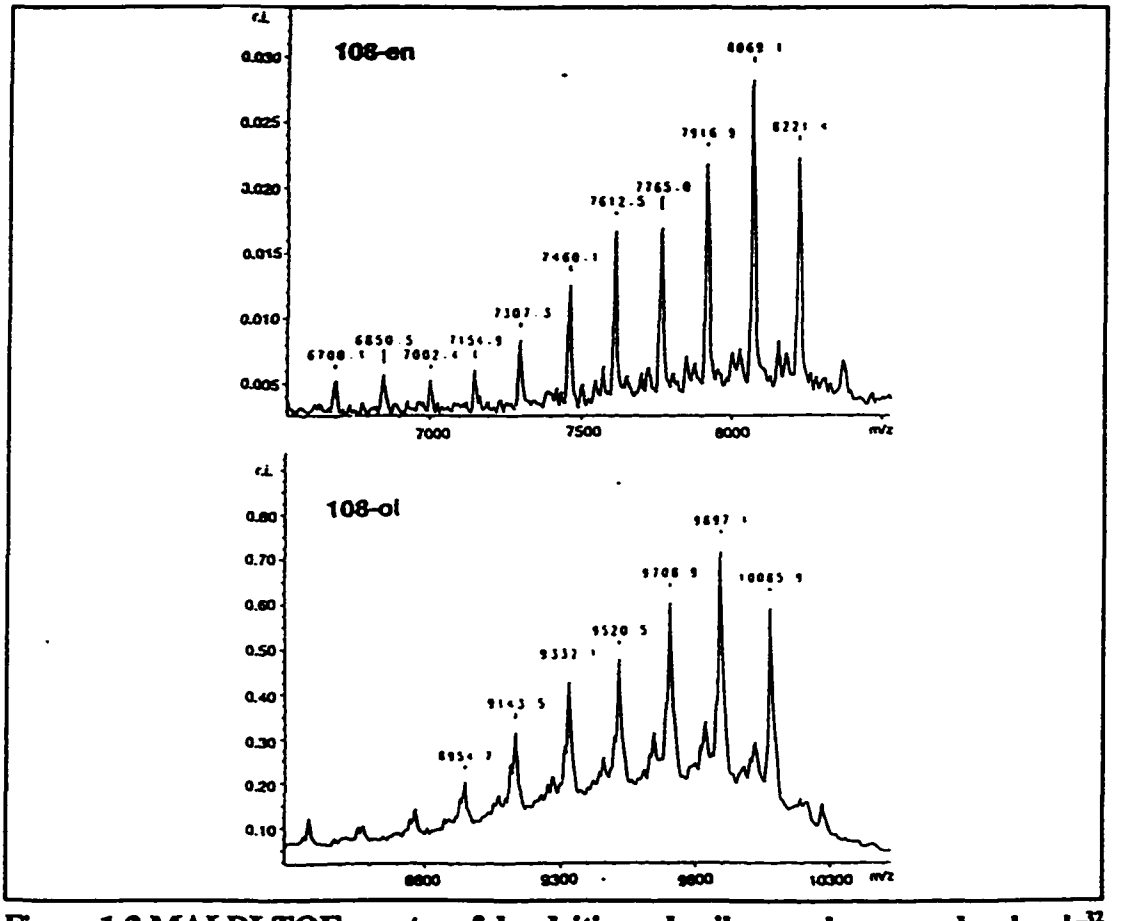


Figure 1.2 MALDI-TOF spectra of dendritic carbosilane poly-ens and poly-ols[32]

1.7.2 Gel Permeation Chromatography

Gel permeation chromatography (GPC), also called size exclusion chromatography (SEC) has been used by most authors involved in dendrimer synthesis. The method uses columns packed with a gel (Figure 1.3) with a narrow distribution of pore sizes. As the molecules pass through the gel the smaller ones permeate the stationary phase preferentially and the highest molecular weight compounds are eluted first.[45] These columns separate fractions on a basis of hydrodynamic volume; this technique is calibrated to polystyrene standards, where a known mass elutes at a fixed volume (elution time). Roovers *et al*[46] illustrated that polystyrene standards are inaccurate for mass determination of carbosilane dendrimers since the shapes of these dendrimers are different from linear polystyrene standards. GPC can still be used as a measure of the polydispersity of the sample to ensure that no gross structural defects have occurred within the assembly. This can be determined by a measure of peak width at half height and from the multiplicity of the peaks.

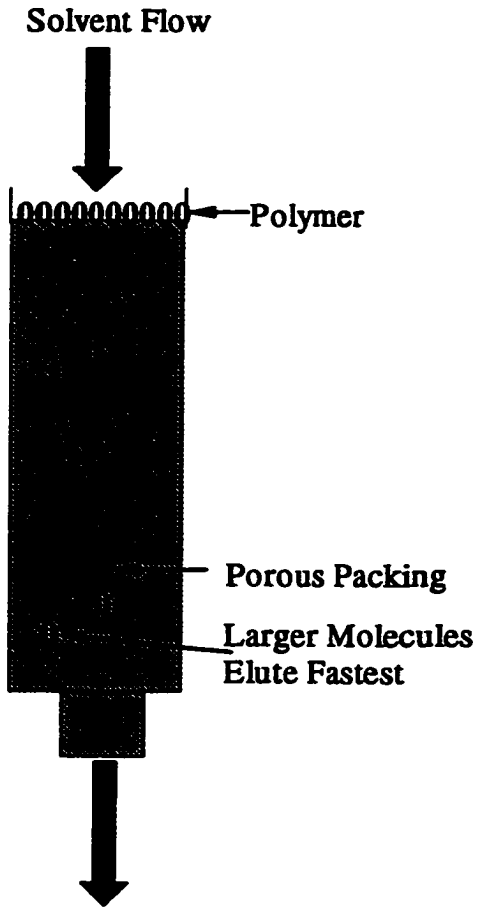
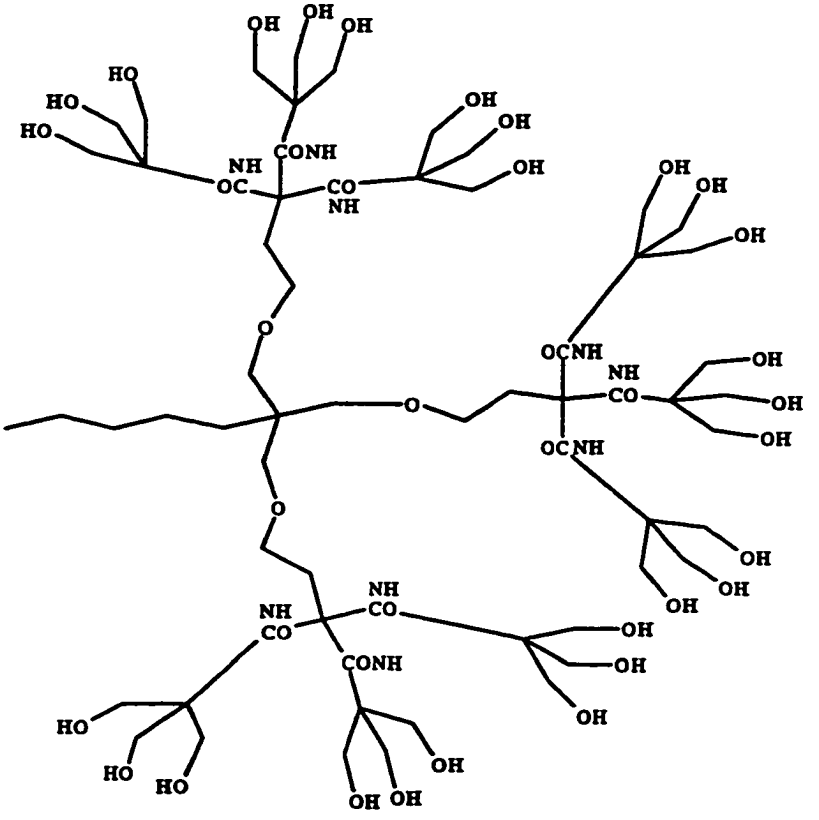


Figure 1.3 Schematic of GPC separation

1.8 Nomenclature of Carbosilane Dendrimers

The nomenclature for dendrimer molecules using the IUPAC system is extremely difficult. For example, the correct name for the molecule synthesised by Newkome *et al*[54] is:

1,19-Dihydroxy-N,N',N"'-tetrakis[2-hydroxyl-1, 1-bis(hydroxymethyl)ethyl]-10-[[4-[[2-hydroxyl-1, 1-bis(hydroxymethyl)ethyl]amino-3,3-bis[[[2-hydroxyl-1,1-bis(hydroxymethyl)ethyl]amino]carbonyl]-4-oxobutoxy]methyl]-2,2,18,18-tetrakis(hydroxymethyl)-4-16-dioxo- 10-pentyl-8, 12-dioxa-3,17-diazanona-decane-5,5,15, 15-tetracarboxamide[3a]



[27]-arborol by Newkome *et al*[54]

This is difficult and cumbersome for both written and verbal communication and so both these authors[54] and Mendenhall *et al*[55] independently devised more systematic methods for naming such large molecules. The fractal nomenclature notation by Mendanhall simplifies the above name to $(HO)_{27}$f(1.NHCO.2O1)C5H, but it may still not be clear to readers what this name implies unless a full understanding of the fractal system is known. The naming begins at the periphery and works inwards towards the core in four parts; terminal group, subscript, connectors and then the core.[55] The fractal name for the molecule implies 27 alcohol groups at the periphery. The connector group then consists of one carbon atom (1) joined to a branching carbon (.), next is the amide link (NHCO) followed by another branching carbon atom (.) and finally two carbons linked *via* an oxygen to another carbon (2O1). All of these are attached to the core which is a five carbon chain that is terminated with protons (C5H).

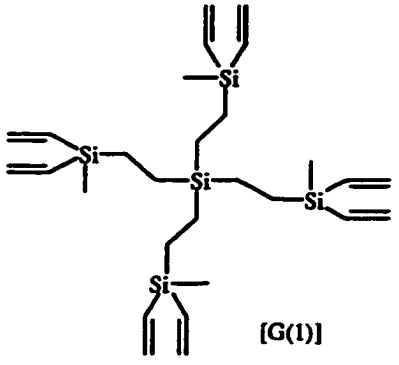
The dendrimers presented in this thesis shall be named differently to the fractal system. In general, dendrimer molecules are given the designation [G(N)] indicative of the generation number reached.[3e] This same generational approach can be applied to carbosilane dendrimers, each successive, isolable compound can be classed as a [G(N.5)] or [G(N)] depending on the extent of iteration achieved.

A nomenclature system for cascade molecules has been proposed by Newkome *et al*[54] where the general scheme is as follows:

$$[Core][(Repeat\ Unit)\ {}^{G}_{N_b}\ (Terminal\ Unit)]_N$$

Where G is the generation number attained; N_b is the branch point multiplicity and N is the

core multiplicity. For example, if the first generation of the carbosilane dendrimer prepared by Roovers *et al*[27] (also see page 14) is written with this formulation it becomes:



[G(1)]

$Si[(CH_2CH_2Si(CH_3))^1{}_2{:}(CH{=}CH_2)]_4$

Roovers' first generation dendrimer

$$\textit{Roovers}: \quad Si[(CH_2CH_2Si(CH_3))^1_2 : (CH{=}CH_2)]_4$$
$$\textit{van der Made}: \quad Si[(CH_2CH_2CH_2Si)^1_3 : (CH_2CH{=}CH_2)]_4$$

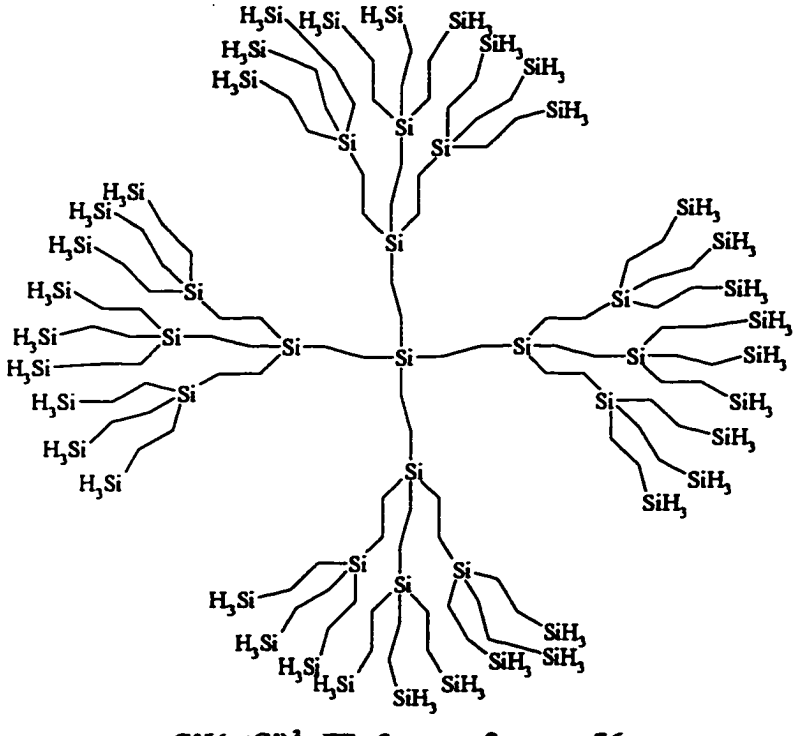
Roovers *et al*[27] initially used tetravinylsilane as the central core, followed by a repeating unit of ethylmethylsilyl spacers and termination with vinyl groups. For van der Made's[28] compound the core used was tetraallylsilane, propylsilyl spacers and then capped with allyl groups. For each the number of terminal groups (Z) may be calculated from $Z = N_b^G \times N$. *i.e.* for Roovers $Z = 2^1 \times 4 = 8$ terminal vinylic groups; whilst for van der Made $Z = 3^1 \times 4 = 12$ terminal allylic groups.

Alternatively, in order to simplify both the repeat units and the terminal groups further the ethylmethylsilyl can be written as etSiMe, and the propylsilyl spacer as prSi; also

simplifying with Vi as vinyl and All as allyl terminal groups.

$$Roovers : Si[(etSi(CH_3)_2^1 : Vi]_4$$
$$van\ der\ Made : Si[(prSi)_3^1 : All]_4$$

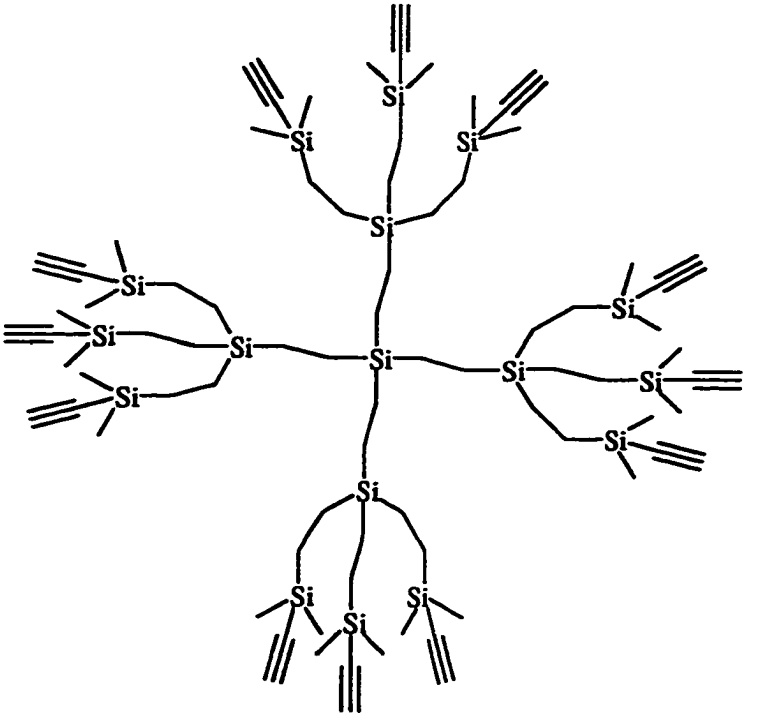
Although these are relatively simple molecules this nomenclature is shown to work for higher generations also. For example, Seyferth *et al*[56] synthesised a series of organosilicon dendrimers with peripheral silicon hydride groups. The procedure again used tetravinylsilane as a core molecule (*c.f.* Roovers[27]), ethylsilyl links between 'shells' and capping with hydride groups. The following shows a third generation molecule which was labelled as 3G-H.[56] Using the naming scheme mentioned the compounds name would shorten to: $Si[(etSi)^3{}_3:H]_4$



$Si[(etSi)^3{}_3:H]_4$ from reference 56

When the branch point multiplicity at the silicon atom changes, or when mixed spacer groups are used this nomenclature also depicts this variation. An example containing both branch point changes and other terminal groups is also seen in work by Seyferth *et al.*[57] The shortened version of this compound would be written as:

$$Si[(etSi)_3^1 : (etSiMe_2)_1^2 : C{\equiv}CH]_4$$



$Si[(etSi)^1_3:(etSiMe_2)^2_1:C{\equiv}CH]_4$

where similar to the previous examples, the number of terminal groups, Z, can be calculated by $Z = N_b^G \times N$. In this example $Z = 1^2 \times 3^1 \times 4 = 12$, and as seen in the diagram of this compound twelve alkyne groups are observed.

1.9 Scope of this Thesis

The work presented in this thesis examines the synthesis and multinuclear NMR characterization of carbosilane dendrimers. This class of compounds has typically been difficult to analyse by proton NMR since the backbone consists of units that appear to be indistinguishable. Initially, a lower symmetry core molecule ($PhSiAll_3$; trifurcate system) will be studied as this contains an internal integration signal for proton NMR spectroscopy, *i.e.* core to peripheral protons *via* 'end-group' counting. Branch point multiplicity at silicon varies using different chlorosilanes (1B, 2B or 3B) in the hydrosilylation reactions. Use of ^{29}Si NMR spectroscopy as a technique to map dendrimeric structures topographically is also examined. Analogous work has been reported by Majoral[14] *et al* (phosphorus containing dendrimers; ^{31}P NMR) and separately by Meijer[58] *et al* (nitrogen dendrimers; ^{15}N NMR). The trifurcate series of compounds will be used to aid in the interpretation of dendritic molecules which have higher core symmetry. This is by comparison of the ^{29}Si NMR spectra which will show hierarchical (generational) signals, that give topographical information about the dendrimer structure. It will also be established that carbosilane based dendrimers can be characterized by conventional multinuclear NMR methodology, and also by techniques more applied to polymers such as GPC; retention times (volumes) *vs* $\log_{10}M_w$ will be plotted and shown to be linear for different silicon branch point multiplicities. These plots (using narrow dispersity samples) will be used as calibration curves for unknown, or alternate, systems centred around the same core molecule.[59]

From the time that this research was initiated many workers have studied carbosilane based dendrimer molecules;[27-32] one aspect of research not extensively studied thus far is the

role of a dendrimer scaffold to facilitate in energy transfer processes.[60] This "light-harvesting"[61] capacity requires that chromophores are present in the structure and the chlorosilyl dendrimer systems will be exploited for this purpose. The reactivity of a silicon chloride bond facilitates substitution with nucleophilic reagents to introduce a variety of different peripheral groups. Specifically for a such a "nano-antenna" approach (*i.e.* for chromophore end-groups) naphthyl units are incorporated as peripheral groups. With the trifurcate series there is also an added opportunity for Ph-Si bond cleavage with trifluoromethanesulphonic acid and subsequent internal group modification.[62] This then shows that an isolable triflate salt, which can then be substituted by a range of alcohols to produce modified core groups, is possible. Also, a digermane series of compounds have been examined as a series of masked trifurcate dendrimers; cleavage of the Ge-Ge bond by oxidative addition provides an unparrelled route into dendrimer core modification. These two routes have been used to modify the core atoms by introducing chromophores into the scaffold. The idea that an energy gradient will allow for an electron transfer process to occur has been explored *via* the use of fluorescence spectroscopy. Peripheral and core manipulation chemistry will be explained with both the Ph-Si (trifurcate) and Ge-Ge (masked trifurcate) series of dendrimers; each series can be directed toward a target molecule that possesses some chromophoric groups. Other peripheral groups have also been synthesised, fluorosilyl peripheries have been examined using LEED spectroscopy in attempts for detection of the dendrimer size.[63]

The final area studied is directed towards hyperbranched polycarbosilanes. Initially hybrid (branch point multiplicity change at silicon) step-wise synthesised compounds are

studied and then compared with small hyperbranched materials suspected to be analogous. This involves the simplest case of hybrid systems that can be generated; a shell expansion from two branches per silicon atom to three branches per silicon atom. As the data from these 'model' compounds is collected, larger hyperbranched materials will also be synthesised and the spectroscopic data is then compared to that from materials produced *via* a controlled iterative route.

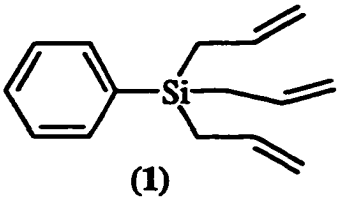
Overall this thesis establishes a general methodology for carbosilane dendrimer synthesis and characterization. The incorporation of silicon is exploited for both its reactivity and also for topographical mapping with the use of ^{29}Si NMR spectroscopy. These techniques will be transposed to aid interpretation of more ambiguous polymeric systems where definitive resolutions are deficient.

CHAPTER TWO

TRIFURCATE CARBOSILANE DENDRIMERS:

MOLECULES WITH AN INTERNAL INTEGRATION SIGNAL

Dendrimer research has primarily focussed on branching from cores which possess high symmetry. [3] The aim of this Chapter is to highlight the usefulness of a lower symmetry core molecule as an aid for characterising topological growth of the macromolecules, specifically by using phenyl triallylsilane (1), $PhSiAll_3$, as a core group.[64]



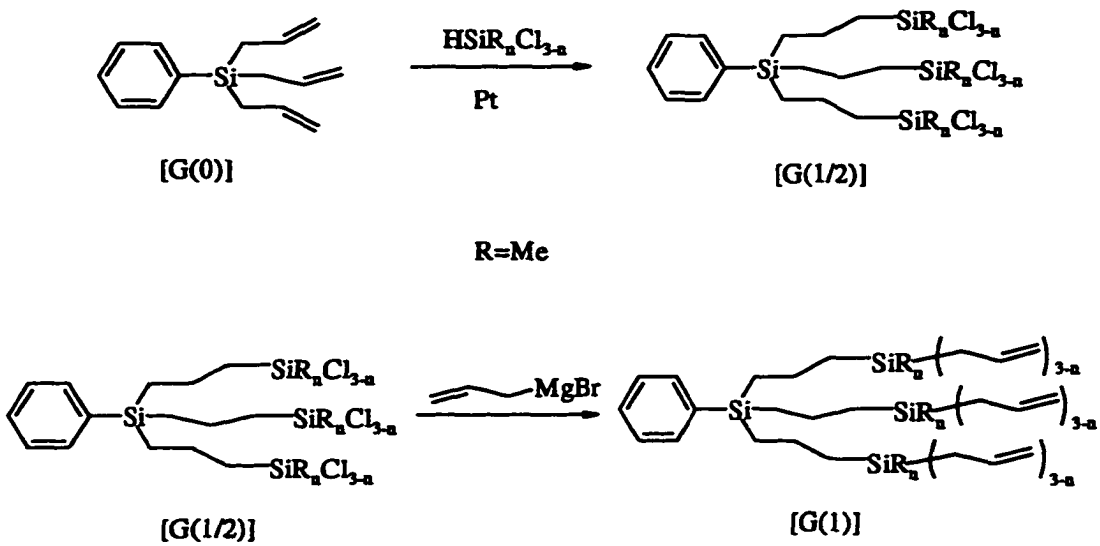
(1)

Phenyl triallylsilane

Strategically this is important since the core molecule contains a phenyl ring, which acts as an internal integration calibration device for ^1H NMR spectroscopy. There is also the potential for core group manipulation *via* phenyl-Si bond cleavage and subsequent group modification at the core.[62]

This chapter focuses on a series of iteratively prepared dendrimers, beginning from a trifurcate core, using various chlorosilanes to assemble the branching units, Scheme 2.1. It also examines ^1H NMR integration for individual shell characterization, using the phenyl signal calibrated to five protons relative to other resonances (*Me*-Si, *Allyl*-Si) as a means for

end group counting. Other techniques will also be considered as a basis for characterization and structural analysis that can then be applied to the other carbosilane systems discussed in the remaining chapters.



Scheme 2.1 Generic carbosilane dendrimer synthesis

The dendrimers synthesised from the trifurcate core are outlined in Table 2.1 and will be discussed in more detail below; this synthesis leads to products that are formed by one-, two- or three-directional branching from the Si branch atoms (1B, 2B or 3B).

Table 2.1 Trifurcate Carbosilane Dendrimers Synthesised

Core	Branching Silane	Generation number G(N)	Series Name
$PhSiAll_3$	$HSiMe_2Cl$	G(1) to G(5)	$PhSi[(prSiMe_2)^N{}_1:All]_3$
$PhSiAll_3$	$HSiMeCl_2$	G(1) to G(4)	$PhSi[(prSiMe)^N{}_2:All]_3$
$PhSiAll_3$	$HSiCl_3$	G(1) to G(5)	$PhSi[(prSi)^N{}_3:All]_3$

Where pr = $CH_2CH_2CH_2$ and All = $CH_2CH{=}CH_2$

2.1 Phenyl triallylsilane[64]

This core molecule has been known for over 50 years and is easily obtained by reaction of phenyl trichlorosilane with an excess of allylmagnesium bromide. For reference purposes its ^{1}H NMR spectrum is illustrated in Figure 2.1, showing the phenyl protons (observed in the range δ 7.5-7.3 ppm), allylic (β at 5.8 ppm (t of t) and α at 4.9 ppm) and the saturated resonances (γ at 1.9 ppm). The ^{13}C NMR spectrum (Figure 2.2) is also simple to assign; the aromatic carbons appear at δ 135.3, 133.8, 129.3 and 127.8 ppm, allylic carbons at δ 134.2, 114.2 ppm, and the methylene signal at 19.5 ppm. The ^{29}Si NMR spectrum (Figure 2.3) is a single resonance, δ -7.97 ppm, typical of silicon with one phenyl ring attached.[65]

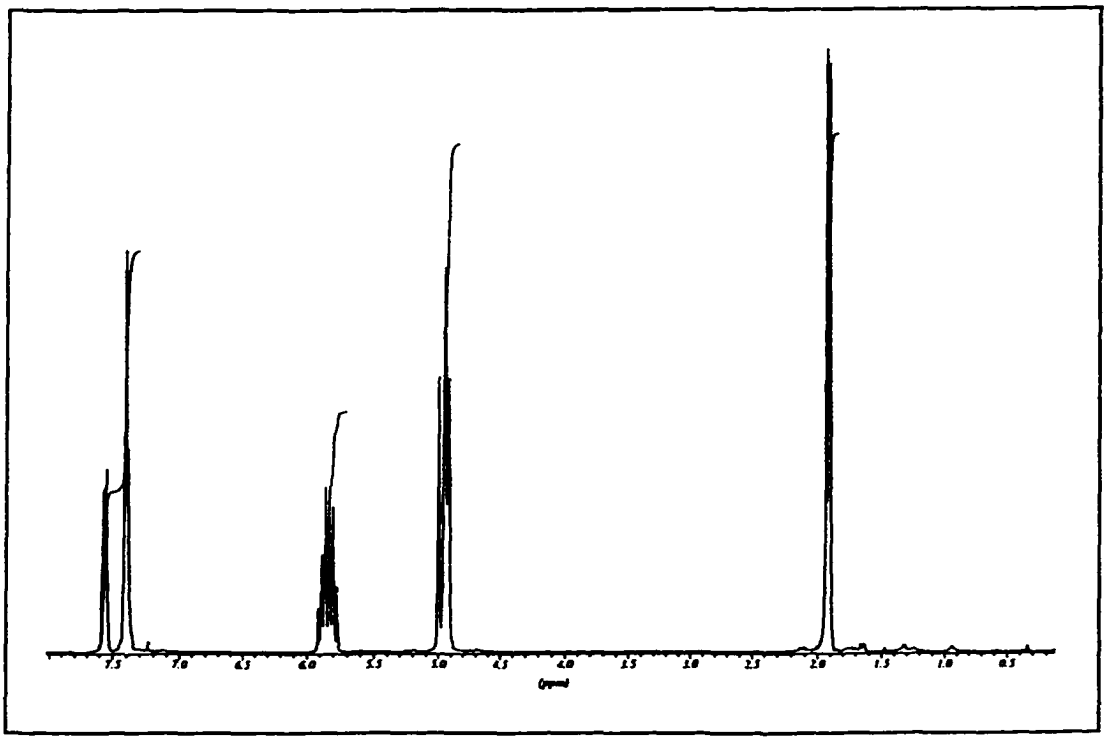


Figure 2.1 ^{1}H NMR spectrum of phenyl triallylsilane $PhSiAll_3$(1)

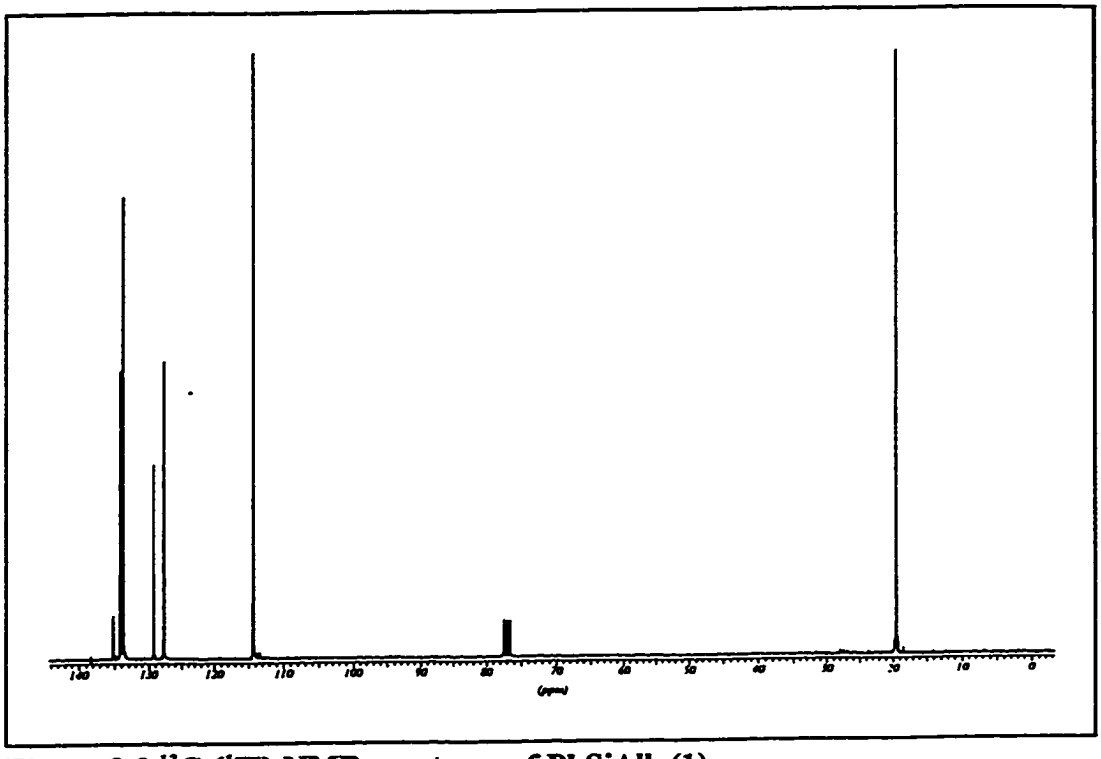


Figure 2.2 ^{13}C-{^{1}H} NMR spectrum of $PhSiAll_3$ (1)

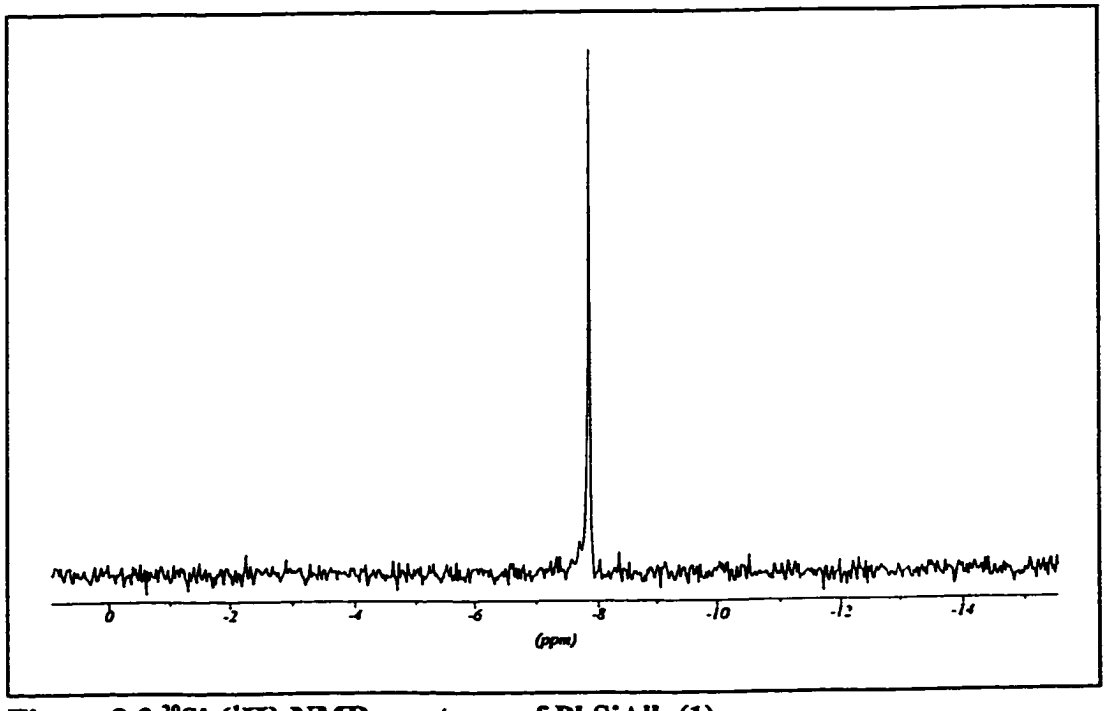
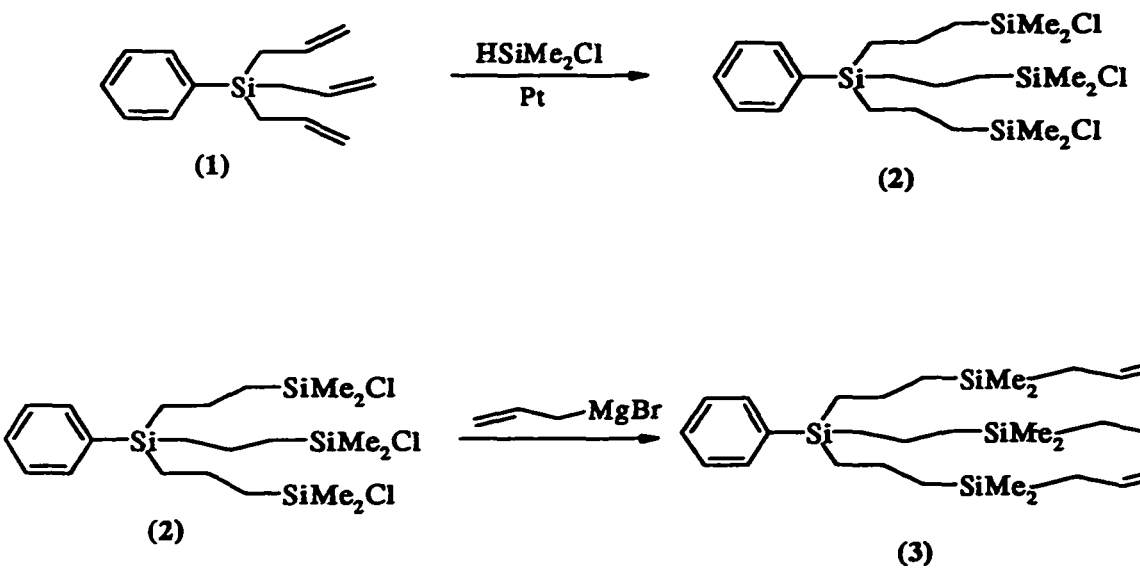


Figure 2.3 ^{29}Si-{^{1}H} NMR spectrum of $PhSiAll_3$ (1)

2.2 One-Directional Branching (1B)

These molecules, which are like linear polymers since the growth from silicon centres extend in one direction only, were synthesised (Scheme 2.2) by hydrosilylation with chlorodimethylsilane ($HSiMe_2Cl$), followed by an alkenylation reaction with allylmagnesium bromide.



(1) (2) (2) (3)

Scheme 2.2 Formation of first generation molecules by 1B branching

Although these molecules are not dendritic, they are useful models to establish how generational connectivity can be observed using multinuclear NMR spectroscopy. Also, since they remain relatively low molecular weight materials, even after a number of iterative growth steps, they are easily characterized by analytical methods used for small molecules (mass spectroscopy and elemental analysis). Single branch carbosilanes (1B) were synthesised to a fifth generation, *i.e.* to a point where the limits of conventional mass spectroscopic

techniques (CI, EI) had been reached. At the same time the relative percentages of constituent elements converged such that no useful distinction between successive generations is possible. To ensure that the reaction had gone to completion, the chlorosilyl product obtained by hydrosilylation, G(0.5)1B (2), was isolated and multinuclear NMR ($CDCl_3$) and IR (as a neat oil between KBr plates) spectra were recorded. The reaction could be judged to be complete by loss of terminal allyl groups, *i.e.* no resonances at δ 5.80 and 4.90 ppm from the unsaturated bond (^{1}H NMR), no C=C stretching absorption at 1630 cm^{-1} (IR).

The spectroscopic data for compound (2) are reported in Table 2.2, where the phenyl resonance is set using data-processing software (WIN-NMR) to five protons for integration and the remaining signals are reported relative to this. The integration values in all data tables have been reported with an error of ± 10%. This value was determined as being the average difference between the actual and calculated integrations reported in Table 2.6 (page 48) for small, discrete compounds that have been fully characterized.

Table 2.2 Selected NMR and IR data for compound (2) $PhSi[(prSiMe_2)^{0.5}_1:Cl]_3$

	Ph	$ClSiCH_2$	CH_2	$Si\text{-}CH_3$	
^{1}H	7.5-7.3	1.48	0.90	0.37	δ ppm
	(=5) *5H*	(6.6±0.7) *6H*	(13.2±1.3) *12H*	(18.7±1.9) *18H*	
^{13}C	137.0, 133.9	23.4	17.6, 16.5	1.80	δ ppm
	128.9, 127.8				
^{1}H Integration (Experimental) *Calculated*					
^{29}Si	31.2 (Si-Cl)	-3.75 (Si-Ph)			δ ppm
IR cm^{-1}	3060 (CH), 2920 (CH), 1250 (Si-C), 470 (Si-Cl)				

The chlorosilyl compound so obtained was then slowly added to an allylmagnesium bromide solution in ether, to complete the formation of the first generation G(1)1B (3). After an aqueous work-up of this reaction mixture a colourless oil was isolated. Multinuclear NMR spectra were recorded as well as IR, mass spectroscopy and elemental analysis (Figures 2.4, 2.5, 2.6); data are given in Table 2.3.

Table 2.3 Spectroscopic and analytical data for compound (3) $PhSi[(prSiMe_2)^1_1:All]_3$

	Ph	=CH	$=CH_2$	CH_2	$Si-CH_3$
^1H	7.5~7.3	5.74	4.80	1.54, 1.38 0.84, 0.59	-0.06 δ ppm
	(=5) *5H*	(2.8±0.3) *3H*	(5.7±0.3) *6H*	(25±1) *24H*	(18.1±0.2) *18H*
^{13}C	137.9, 135.2 128.6, 127.6	134.0	112.5	23.6, 19.7 18.3, 17.3	-3.63 δ ppm
Integration (Experimental) *Calculated*					
	^{29}Si	0.75 ($Si-CH_3$)	-3.93 (Si-Ph)	δ ppm	
	IR[a]	3060, 2910, 1625, 1250 cm^{-1}			
	MS[b]	527 (M - 1), 513 (Base Peak), 488 (M - Ph)			
	Anal.[c]	Calcd for $C_{30}H_{56}Si_4$: C, 68.18; H, 10.61. Found: C, 67.37; H, 10.54.			

[a]Thin film between KBr plates [b]Chemical Ionisation [c] the carbon percentage may be low due to interference from silicon

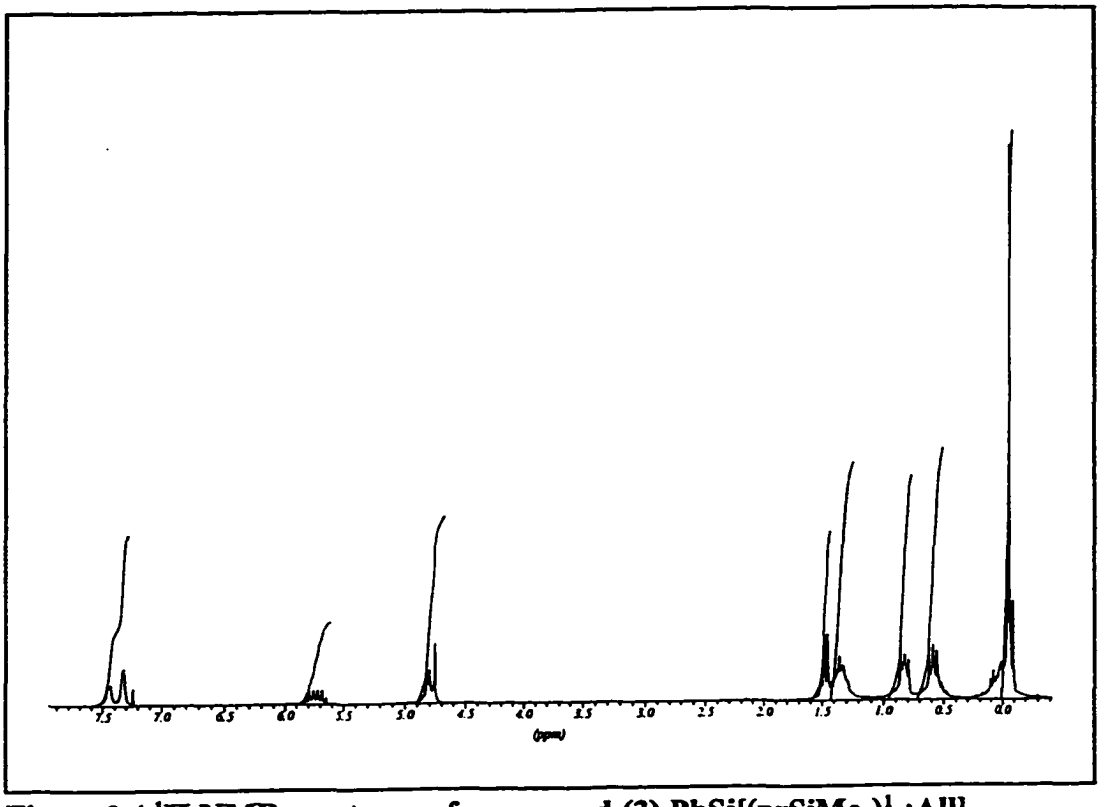


Figure 2.4 ^{1}H NMR spectrum of compound (3) $PhSi[(prSiMe_2)^1_1:All]_3$

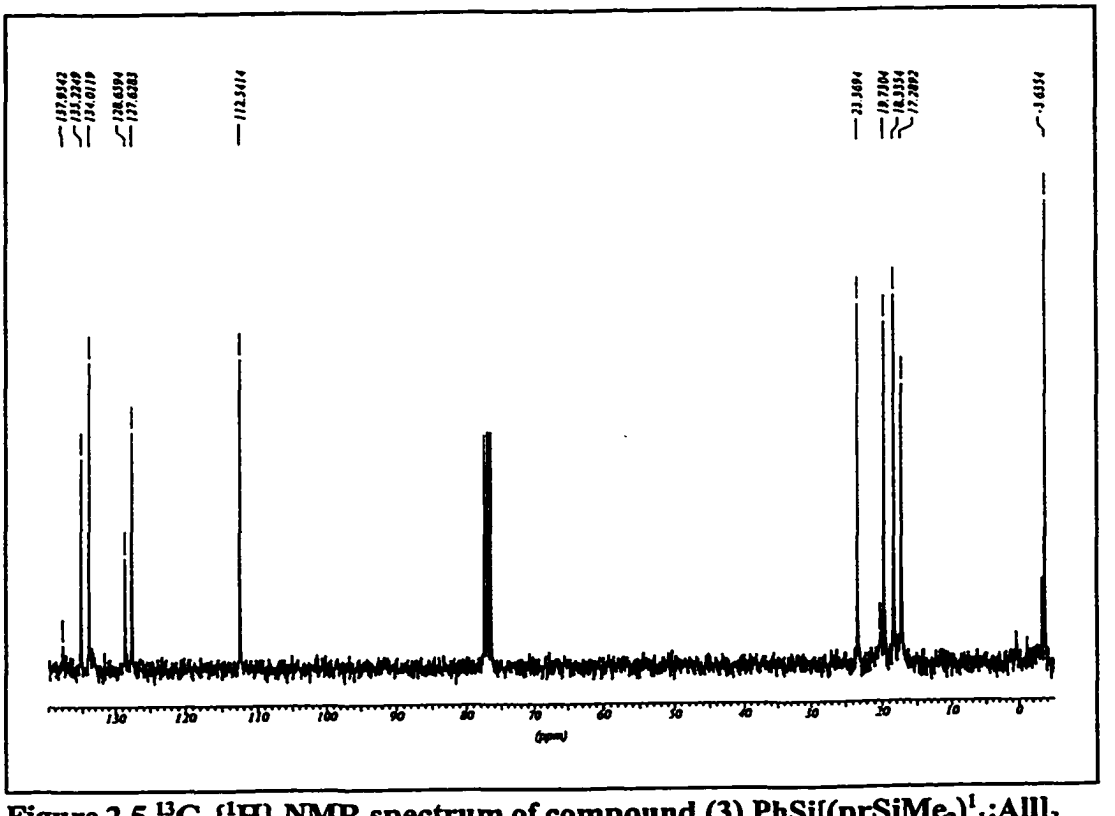


Figure 2.5 ^{13}C-{^{1}H} NMR spectrum of compound (3) $PhSi[(prSiMe_2)^1_1:All]_3$

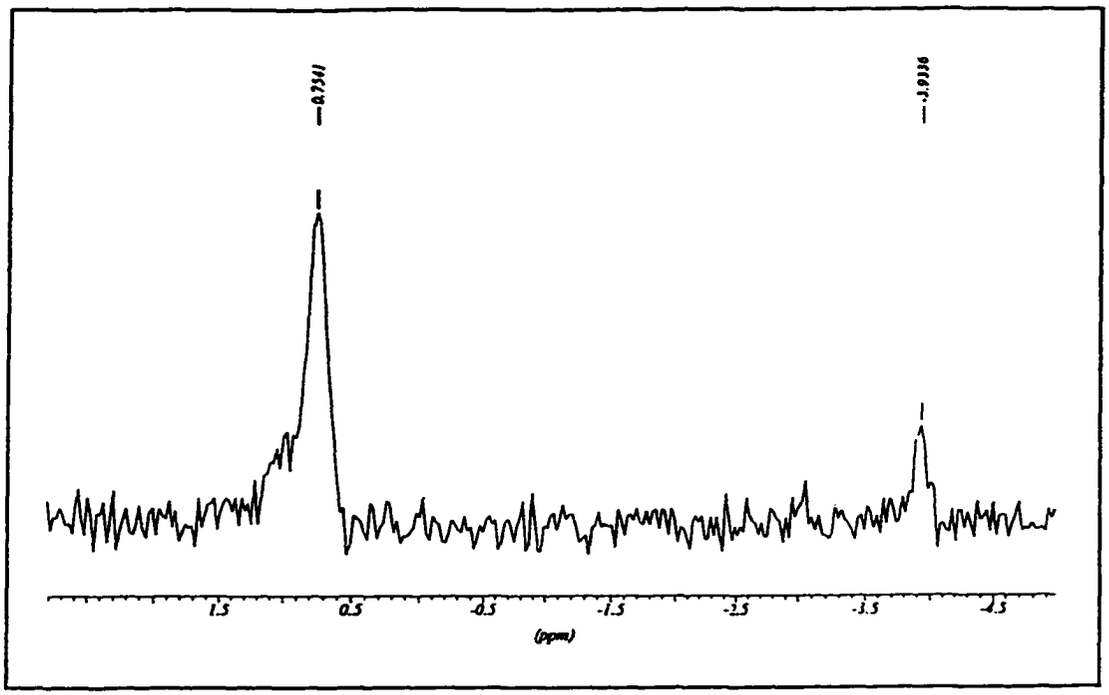


Figure 2.6 ^{29}Si-{^{1}H} NMR spectrum of compound (3) PhSi[(prSiMe$_2$)$^1_1$:All]$_3$

Data for this compound (3) is consistent with the formulation shown above. The allyl resonances integrate within experimental error to the five phenyl protons. Chemical ionisation mass spectroscopy shows a base peak at 513 amu which indicates the loss of a methyl group from the product; the peak at 488 amu corresponds to the loss of the phenyl ring. Elemental analysis of these compounds is problematic as silicon interferes with carbon analysis, this accounts for the lower than expected carbon percentage.

Hydrosilylation of compound (3) using an excess of chlorodimethylsilane ensured complete addition to the unsaturated bonds. Selected ^{1}H NMR chemical shifts and integration values (relative to the five phenyl ring protons) for this new intermediate compound (4) (Figure 2.7) are reported in Table 2.4. Further analyses of this air-sensitive intermediate, ^{13}C and ^{29}Si NMR resonance positions, are highlighted in Table 2.5. Other

chlorosilyl terminated compounds are also shown in Figure 2.7; selected NMR data for these intermediate derivatives G(N.5) are reported in Tables 2.4 and 2.5.

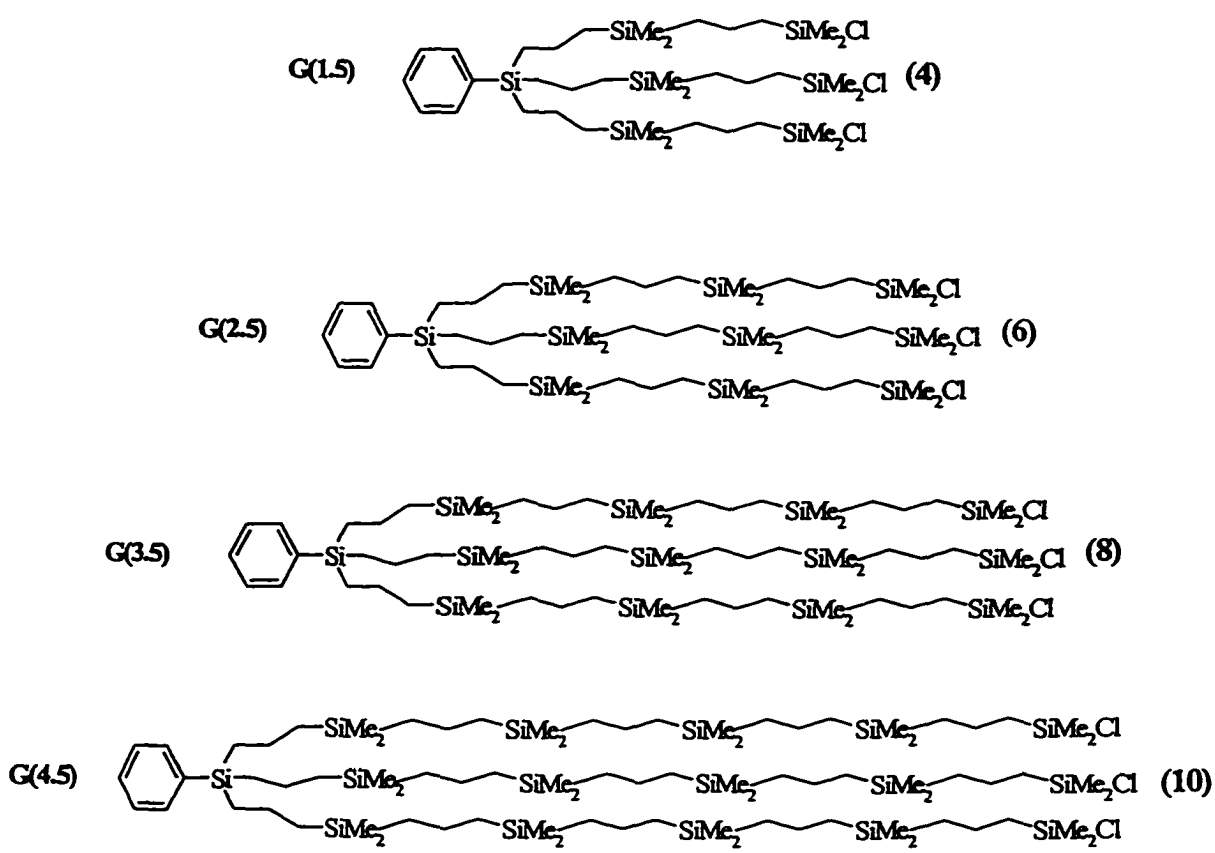


Figure 2.7 Structures of chlorosilyl compounds (4), (6), (8) and (10) $PhSi[(prSiMe_2)^N{}_1{:}Cl]_3$

Table 2.4 Selected ^{1}H NMR data for $PhSi[(prSiMe_2)^{N}_{1}:Cl]_3$ compounds

Compound		Ph	CH_2	$Si-CH_3Cl$	$Si-CH_3$
δ ppm	G(N)	7.5-7.3	1.3-0.55	0.38	δ ppm
(4)	(1.5)	(=5)*5H*	(40±4)*36H*	(19±2)*18H*	-0.07 (19±2)*18H*
(6)	(2.5)	(=5)*5H*	(57±6)*54H*	(19±2)*18H*	-0.06, -0.09 (36±4)*36H*
(8)	(3.5)	(=5)*5H*	(72±7)*72H*	(19±2)*18H*	-0.04, -0.08, -0.10 (60±6)*54H*
(10)	(4.5)	(=5)*5H*	(98±10)*90H*	(20±2) *18H*	-0.06, -0.07, -0.08, -0.10 (64±6)*72H*

Integration (Experimental) *Calculated*

Table 2.5 Selected ^{13}C and ^{29}Si NMR data for $PhSi[(prSiMe_2)^{N}_{1}:Cl]_3$ carbosilanes

		^{13}C δ ppm	^{29}Si δ ppm		
Compound	G(N)	$Si-CH_3$	Si-Cl	$Si-CH_3$	Si-Ph
(4)	(1.5)	1.80. -3.24	31.2	1.12	-3.95
(6)	(2.5)	1.80, -3.2, -3.23	31.3	1.12, 0.98	-3.98
(8)	(3.5)	1.80, -3.29, -3.35	31.2	1.12, 0.97	-3.98
(10)	(4.5)	1.80, -3.17, -3.24	31.2	1.10, 0.94	-4.0

Iteration of the alkenylation reaction produced allyl terminated compound (5) (Figure 2.8) which was also examined by multinuclear NMR spectroscopy (Table 2.6 and 2.7), mass spectroscopy (Table 2.8) and elemental analysis (Table 2.9). Subsequent compounds with allyl peripheries are also shown in Figure 2.8 and selected analytical results are reported in Tables 2.6-2.9.

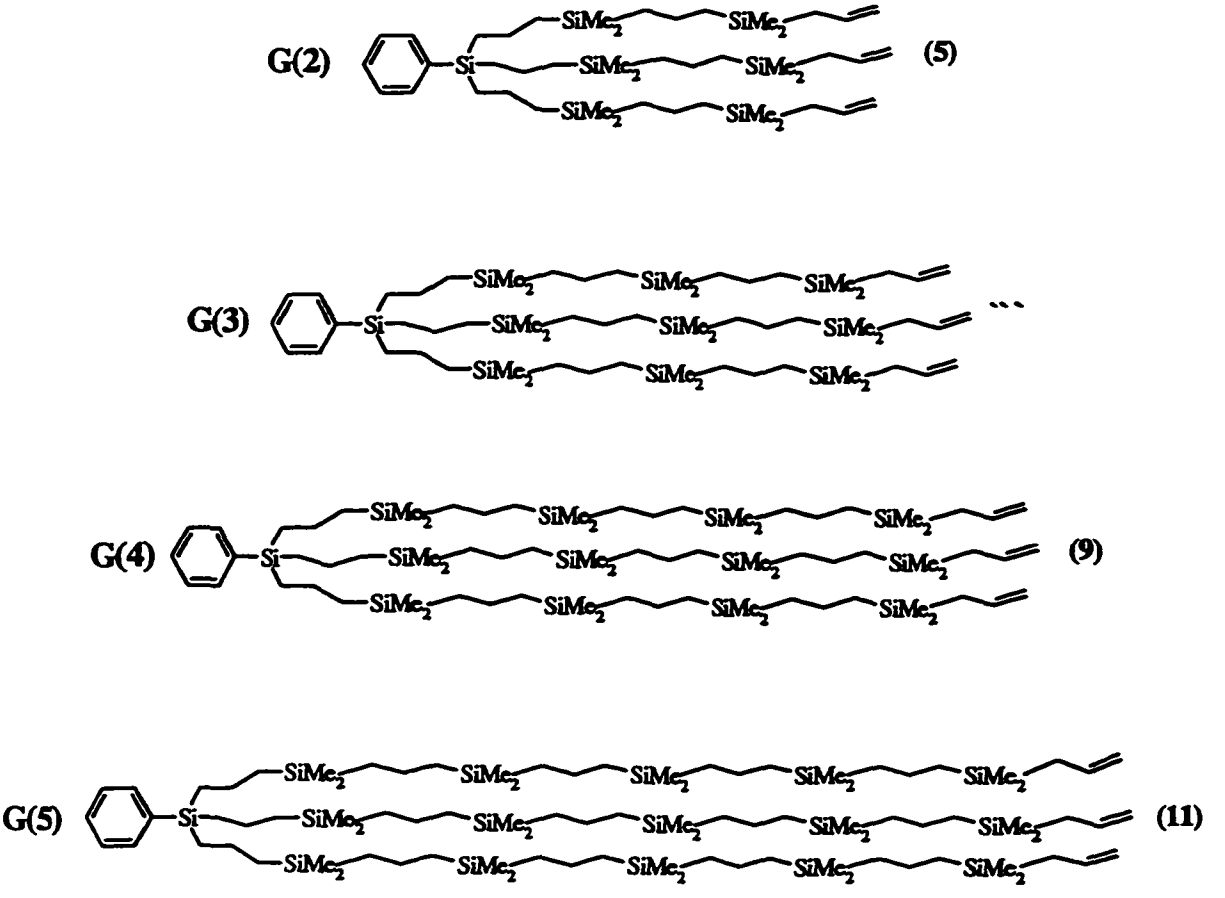


Figure 2.8 Structures of carbosilane compounds (5), (7), (9) and (11) $PhSi[(prSiMe_2)^N_1:All]_3$

Table 2.6 ^{1}H NMR data for allyl compounds (5), (7), (9) and (11)

$PhSi[(prSiMe_2)^{N}_{1}:All]_3$

		Ph	-CH=	$=CH_2$	CH_2	Si-CH_3
δ ppm		7.5-7.3	5.74	4.80	1.5-0.5	
Compound	G(N)					
(5)	(2)	(=5)*5H*	(3.0±3)*3H*	(6.1±6)*6H*	(42±4)*42H*	-0.04 -0.08(36±4)*36H*
(7)	(3)	(=5)*5H*	(3.3±3)*3H*	(5.6±6)*6H*	(92±9)*60H*	-0.04, -0.08, -0.10(75±8)*54H*
(9)	(4)	(=5)*5H*	(3.2±3)*3H*	(6.5±6)*6H*	(80±8)*78H*	0.06, -0.03, -0.08, -0.10(80±8)*72H*
(11)	(5)	(=5)*5H*	(3.0±3)*3H*	(6.4±6)*6H*	(109±11)*96H*	0.06, -0.03, -0.08, -0.09(106±11)*90H*

Integration (Experimental) *Calculated*

Table 2.7 ^{13}C and ^{29}Si spectroscopic data for compounds (5), (7), (9) and (11)

$PhSi[(prSiMe_2)^{N}_{1}:All]_3$

Compound	G(N)	^{13}C δ ppm	^{29}Si δ ppm
(5)	(2)	-3.2, -3.4	0.98, 0.78, -3.95
(7)	(3)	-3.2, -3.6	0.98, 0.78, -3.95
(9)	(4)	-3.2, -3.6	0.98, 0.78, -3.95
(11)	(5)	-3.2, -3.6	0.98, 0.78, -3.95

The data collected for these compounds clearly shows how the core phenyl ring hydrogens can be used as a basis for 'end-group' counting. This is further aided in this series by the methyl resonances at each branch point. All compounds show similar NMR patterns for the terminal allyl groups as in Figure 2.9. Hierarchical methyl signals are seen upon increasing generation number as a major distinction between successive compounds.

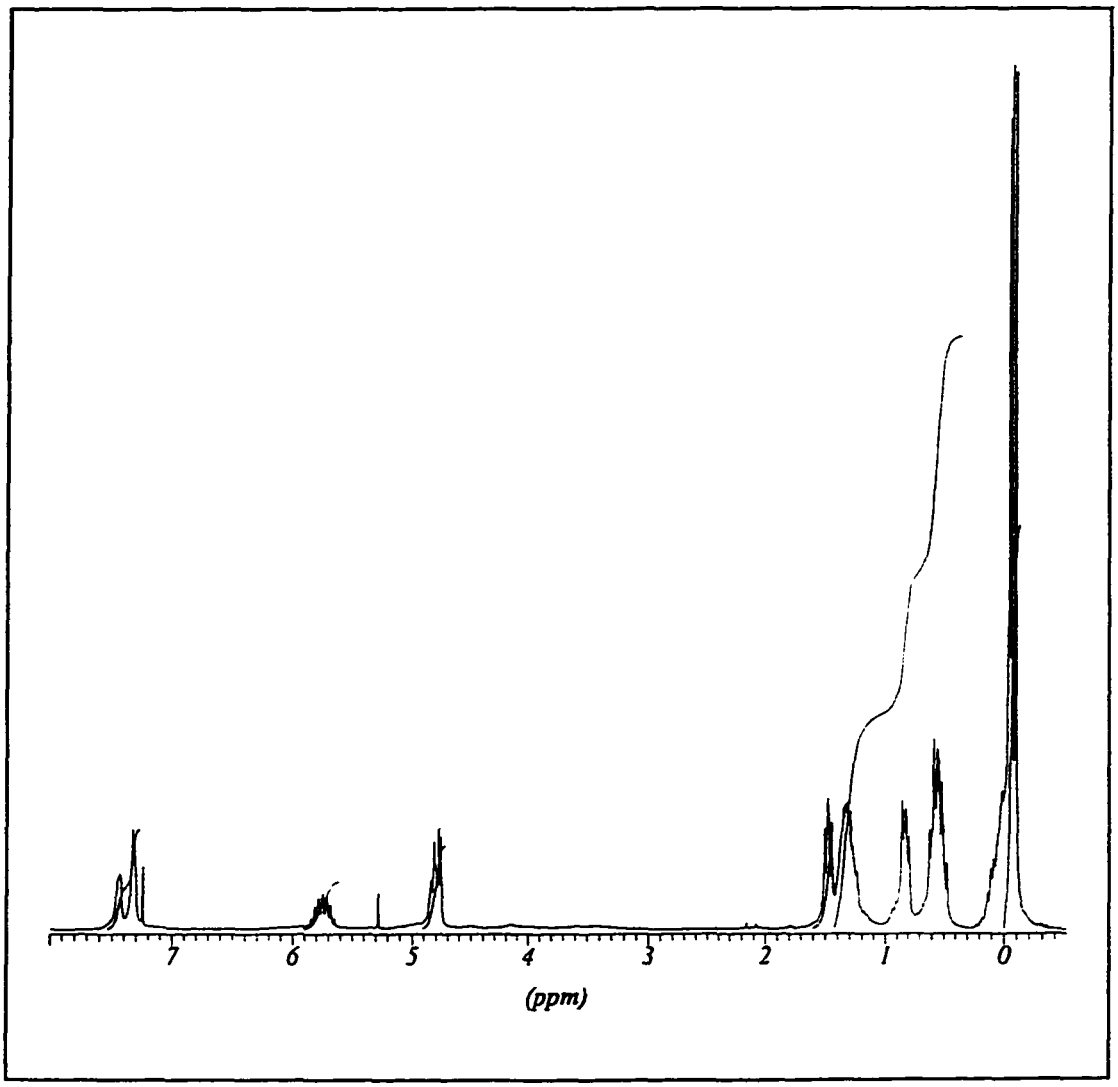


Figure 2.9 ^{1}H NMR spectra of compound (7) PhSi[(prSiMe$_2$)$^2_1$:All]$_3$

The ^{13}C NMR spectra were also recorded, there are clearly distinct resonances for the first and second generations. At the third generation collapse of these resonances is seen, with the exterior signal appearing further downfield from the two interior sites. For the ^{29}Si NMR spectra similar patterns arise; for the first two generations distinct resonances are seen at δ 0.97 and 0.76 ppm relative to TMS. At the third generation the two interior signals collapse into one peak with the exterior signal still appearing at δ 0.96 ppm, the trifurcate system has the phenyl-silicon signal permanently at δ -3.95 ppm.[65] Use of an NMR active heteroatom at the branch site within a dendrimer framework has been seen previously. For example, using ^{31}P NMR spectroscopy Majoral *et al*[14f] showed that they could determine partial structures of the materials generated as shown in Figure 2.10.

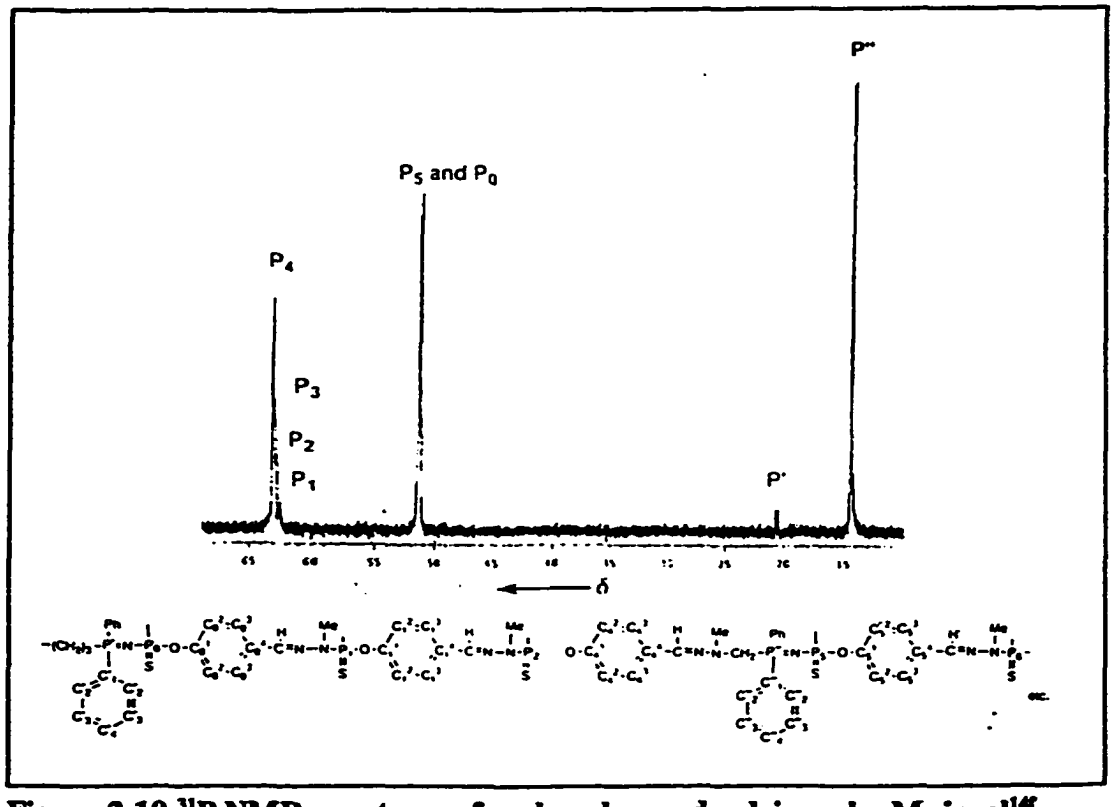


Figure 2.10 ^{31}P NMR spectrum of a phosphorus dendrimer by Majoral[14f]

Since these materials are relatively low in molecular mass, spectroscopic data was obtained on all five generations using either CI/methane or EI, Table 2.8.

Table 2.8 Selected mass spectral data for trifurcate linear carbosilanes $PhSi[(prSiMe_2)^N{}_1:All]_3$

Compound	G(N)	Calculated	Found
(3)	(1)	528	(CI, Methane): **527** (M^+ - 1), 513, 488
(5)	(2)	828	(CI, Methane): **827** (M^+ - 1), 812, 771, 756
(7)	(3)	1130	(CI, Methane): **1130** (M^+), 1088, 1052, 790
(9)	(4)	1431	(EI): **1430** (M^+ - 1), 1415, 1372, 1354
(11)	(5)	1730	(EI): **1728** (M^+ - 2), 1611, 1538, 1464

Clearly noticeable in the low generation compounds is an intact molecular ion which shows loss of allyl, methyl or phenyl units; at the fifth generation the molecular ion is only weakly detected whilst loss of larger units (mass of ≈ 100 amu), such as allyl dimethylsilyl groups, is more readily observed.

Elemental analysis for dendrimers is problematic since the higher generations are simply a repeat of identical structural units; there comes a point where the percentage present of each element converges to a plateau, seen in Table 2.9. The problem of converging ratios will be seen later, when the limits for unequivocal analysis is reached far more rapidly with increasing branch point topologies.

Table 2.9 Elemental analyses for allyl terminated trifurcate carbosilanes

$PhSi[(prSiMe_2)^N{}_1:All]_3$

	G(N)	Composition	% Calcd.	% Found
(5)	G(2)	$C_{45}H_{92}Si_7$:	C, 65.22; H, 11.11	C, 65.17; H, 11.04
(7)	G(3)[a]	$C_{60}H_{128}Si_{10}$:	C, 63.83; H, 11.35	C, 62.85; H, 11.24
(9)	G(4)	$C_{75}H_{164}Si_{13}$:	C, 63.02; H, 11.54	C, 62.94; H, 11.63
(11)	G(5)	$C_{90}H_{200}Si_{16}$:	C, 62.42; H, 11.63	C, 62.16; H, 11.59

[a]Repeated attempts for analysis of this compound failed to give satisfactory carbon results.

GPC chromatograms were recorded in chloroform solution, Table 2.10, to observe the polydispersity of these compounds. Since adequate mass spectra and elemental analysis were obtained the masses found were used in the plots of retention time *vs* the logarithm of the nominal molecular mass (Figure 2.11).

Table 2.10 GPC data for linear trifurcate carbosilanes in $CHCl_3$ solution

$PhSi[(prSiMe_2)^N{}_1:All]_3$

Compound	G(N)	Mw	$\log_{10}$Mw	Time (min)	Peak Width[a]
(3)	G(1)	528	2.723	11.50	± 0.12
(5)	G(2)	828	2.918	11.30	± 0.12
(7)	G(3)	1128	3.052	11.10	± 0.12
(9)	G(4)	1428	3.154	11.00	± 0.12
(11)	G(5)	1728	3.237	10.85	± 0.12

[a] measured as the peak width at half height in minutes

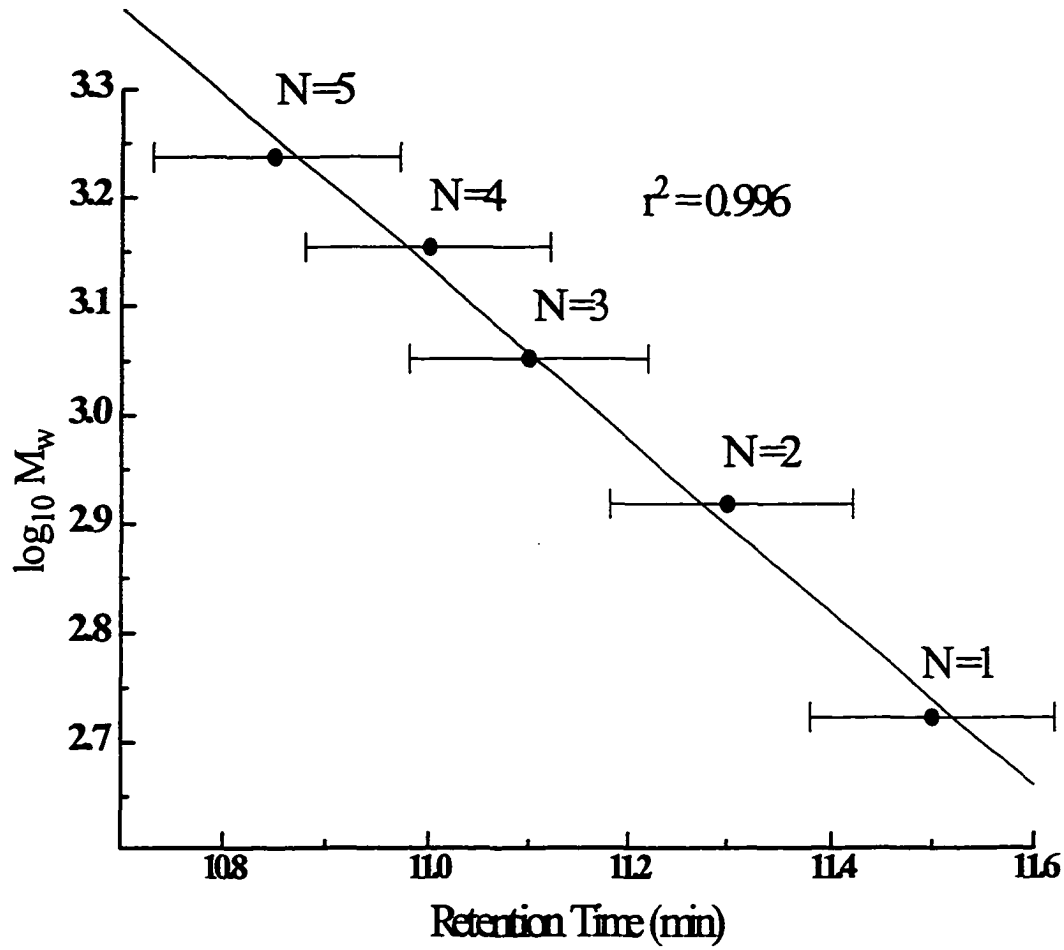
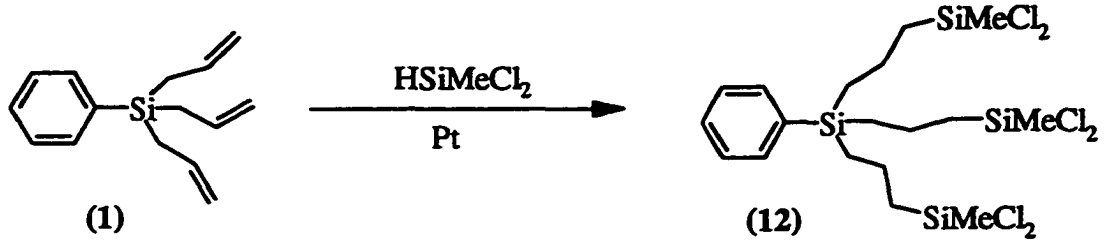


Figure 2.11 GPC data for trifurcate carbosilanes: $Ph[(prSiMe_2)^N{}_1:All]_3$

This plot is a calibration curve for this series of carbosilane dendrimers, with an r^2 of 0.966, which may be useful for future analysis of other linear trifurcate carbosilane systems synthesised. More importantly this plot is linear for the carbosilane series, which for low mass polystyrene standards is not the case. A similar plot for polystyrene standards is not linear because in solution these PS standards have been described as wormlike molecules.[59]

2.3 Two-Directional Branching (2B)

This series of compounds is analogous to those synthesised by Roovers *et al*[27] and Kim *et al*[31] where dichloromethylsilane has been used in the hydrosilylation reaction. This produces branch points in two directions, 2B, rather than in a linear direction; Scheme 2.3 shows the initial reaction of phenyl triallylsilane with dichloromethylsilane.



Scheme 2.3 Synthesis of chlorosilyl intermediate (12) PhSi[(prSiMe)$^{6,5}_{2}$:Cl]$_3$

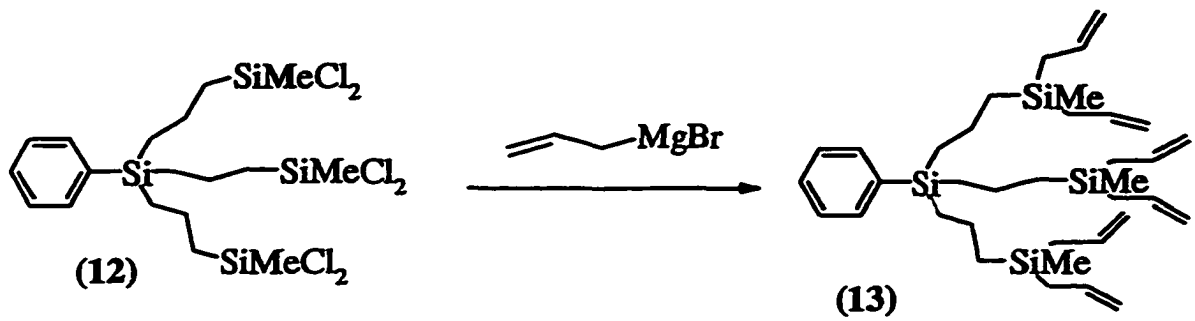
The product (12) from this reaction was isolated and multinuclear NMR and IR spectra were recorded to ensure complete addition of silane to the unsaturated bonds. The ^{1}H NMR shows the phenyl region at δ 7.5-7.3 ppm, calibrated to five protons as before, three distinct methylene regions between δ 1.60-0.95 ppm and a single Si-C*H*$_3$ peak at δ 0.73 ppm, which integrate within experimental error to the calculated ratio of 5:6:6:6:9, Table 2.11. The resonance assigned as the Si(C*H*$_3$)Cl$_2$ protons lies further downfield than those with only one peripheral chlorine atom, since the electronegative chlorine atoms deshield these protons.

Table 2.11 Selected spectral data for compound (12) $PhSi[(prSiMe)^{0.5}_2:Cl]_3$

	Ph	CH_2	Si-CH_3
^1H	7.5-7.3	1.60, 1.20, 0.95	0.73 δ ppm
	(=5) *5H*	(18±1.8) *18H*	(9±0.9) *9H*
^{13}C	136.0, 133.9	25.7, 17.2, 15.7	5.41 δ ppm
	129.2, 127.9		
Integration (Experimental) *Calculated*			
^{29}Si δ ppm	32.1 (Si-Cl)	-3.59 (Ph-Si)	
IR cm^{-1}	3060, 2920, 1260, 535, 470		

The ^{13}C and ^{29}Si NMR spectra (Appendix A) also show indicative resonances; again the ring carbons are observed and the silicon methyl resonance is observed at δ 5.41 ppm, downfield from TMS due to the presence of two chlorine atoms. The Ph-*Si* signal is seen at δ -3.6 ppm similar to the linear G(0.5)1B analogue, and no noticeable difference is seen for the dichloromethylsilyl signal at δ 32.1 ppm in the ^{29}Si NMR spectrum.[65]

This chlorosilyl product is reacted with an excess of allylmagnesium bromide solution in ether, Scheme 2.4, and the excess Grignard solution was quenched with ammonium chloride solution. After an extraction and removal of all residual volatile materials an oil remained in 73% yield (13). This was again analysed by multinuclear NMR spectroscopy (Figures 2.12-2.14), IR, mass spectroscopy and elemental analysis, Table 2.12.



Scheme 2.4 Synthesis of G(1)2B two branch point dendrimer from $PhSiAll_3$

Table 2.12 Selected spectral data for compound (13) $PhSi[(prSiMe)^1_2:All]_3$

	Ph	=CH	$=CH_2$	γCH_2	CH_2	$Si-CH_3$
^1H	7.5~7.3	5.73	4.79	1.52	1.38-0.63	-0.054
	(=5)	(5.6±0.2)	(11.5±0.3)	(11.9±0.3)	(17.3±0.4)	(8.9±0.2)
	5H	*6H*	*12H*	*12H*	*18H*	*9H*
^{13}C	137.6, 133.9	134.7	113.0	21.7	18.2, 17.9	-5.8
	128.7, 127.6				17.3	

Integration (Experimental) *Calculated*

^{29}Si	0.24 ($Si-CH_3$) -3.94 (Si-Ph)
[a]IR cm^{-1}	3060, 2910, 1625, 1250, 590
[b]MS	607 (M^+ + 1), 591 (M^+ - Me), 564 (M^+ - allyl), 529 (M^+ - Ph)

Anal. Calcd for $C_{35}H_{62}Si_4$: C, 71.29; H, 10.23. Found: C, 70.82; H, 9.85

[a]Thin film between KBr plates [b]Chemical Ionisation (Methane)

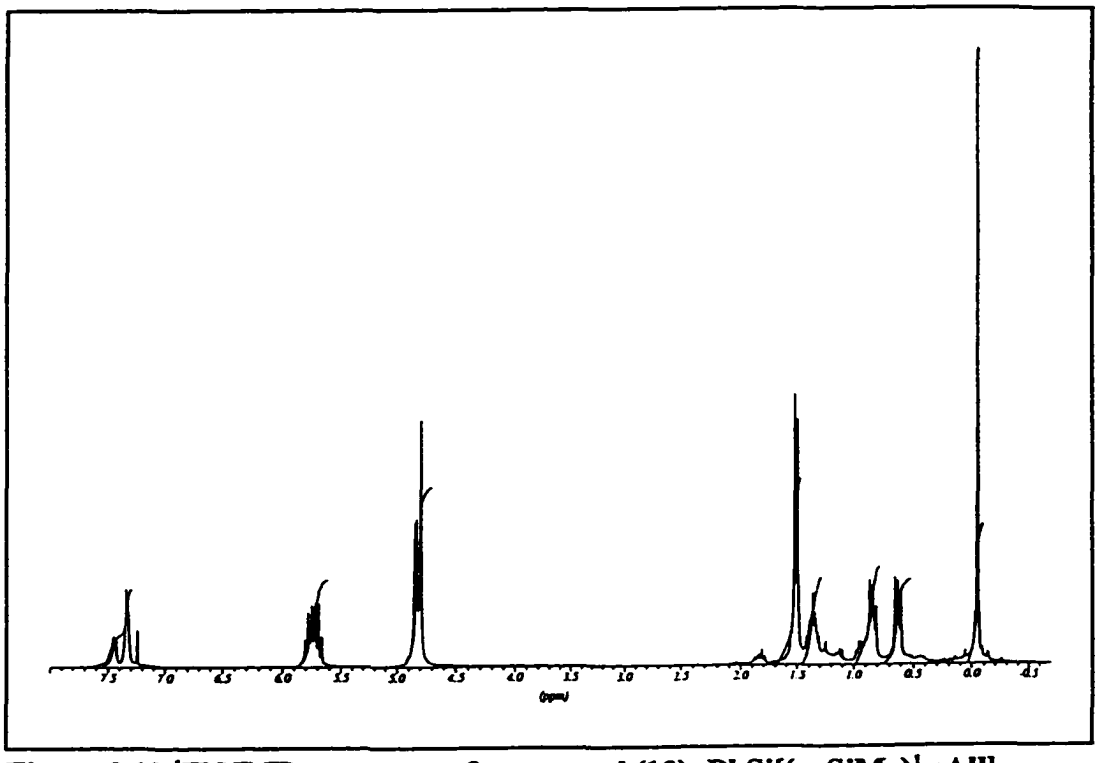


Figure 2.12 ^{1}H NMR spectrum of compound (13) $PhSi[(prSiMe)^{1}_{2}:All]_{3}$

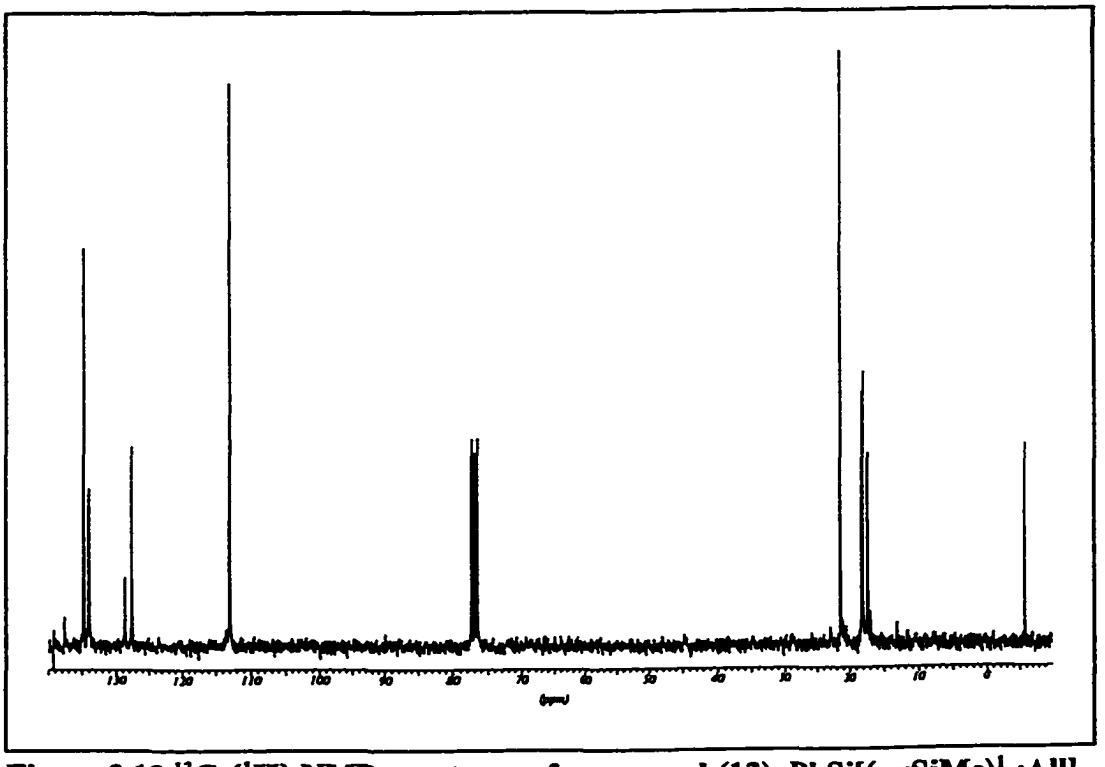


Figure 2.13 ^{13}C-{^{1}H} NMR spectrum of compound (13) $PhSi[(prSiMe)^{1}_{2}:All]_{3}$

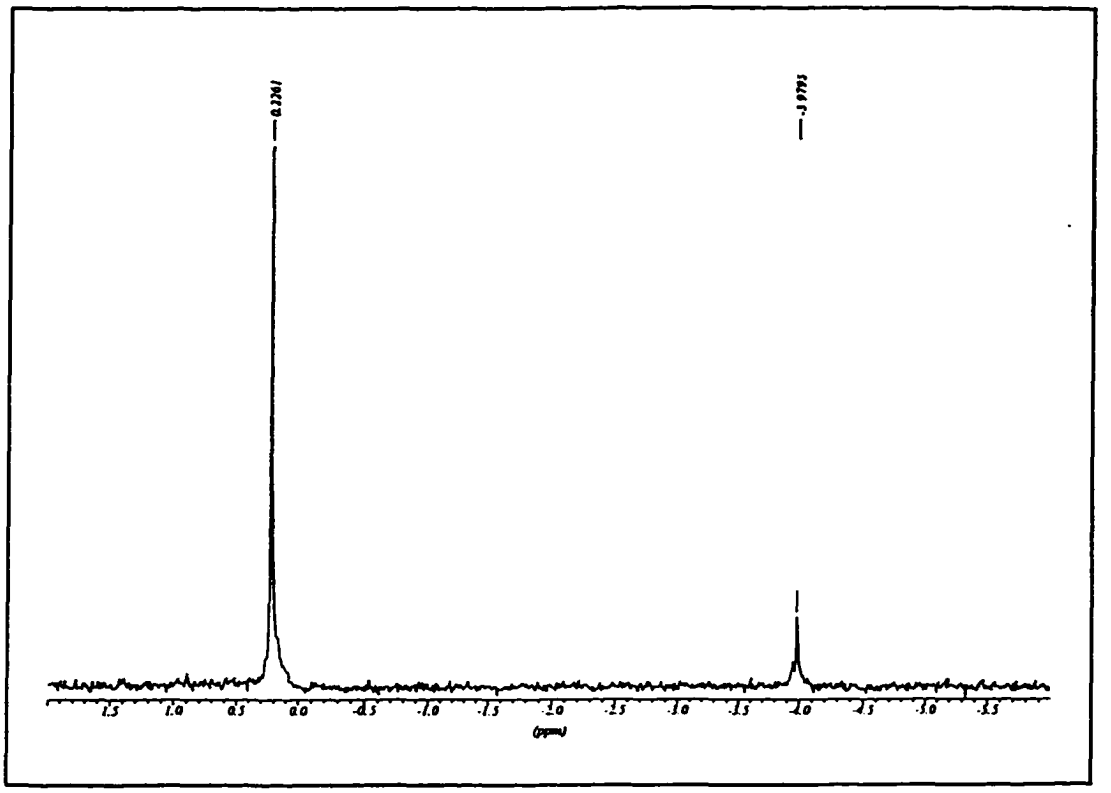
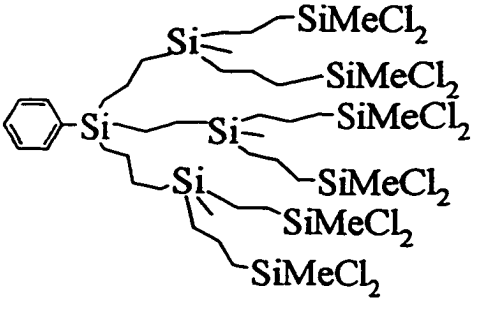
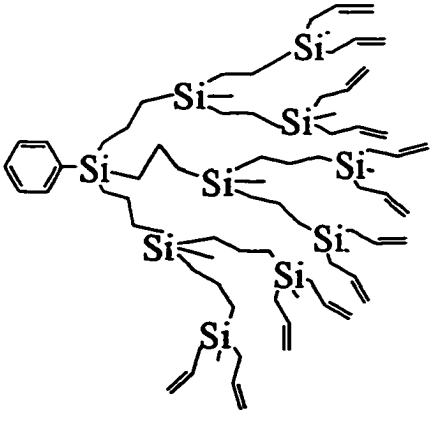


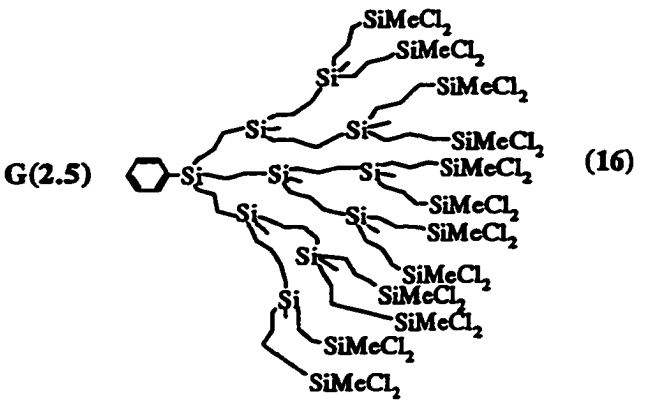
Figure 2.14 ^{29}Si-{^{1}H} NMR spectrum of compound (13) PhSi[(prSiMe)$^{1}_{2}$:All]$_3$

From the NMR spectra (Figures 2.12-14) compound **(13)** shows very distinctive resonances in each type of nucleus. The proton NMR integrates within experimental error, phenyl protons relative to peripheral signals, to the calculated ratio. The ^{13}C NMR exhibits a simple spectrum for the phenyl ring, allylic carbons and three single peaks for the methylenes. The silicon methyl resonance is observed at δ -5.7 ppm which is further upfield than the linear derivatives. Also in the silicon NMR the *Si*-Me resonance is seen further upfield at δ 0.26 ppm, with the Ph-*Si* peak again at δ -4.0 ppm. Both mass spectral and elemental analysis are consistent with the formulation expected for this compound. The mass spectrum shows loss of methyl, allyl and phenyl groups as 15, 41 and 77 amu respectively.

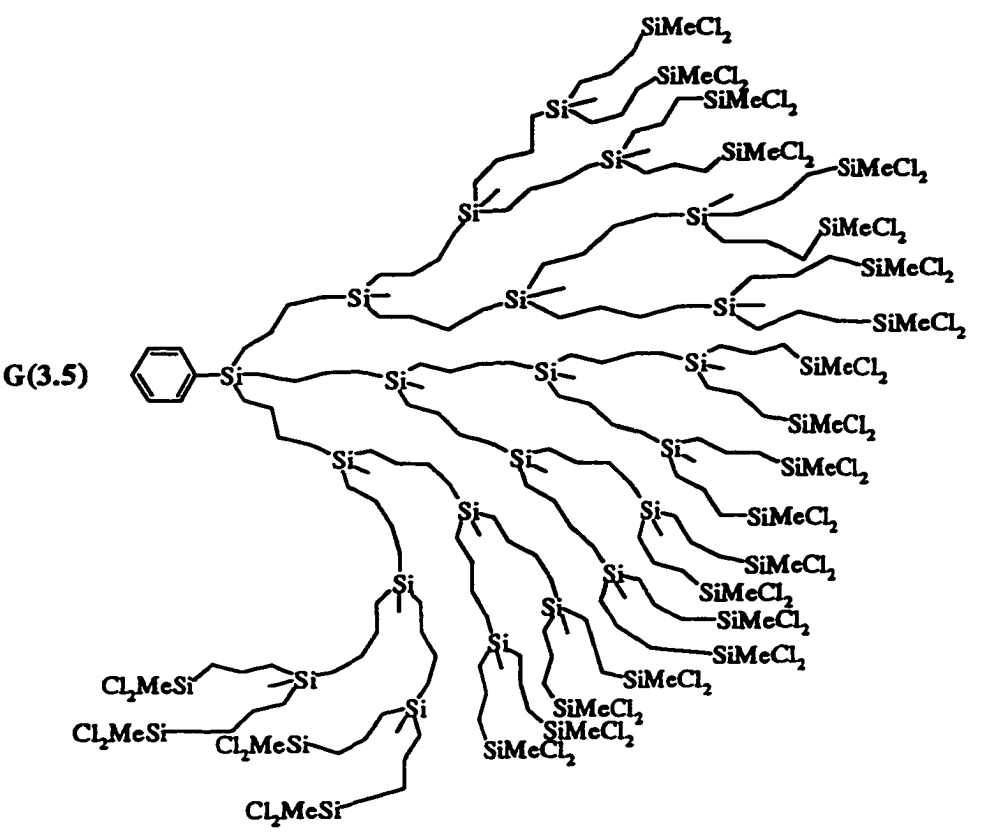
Repetition of these reactions, hydrosilylation and the subsequent alkenylation, is performed; initially on this first generation molecule to give a chlorosilyl intermediate, G(1.5) **(14)**, followed by the allyl terminated compound, G(2) **(15)**, shown below. Further iteration produces the G(N.5) chlorosilyl intermediates **(16)** and **(18)** seen on the following page, and also the air-stable allyl dendrimers, G(N) **(17)** and **(19)**, whose structures are illustrated on page 66. Each compound is isolated and NMR spectra were recorded to ensure that complete reactions had occurred at each stage. Selected spectroscopic data for the dichloromethylsilyl derivatives are shown in Table 2.13.

G(1.5)  **(14)**

G(2)  **(15)**



(16)



(18)

Table 2.13 Selected NMR data for PhSi[(prSiMe)$^{N}_{2}$:Cl]$_3$ carbosilane compounds (14), (16) and (18)

^{1}H	Ph	CH_2	Si-CH_3Cl_2	Si-CH_3
δ ppm G(N)	7.5-7.3	1.60-0.95	0.75	
(14) G(1.5)	(=5) *5H*	(54±5) *54H*	(18±2) *18H*	-0.60 (9±0.9) *9H*
^{13}C δ ppm			5.44	-5.17
(16) G(2.5)	(=5) *5H*	(198±20)	(36±4)	0.10--0.21 (27±3)
		126H	*36H*	*27H*
^{13}C δ ppm			5.44	-5.01, -5.13
(18) G(3.5)	(=5) *5H*	(290±30)	(72±7)	0.10--0.21 (63±6)
		270H	*72H*	*63H*
^{13}C δ ppm			5.44	-5.01, -5.13

Integration (Experimental) *Calculated*

^{29}Si δ ppm	G(N)	Si-Cl	Si-CH_3	Si-Ph
(14)	G(1.5)	32.2	1.51	-3.98
(16)	G(2.5)	32.2	1.51	-3.98
(18)	G(3.5)	32.2	1.51, 0.98	-3.98

Chemically distinct Si-C*H*$_3$ resonances are observed in these compounds and these proton integration values increase relative to the five phenyl protons as the shells grow. The chemical shifts of the interior methyl signals move upfield in the ^{1}H NMR and downfield in both ^{13}C and ^{29}Si NMR spectra with increasing G(N), analogous to similar observations in the linear trifurcate carbosilanes. The aliphatic integration for the larger generation compounds, **(16)** and **(18)**, are above the calculated values. This is possibly as a result of solvent

(hexanes) inclusion within the structure, the hexanes may have become trapped in these branched molecules and is difficult to remove. This could be caused by chain entanglement which prevents the solvent from escaping, even under high vacuum. Meijer *et al*[66] have successfully encapsulated probes within the interior of several amine based dendrimers; this was achieved by careful control of pH which they attributed to the dendrimer chains contracting (entangling) around the probe.

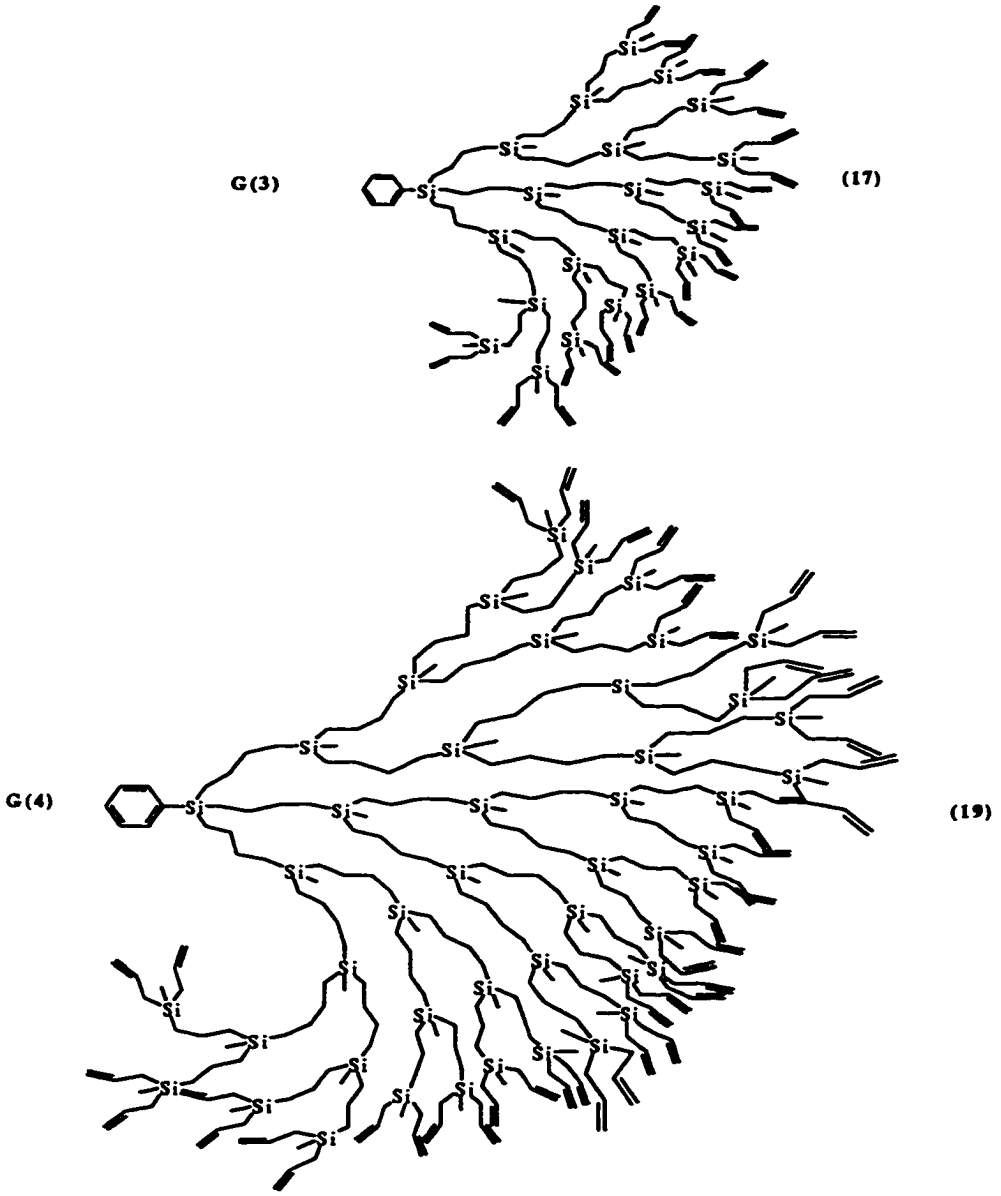


Table 2.14 Selected NMR data for PhSi[(prSiMe)$^{N}_{2}$:All]$_3$ carbosilane dendrimers (15), (17) and (19)

^{1}H		Ph	=CH	Si-CH$_3$
δ ppm	G(N)	7.5-7.3	5.75	
(15)	G(2)	(=5) *5H*	(11±1) *12H*	-0.04 (17.8±2) *18H* -0.12, -0.14 (7.8±8) *9H*
^{13}C δ ppm				-5.0, -5.8
(17)	G(3)	(=5) *5H*	(29±3) *24H*	-0.03 (33±3) *36H*, -0.06 (28±3) *18H*, -0.09 (12±1.2) *9H*
^{13}C δ ppm				-4.98, -5.33, -5.74
(19)	G(4)	(=5) *5H*	(41±4) *48H*	-0.03 (65±7)*72H*, -0.06 (59±6) *36H*, -0.09 (27±3) *27H*
^{13}C δ ppm				-4.98, -5.33, -5.74

Integration (Experimental) *Calculated*

	^{29}Si δ ppm	G(N)	Internal	Si-CH$_3$	Si-Ph
(15)		G(2)	1.01, 0.93	0.24	-4.06
(17)		G(3)	0.99, 0.73	0.26	-3.98
(19)		G(4)	0.99, 0.73	0.26	-3.98

A full proton NMR spectrum of compound (15) is shown in Figure 2.15, which gives integration consistent with the formulation proposed. The methylsilyl region shows three peaks (two separate internal methyls at δ -0.12 and -0.14 ppm), integration ratio of 2:1, which is consistent with the data found in both ^{13}C NMR and ^{29}Si NMR spectra. The carbon NMR also showed two resonances for the interior group, possibly due to the steric influence associated with adding the extra shell onto the periphery. The same observation is noted in the silicon spectra; two separate resonances for the interior methylsilyl group and one single peak for the peripheral silicon.

An enlargement of the methyl region for compound (17) (Figure 2.15 inset) shows the interior groups as chemically distinct for the separate shells; ^{1}H integration suggests these methylsilyls are generationally distinct. Similarly the ^{13}C and ^{29}Si NMR spectra show the same phenomena (Appendix A), it appears that each successive shell is chemically independent from the others. With the fourth generation, **$PhSi[(prSiMe)^{4}_{2}:All]_{3}$ (19)**, this layer structure collapses and overlap of the two interior peaks is observed (Figure 2.15 inset). The possibility of solvent (hexanes) inclusion is again noted since the aliphatic resonances integrate to larger values than calculated.

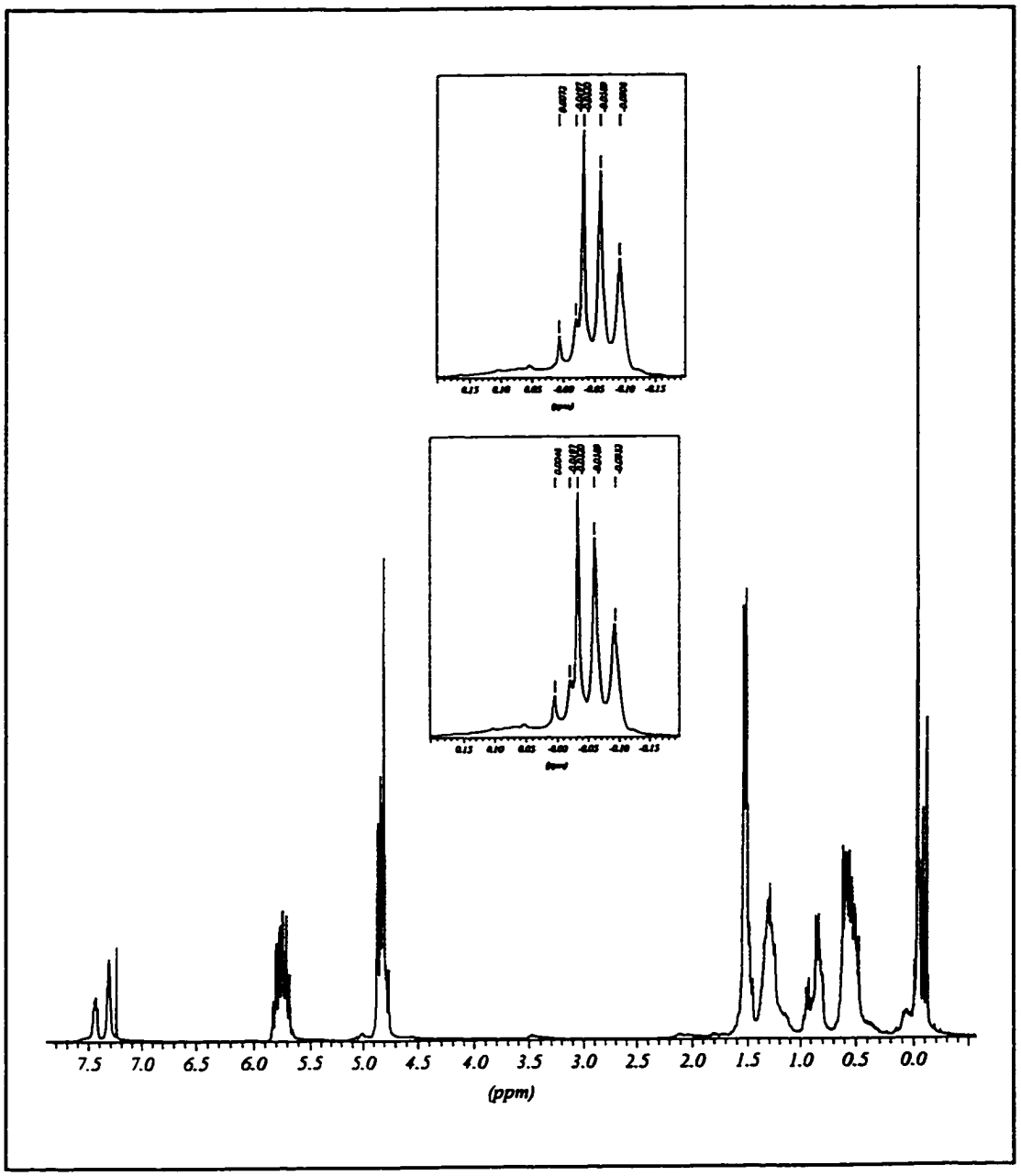


Figure 2.15 ^{1}H NMR spectra of PhSi[(prSiMe)$^{N}_{2}$:All]$_3$ compounds N =2 (15) full scale; N =3 (17) lower inset and N =4 (19) upper inset

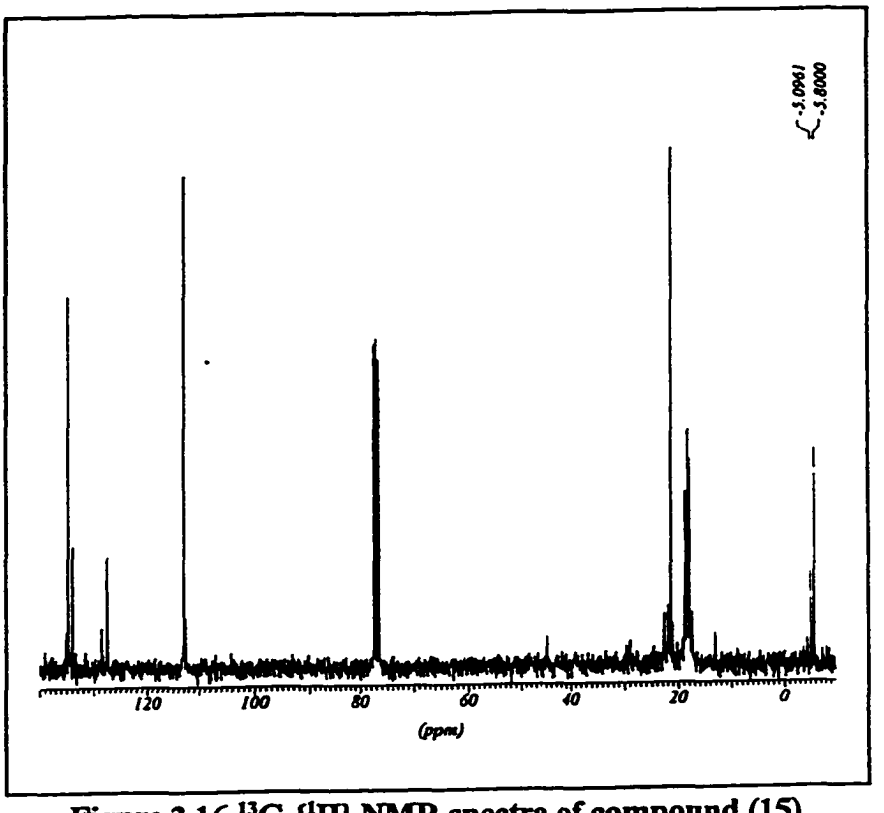


Figure 2.16 ^{13}C-{^{1}H} NMR spectra of compound (15) PhSi[(prSiMe)$^{2}_{2}$:All]$_3$

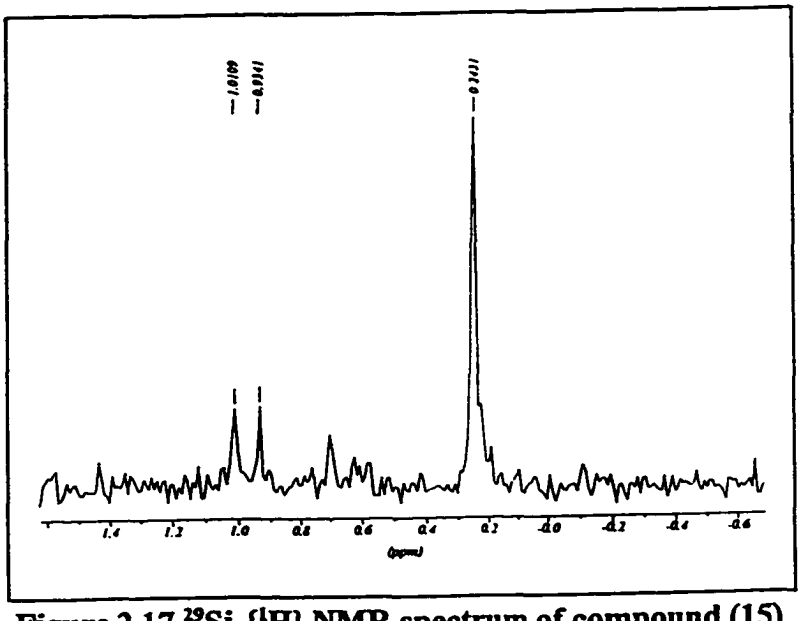


Figure 2.17 ^{29}Si-{^{1}H} NMR spectrum of compound (15) PhSi[(prSiMe)$^{2}_{2}$:All]$_3$

These air-stable allyl compounds have also been analysed by GPC in chloroform solution. The chromatograms showed the polydispersity of these materials to be very narrow as judged by the peak width at half height. A plot of the retention time *vs* $\log_{10}M_w$ for this series of compounds was a straight line, $r^2 = 0.980$. This linearity is an important aspect, it implies that the same extent of shell closure is found for all generations; they are discrete molecules that elute distinctly from each other, Figure 2.17.

Table 2.15 GPC data for $PhSi[(prSiMe)^N_2:All]_3$ dendrimers in $CHCl_3$ solution

Compound	$PhSiAll_3$ 2B G(N)	M_w	$\log_{10}M_w$	Time (min)	Peak Width[a]
(13)	G(1)	606	2.782	11.50	± 0.13
(15)	G(2)	1362	3.134	11.25	± 0.16
(17)	G(3)	2874	3.458	10.70	± 0.17
(19)	G(4)	5898	3.771	10.10	± 0.22

[a] measured as the peak width at half height in minutes

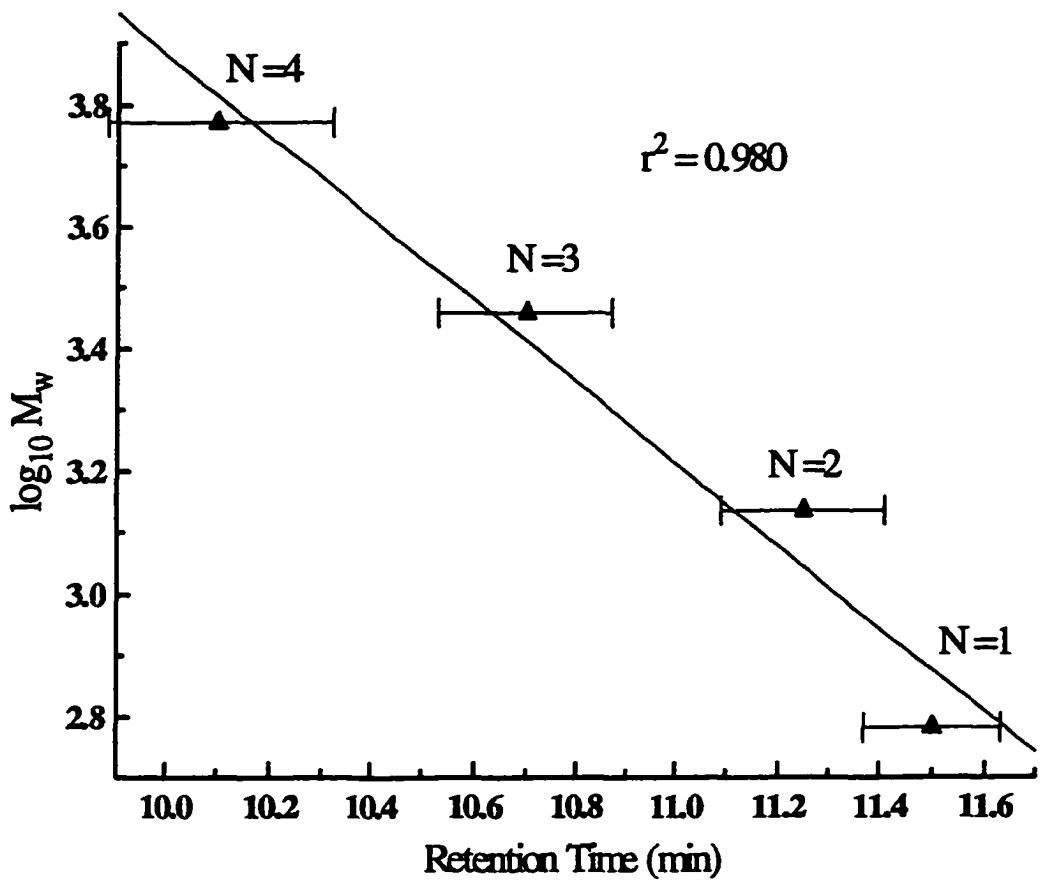
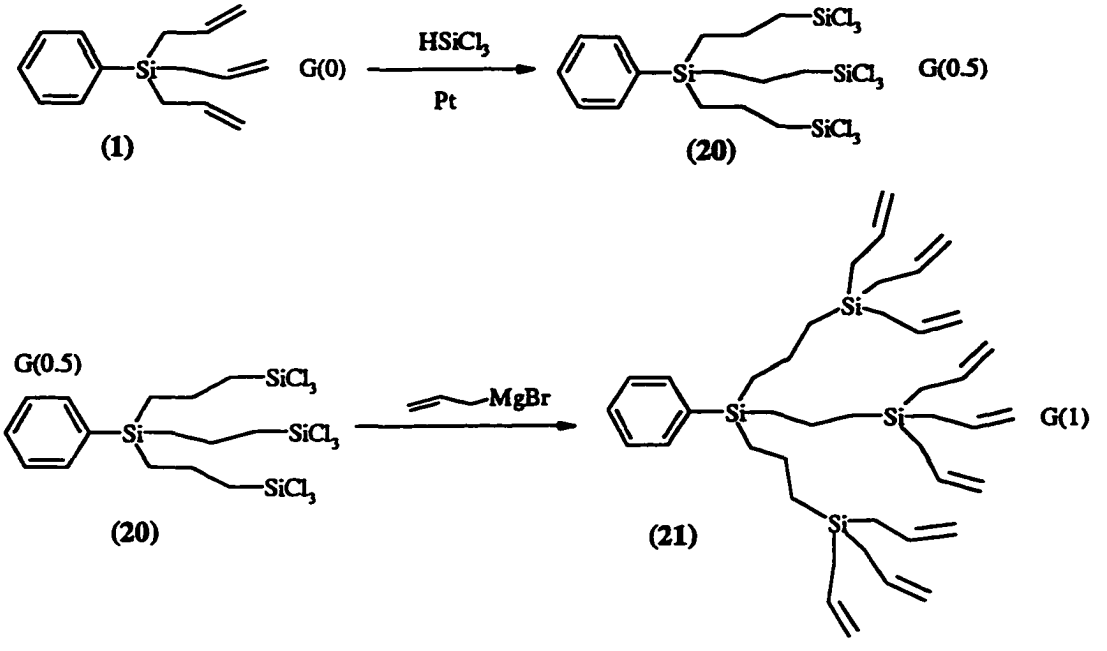


Figure 2.18 Plot of retention time *vs* $\log_{10}M_w$ for $Ph[(prSiMe)^N{}_2:All]_3$ dendrimers

2.4 Three-Directional Branching (3B)

The synthesis of trifurcate dendrimers with three branching points per silicon atom is shown in Scheme 2.5. These compounds do not possess methyl groups attached to silicon atoms and integration of the phenyl ring protons to the peripheral groups becomes the only method for end group analysis. Hydrosilylation of phenyl triallylsilane using trichlorosilane, in the presence of CPA catalyst and subsequent isolation of the product yields compound **(20)**. Both NMR and IR spectra showed no allylic groups present, suggesting completion of the reaction.



Scheme 2.5 Synthesis of carbosilane with three branch points per silicon (21) $PhSi[(prSiMe)^1_3:All]_3$

NMR and IR spectral data for this moisture sensitive compound are reported in Table 2.16. The aliphatic protons integrate to the calculated ratio of 5:18.4 (relative to the five phenyl protons), with the methylene closest to the silicon trichloride moiety being the furthest downfield due to shielding from the chlorine atoms, Figure 2.19.

Table 2.16 Selected NMR and IR data for compound (20) $Ph[(prSi)^{0.5}_3:Cl]_3$

^1H δ ppm	7.5-7.3 (=5) *5H*, 1.9-0.4 (18.4±1.8)*18H*
^{13}C δ ppm	134.2, 133.8, 129.9, 129.6, 128.2, 28.3, 28.2, 23.8, 18.9, 17.5, 17.2, 17.0, 16.0, 15.2
^{29}Si δ ppm	12.0, 11.9, 11.2, -3.5
IR cm^{-1}	3060, 2090, 1250, 570, 460

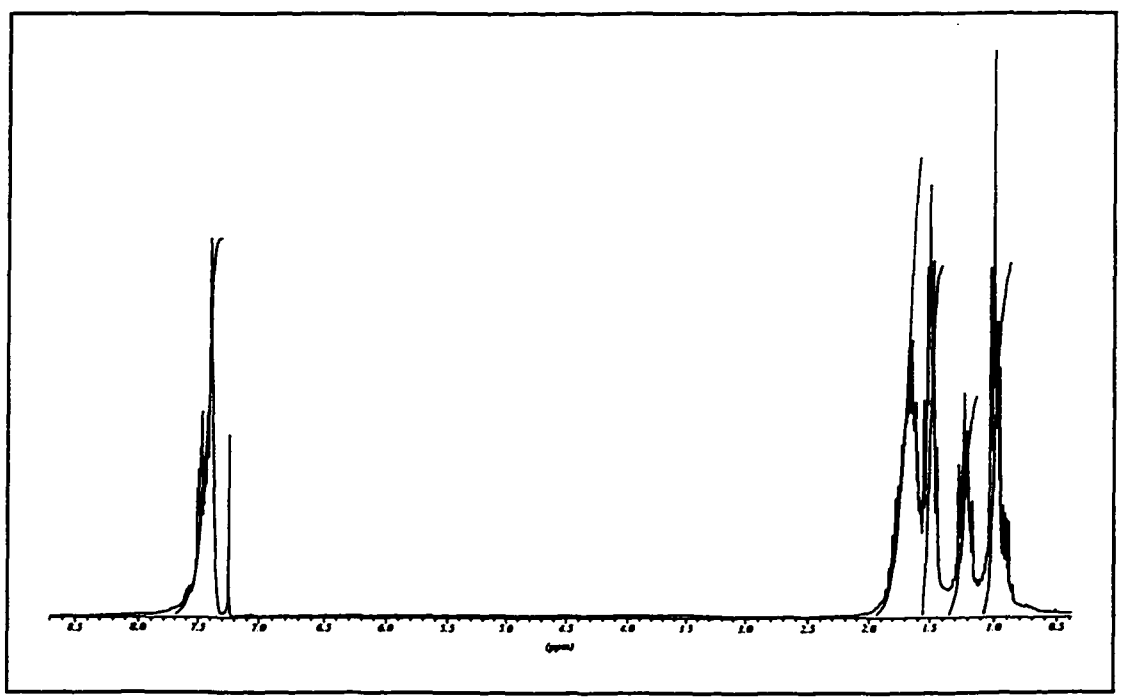


Figure 2.19 ^1H NMR spectrum of compound (20) $Ph[(prSi)^{0.5}_3:Cl]_3$

Carbon-13 NMR (Appendix A) has also provided very useful information in the analysis of trichlorosilyl terminated products. The hydrosilylation product **(20)** shows peaks which are indicative of saturated carbon atoms. However, it appears that there may be a steric effect from having three peripheral chlorine atoms attached to each silicon as nine separate methylene resonances are observed in this spectrum, Table 2.16.

Silicon-29 NMR chemical shift data, Table 2.16, has been of extreme importance in carbosilane dendrimer studies. In the hydrosilylation product **(20)** signals are observed and assigned as the *Si*-Cl_3 and the *Si*-Ph (Appendix A). These multiple downfield silicon resonances may possibly be accounted for by steric effects from the large trichlorosilyl end group. This would place each peripheral group into a fixed position, not free to rotate, and thus they may appear as separate signals.

Since the ^{1}H NMR and IR spectra showed no evidence for any unsaturated groups, the product **(20)** was slowly added to an excess solution of Grignard reagent. The product **(21)** from this reaction was then analysed in a similar manner as previous examples. For the ^{1}H NMR spectrum the allylic resonances reappear at δ 5.8 (β) and 4.8 (α) ppm with the methylene attached to Si at δ 1.5 (γ) ppm respectively. There are also three separate methylene proton resonances at δ 1.4-0.4 ppm which integrate correctly relative to the phenyl signal at δ 7.5-7.3 ppm, five protons, and also with the exterior allylic signals, Table 2.17 (Figure 2.20).

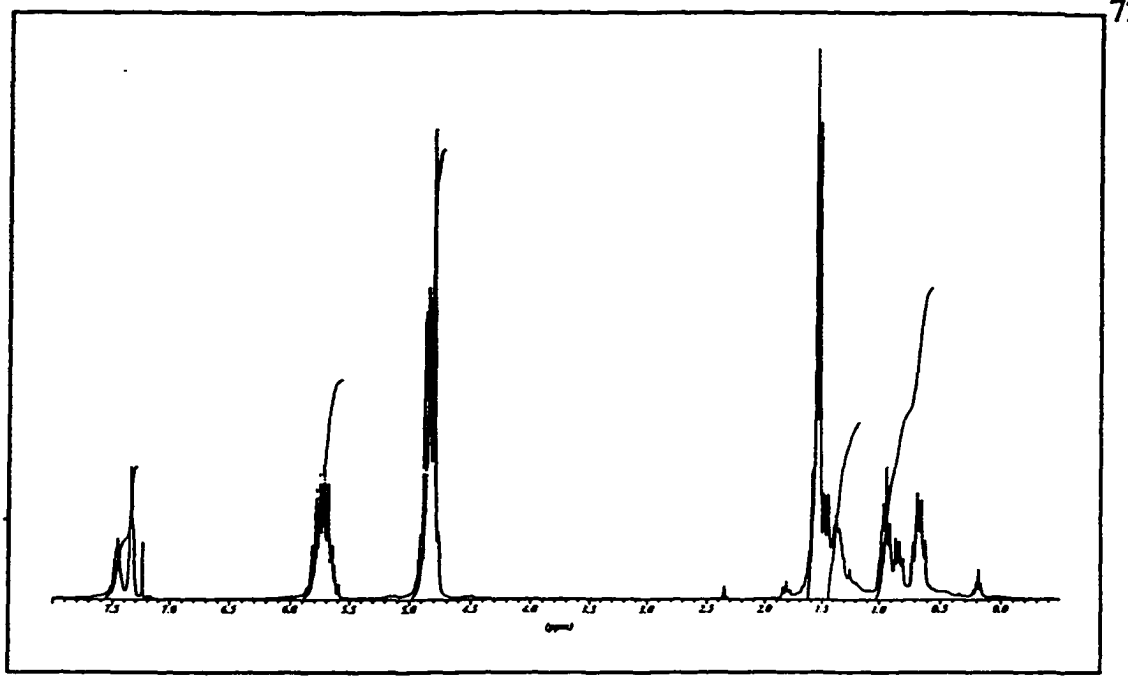


Figure 2.20 ^{1}H NMR spectrum of compound (21) Ph[(prSi)$^1_3$:All]$_3$

Table 2.17 Selected NMR data for compound (21) Ph[(prSi)$^1_3$:All]$_3$

	Ph	=CH	$=CH_2$	CH_2
^{1}H δ ppm	7.5-7.3 (=5)	5.74 (8.2±0.8)	4.84 (17±1.8)	1.53 (17.5±1.8) *18H*
	5H	*9H*	*18H*	1.4-0.4 (18.4±1.8) *18H*
^{13}C δ ppm	135.3, 133.8	134.7	113.0	20.7, 19.6, 19.1, 18.6-16.5
	129.4, 127.8			
Integration (Experimental) *Calculated*				
^{29}Si-NMR δ ppm		-1.10 ($Si-All_3$)		-3.97 (Si-Ph)

Multiple methylene resonances also appear in the ^{13}C NMR for this first generation product, Figure 2.21. These multiple peaks may be rationalized by considering the steric bulk associated with addition of three terminal allyl moieties. This would cause the interior methylene carbons to be distinguishable from each other and appear as nine separate resonances in the spectrum.

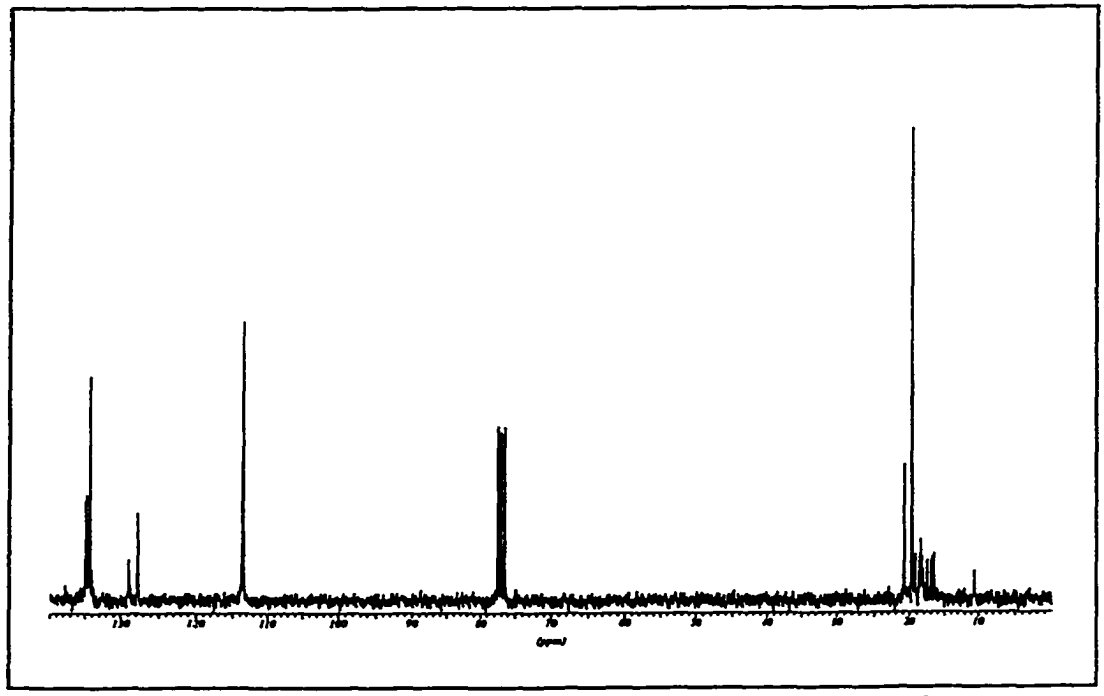


Figure 2.21 ^{13}C-{^{1}H} NMR spectrum of compound (21) $Ph[(prSi)^{1}_{3}:All]_{3}$

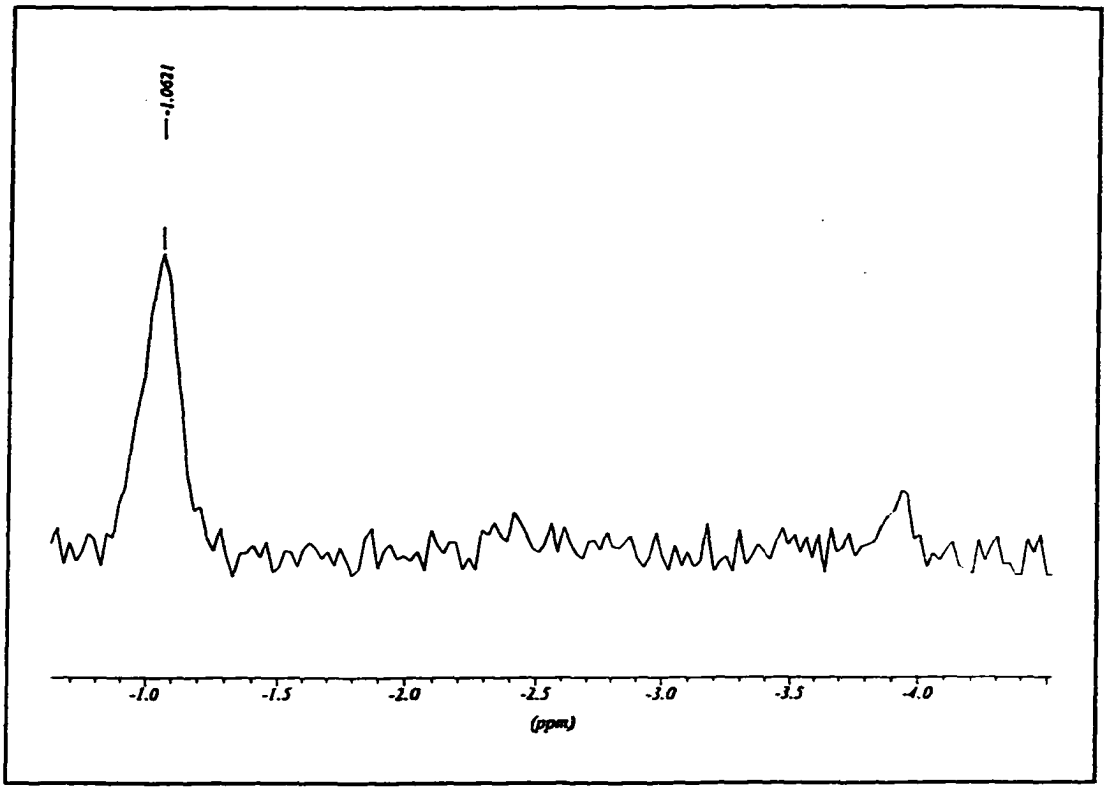
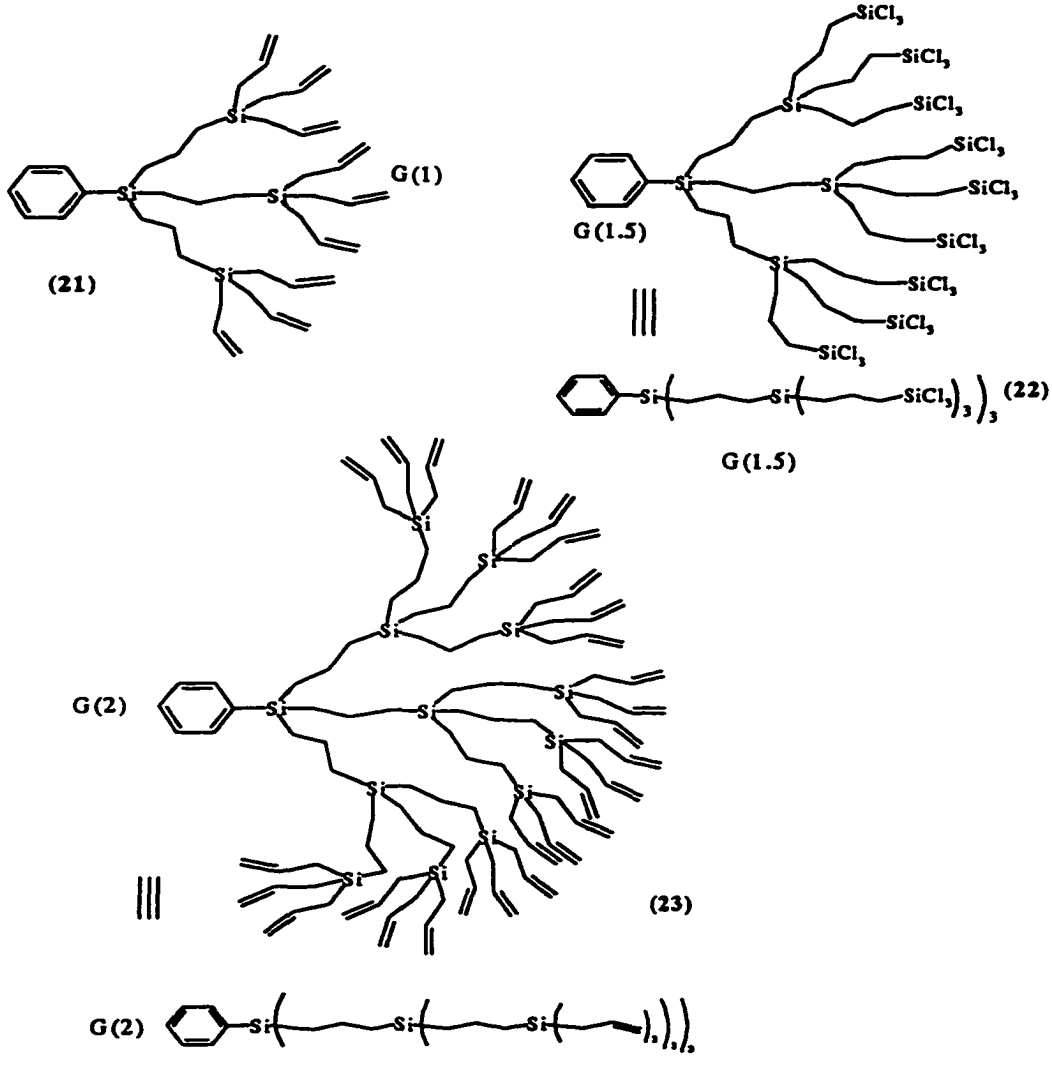
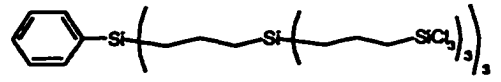


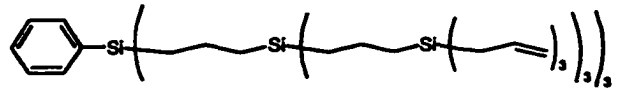
Figure 2.22 ^{29}Si-{^{1}H} NMR spectrum of compound (21) Ph[(prSi)$^{1}_{3}$:All]$_3$

The ^{29}Si NMR spectrum (Figure 2.22) is also consistent with the formulation predicted, although with this spectrum the signal to noise ratio is poor and the Ph-*Si* resonance is not very well resolved. There are two signals observed, one at δ -3.97 ppm assigned as the Ph-*Si* group and the other at δ -1.10 ppm for the terminal *Si*-allyl group. Mass spectral analysis of compound (21), using CI/Methane as the ionisation method, shows a molecular ion at 684 m/z units and subsequent fragmentation patterns that arise from the loss of allylic groups (643, 602 amu) or a benzene ring (607 amu) respectively. Elemental analysis of this compound is also reasonably consistent with its formulation; Anal. Calcd for $C_{42}H_{68}Si_4$: C, 73.68; H, 9.94. Found: C, 74.30; H, 10.00.

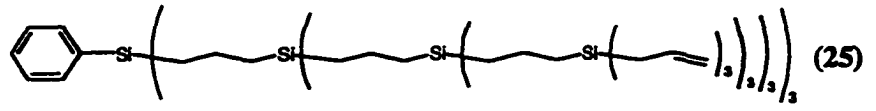
The synthesis is repeated iteratively, hydrosilylation with trichlorosilane followed by alkenylation with allylmagnesium bromide, and as in prior branching examples (1B and 2B) the chlorosilyl and the allylsilyl terminated derivatives were individually isolated and characterised by multinuclear NMR spectroscopy. For the chlorosilyl intermediates, loss of the terminal allylic groups was determined by ^{1}H NMR spectroscopy (Table 2.18) and IR spectroscopy. The interior phenyl resonance was used as an internal integration handle to present a quantitative view on the completeness of each hydrosilylation reaction.

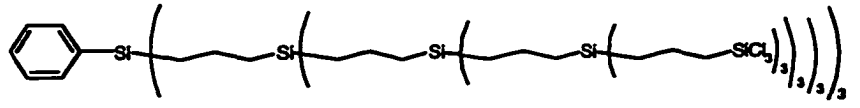


G(1.5)  (22)

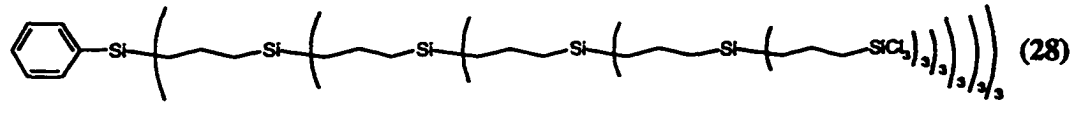
G(2)  (23)

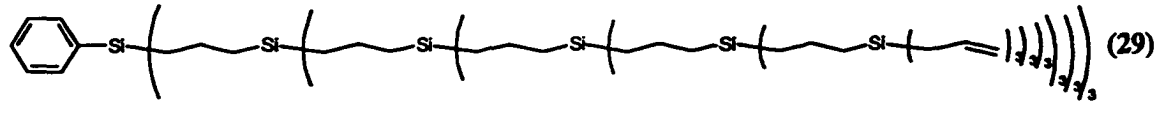
G(2.5)  (24)

G(3)  (25)

G(3.5)  (26)

G(4)  (27)

G(4.5)  (28)

G(5)  (29)

Ph[(prSi)$^{N}_{3}$:Cl/All]$_3$ dendrimers synthesised

Table 2.18 Selected spectral data for PhSi[(prSi)$^{N}_{3}$:Cl]$_3$ trifurcate dendrimers

		^{1}H NMR integrations		
		Ph	CH_2	^{29}Si δ ppm
δ ppm	G(N)	7.5-7.3	1.1-0.4	
(22)	G(1.5)	(=5) *5H*	(72±7) *72H*	12.0, 0.98, -4.00
(24)	G(2.5)	(=5) *5H*	(230±23) *234H*	12.0, 0.98, 0.04, -4.00
(26)	G(3.5)	(=5) *5H*	(700±70) *720H*	12.0, 0.98, 0.04, -0.40, -4.00
(28)	G(4.5)	(=5) *5H*	(2000±200) *2178H*	12.0, 0.98, 0.04, -0.40

Integration (Experimental) *Calculated*

Table 2.19 Selected spectral data for PhSi[(prSi)$^{N}_{3}$:All]$_3$ trifurcate dendrimers

		^{1}H NMR integrations		
		Ph	=CH	^{29}Si δ ppm
δ ppm	G(N)	7.5-7.3	5.80	
(23)	G(2)	(=5) *5H*	(25±2.5) *27H*	-0.37, -1.06, -4.00
(25)	G(3)	(=5) *5H*	(80.2±8) *81H*	0.14, -0.37, -1.10, -4.00
(27)	G(4)	(=5) *5H*	(253±25) *243H*	0.77, 0.14, -0.40, -1.10, -4.00[a]
(29)	G(5)	(=5) *5H*	(800±80) *729H*	0.77, 0.14, -0.37, -0.40, -1.10

Integration (Experimental) *Calculated* [a]very weak signal

The ^{1}H NMR spectra of the allyl terminated dendrimers (Figures 2.23-2.25) were analysed and the integration ratios of the peripheral =C*H* groups relative to the phenyl ring protons are reported in Table 2.19. Since there are no methyl groups attached to these silicon branches the integration analysis relies solely on the five phenyl ring protons relative to the number of peripheral groups. This also means that no cross-checking can be applied, *i.e.* phenyl:β-allyl:methyl as in the 1B and 2B examples, and the error in this 3B series may be greater than in the previous two instances.

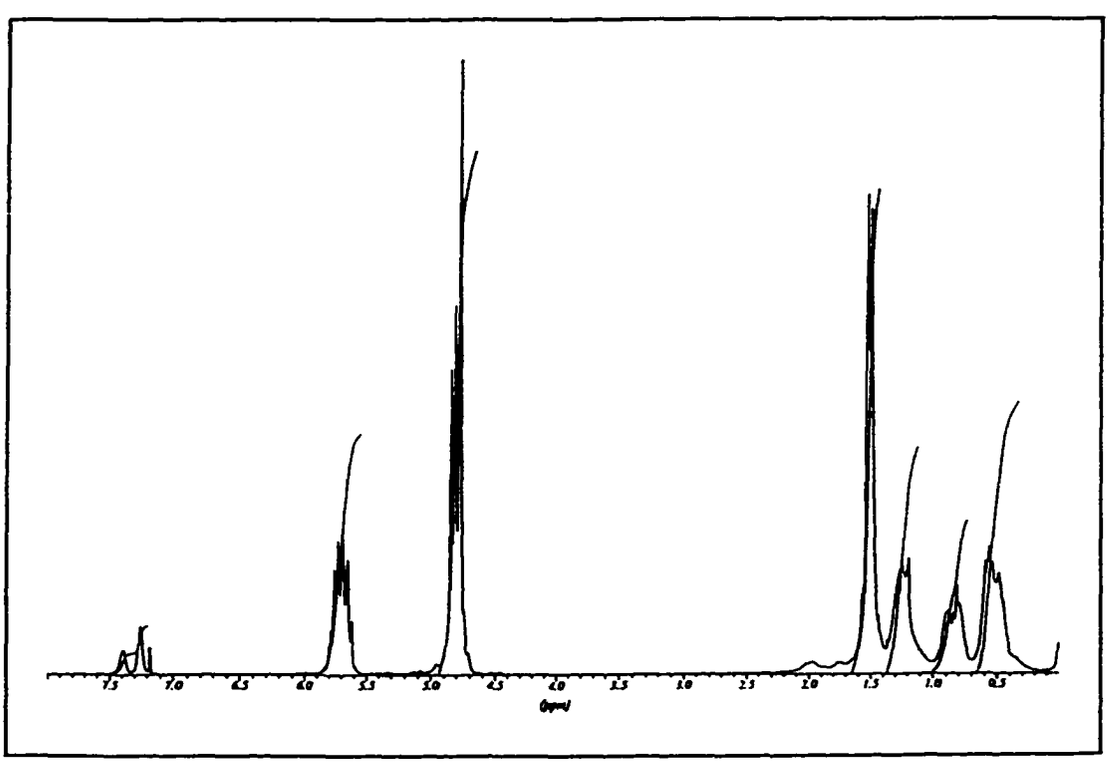


Figure 2.23 ^{1}H NMR spectrum of compound (23) PhSi[(prSi)$^2_3$:All]$_3$

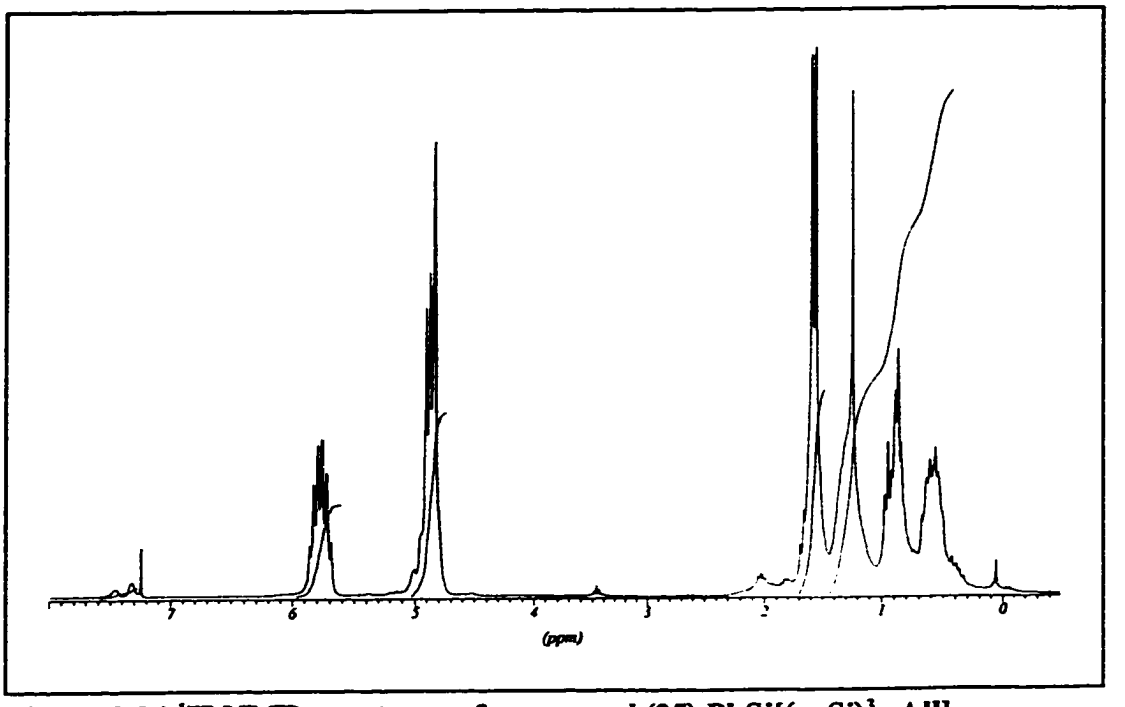


Figure 2.24 ^{1}H NMR spectrum of compound (25) PhSi[(prSi)$^3_3$:All]$_3$

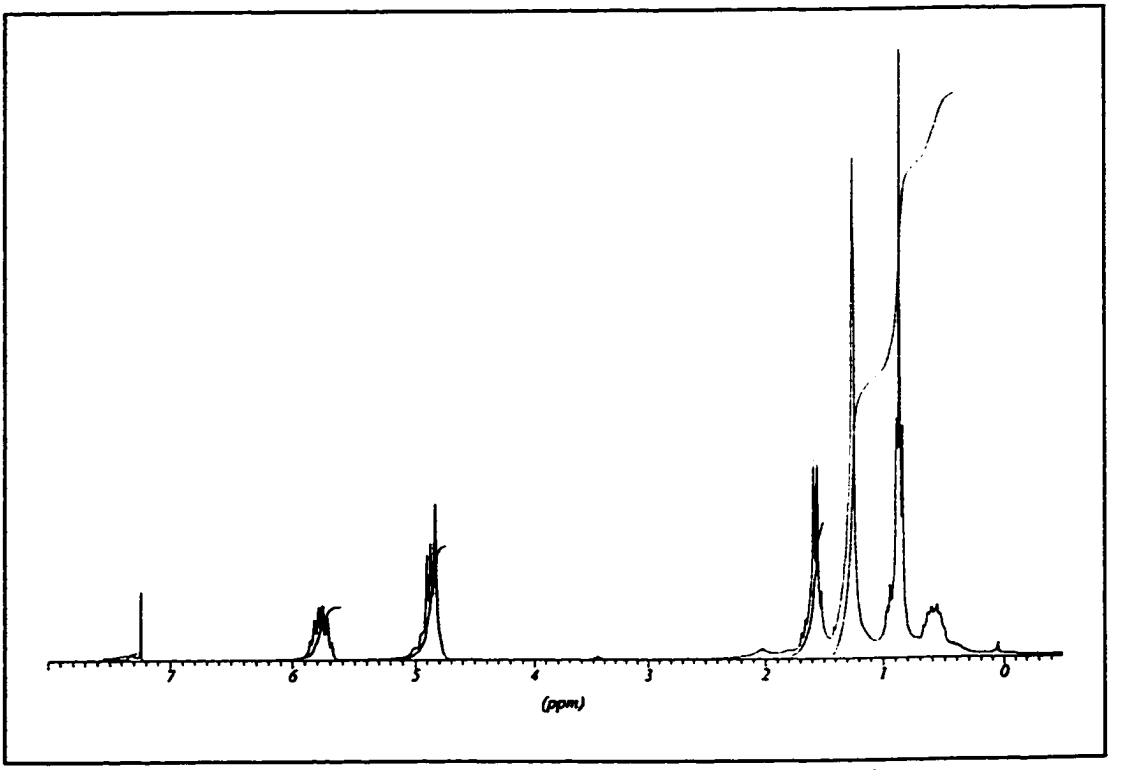


Figure 2.25 ^{1}H NMR spectrum of compound (27) PhSi[(prSi)$^4_3$:All]$_3$

The ^{1}H NMR spectrum of the third generation is shown (Figure 2.24) and at this stage it is already difficult to distinguish the phenyl signal on a full scale spectrum. The integration of this aromatic signal to the peripheral allyl resonances is in the ratio of 5:80.2 compared with the calculated value of 5:81. This is within a reasonable experimental error that can be obtained *via* proton NMR integration which, for these oils that contain a large number of peripheral groups, is estimated at 10%. Also seen in the NMR of the third generation is inclusion of 2-propanol at δ 3.5 and 1.25 ppm. Proton NMR integrations of the aliphatic regions become unreliable when inclusion occurs since it is not always possible to completely remove all traces of residual solvents such as hexanes, 2-propanol, and ethyl acetate.

Equally important are the ^{29}Si NMR shifts, Table 2.19, for the allylsilane compounds; these show distinctive resonances that are indicative of a hierarchical structure, examples of the third and fourth generations are shown in Figures 2.26 and 2.27. As the generation number increases the chemical shifts of the respective silicon signals appear to be generationally dependant, the intensity of the signal is proportional to the relative amounts of silicon within each shell. The outermost silicon signal remains consistent at δ -1.10 ppm while the interior silicon branches move progressively downfield, with diminishing intensity, as each shell is added. The core group phenylsilyl signal remains unperturbed at δ -4.0 ppm. This phenomena is not unique to carbosilane dendrimers; Majoral *et al*[14] reported similar generational behaviour for phosphorus containing dendrimers (see page 54), and Meijer *et al*[58] found analogous behaviour with nitrogen containing materials. For this set of trifurcate carbosilane molecules this behaviour is only observed to a fifth generation, further shell expansion after this results in loss of any interior signals into the baseline.

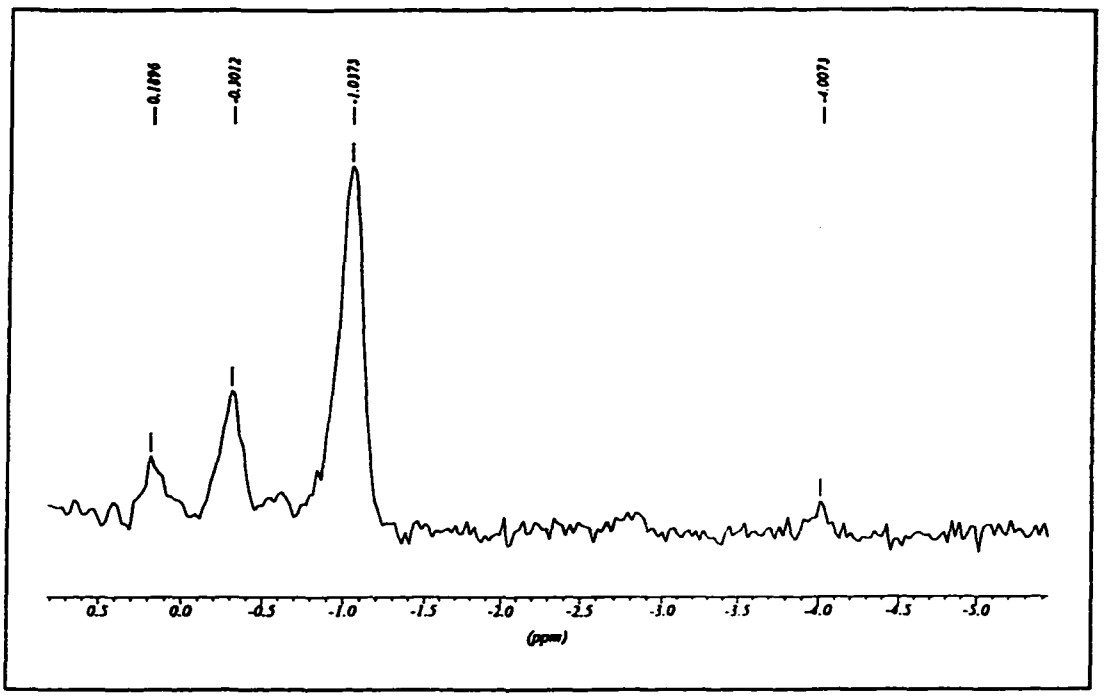


Figure 2.26 ^{29}Si-{^{1}H} NMR spectrum of compound (25) PhSi[(prSi)$^{3}_{3}$:All]$_3$

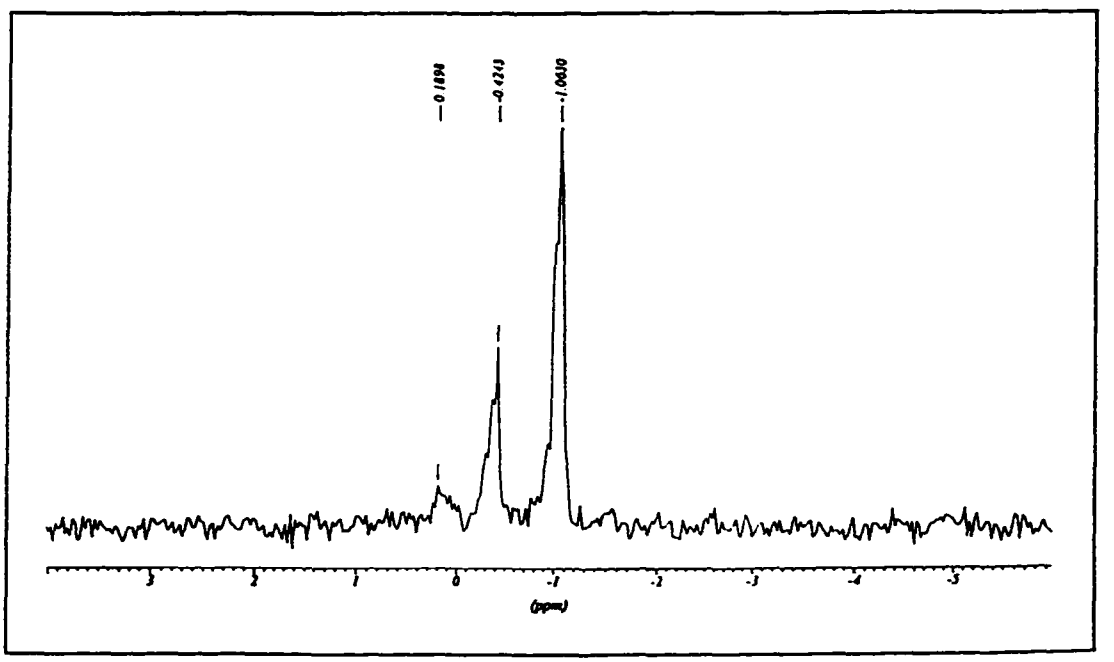


Figure 2.27 ^{29}Si-{^{1}H} NMR spectrum of compound (27) PhSi[(prSi)$^{4}_{3}$:All]$_3$

As with the two previous topologies GPC data has been obtained and for each generation shows that the polydispersity of each sample is narrow. Adequate mass spectroscopy was only found for the first generation; the calculated molecular mass of the second generation is 2052 amu and conventional techniques (CI and EI) could not provide any useful data. GPC data is highlighted in Table 2.20 for the successive G(N) generations of this triply branched trifurcate system. The linear plot of retention time *vs* molecular mass (Figure 2.28) is analogous to the two previous series of compounds analysed by GPC chromatography.

Table 2.20 GPC data for $PhSi[(prSi)^{N}_{3}:All]_3$ carbosilane dendrimers in $CHCl_3$

Compound	G(N)	M_w	$\log_{10}M_w$	Time (min)	Peak Width[a]
(21)	G(1)	684	2.835	8.70	± 0.15
(23)	G(2)	2052	3.312	7.90	± 0.17
(25)	G(3)	6156	3.789	6.80	± 0.17
(27)	G(4)	18468	4.266	5.90	± 0.30
(29)	G(5)	55404	4.743	4.90	± 0.60

[a] measured as the peak width at half height in minutes

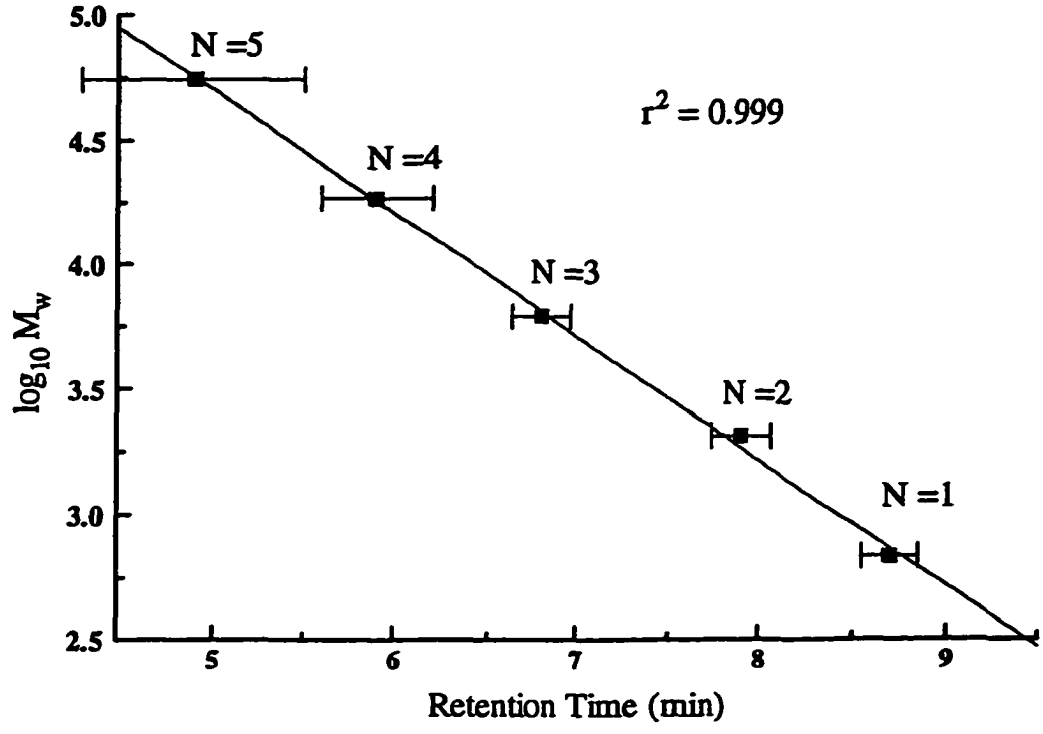


Figure 2.28 Plot of retention time *vs* $\log_{10}M_w$ for $Ph[(prSi)^N_3:All]_3$ dendrimers

2.5 Diphenyl diallylsilane[65] as a Core Molecule

The use of a trifurcate core molecule, that possess an internal integration signal, has proved to be a useful starting point for dendrimer growth. Unfortunately this phenyl signal becomes unreliable for ^1H integration after the fourth generation when investigating the triply branching silanes, 3B. Therefore, a core that contains more phenyl protons would aid the integration analysis of larger generations and so diphenyl diallylsilane (**30**), with ten phenyl protons, was seen as a reasonable alternative, *i.e.* a "bifurcate" system. The ^1H NMR spectrum of this core molecule (Figure 2.29) shows that these phenyl resonances are now

much larger than in the trifurcate system and some residual ether solvent is also seen (δ 3.9 and 1.3 ppm). Some selected NMR data are reported in Table 2.21.

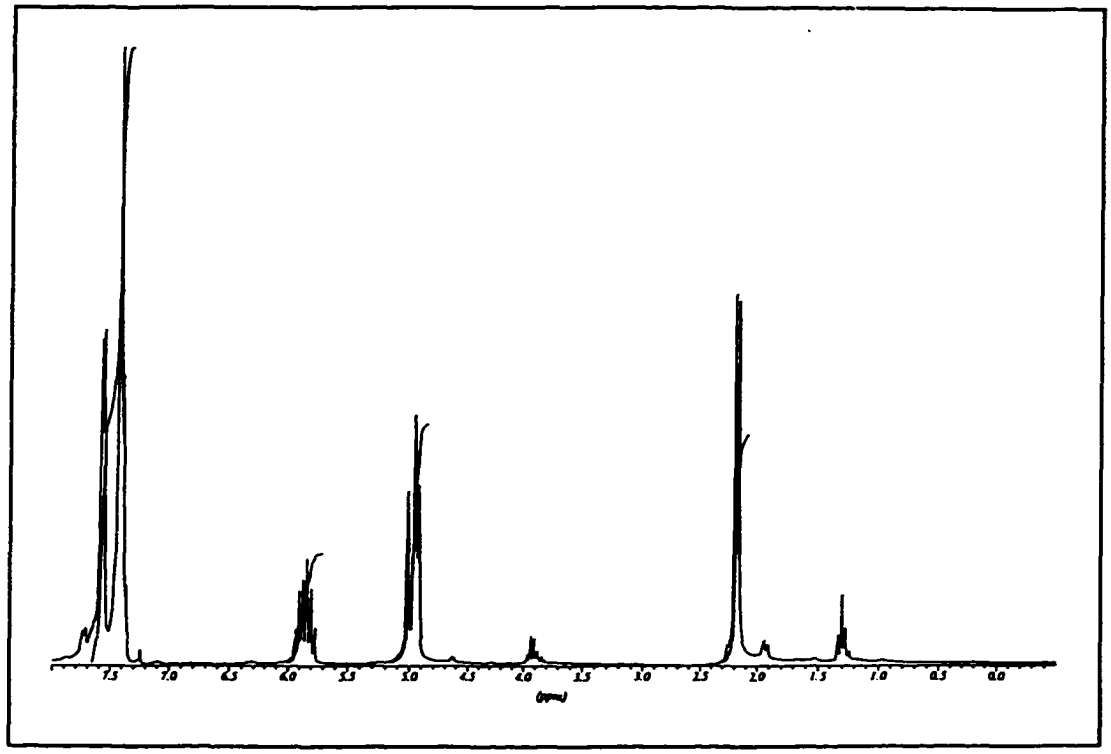
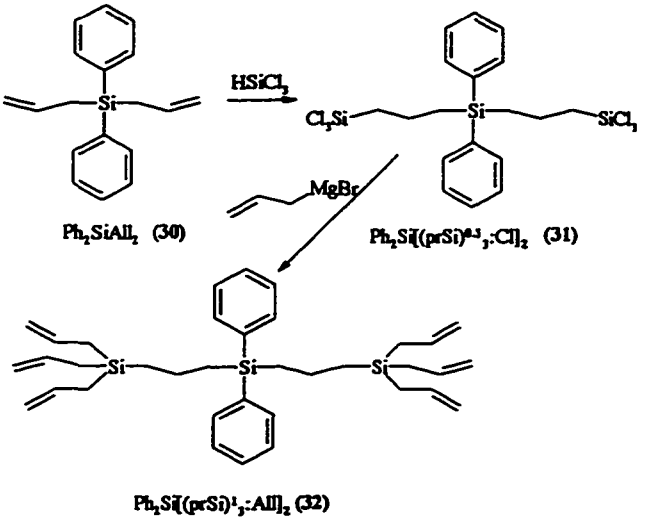


Figure 2.29 ^{1}H NMR spectrum of compound (30) Ph_2SiAll_2

Table 2.21 Spectral data for diallyl diphenylsilane (30) Ph_2SiAll_2

	Ph	=CH	$=CH_2$	CH_2
^{1}H δ ppm	7.5-7.3	5.8	4.8	2.2
	(=10) *10H*	(2±0.2) *2H*	(4±0.4) *4H*	(4±0.4) *4H*
^{13}C δ ppm	134.9, 134.8	133.7	114.7	19.9
	130.1, 129.4			
	127.7			
^{29}Si δ ppm	-11.80			

This molecule was firstly hydrosilylated with trichlorosilane and the intermediate trichlorosilyl compound was isolated and characterized. Proton NMR and IR spectra did not show any unsaturated resonances remaining (Table 2.22) and so the trichlorosilyl was then reacted with allylmagnesium bromide, Scheme 2.6. Isolation of the product from the latter reaction indicated that a first generation compound **(32)** had been formed, some selected NMR data are highlighted in Table 2.23.



Scheme 2.6 Formation of bifurcate G(1) $Ph_2Si[(prSi)^1{}_3:All]_3$

Table 2.22 Selected spectral data for compound (31) $Ph_2Si[(prSi)^{0.5}{}_3:Cl]_2$

	Ph	CH_2	^{29}Si δ ppm
^{1}H δ ppm	7.8-7.4 (=10) *10H*	1.9-1.3 (12±0.5) *12H*	
^{13}C δ ppm	134.8, 134.3	28.2, 17.2, 15.5	12.15 (Si-Cl)
	129.6, 128.1		-7.81 (Si-Ph)
IR cm^{-1}	3060, 2920, 1250, 570, 460		

Integration (Experimental) *Calculated*

Table 2.23 Selected spectral data for compound (32) $Ph_2Si[(prSi)^1_3:All]_2$

	Ph	=CH	$=CH_2$	CH_2	CH_2
^1H δ ppm	7.6-7.3	5.80	4.85	1.50	1.4~0.4
	(=10) *10H*	(6±0.6) *6H*	(12±1.2) *12H*	(12±1.2) *12H*	(12±1.2) *12H*
^{13}C δ ppm	135.0, 134.8	134.4	113.5	19.6	18.1, 17.5
	129.3, 127.8				16.4
^{29}Si δ ppm	1.09 ($SiAll_3$)		-7.91 (Si-Ph)		

Integration (Experimental) *Calculated*

2.6 Summary

The results discussed in Sections 2.3-2.6 demonstrate how multinuclear NMR spectroscopy can be used as an internally consistent means for dendrimer characterization. For the dendritic trifurcate carbosilane compounds, the core phenyl fragment acts as a calibration signal in the proton NMR to make possible end-group counting for a variety of different carbosilane branch topographies. In low branch morphologies (1B or 2B) this signal remains distinguishable for all the generations investigated (up to G(3)). By contrast, the same approach becomes impractical at higher than the fourth generation dendrimer for the 3B series because of the large population of peripheral groups. Use of a bifurcate (diphenyl) core molecule may help integration ratios for larger generations.

Silicon-29 NMR spectroscopy has been shown to be a powerful analytical probe for carbosilane dendrimers. In the linear series of molecules (1B), overlap of ^{29}Si signals due to interior *Si*-Me_2 was observed at low generation numbers, but the core *Si* atom as well as the Si_N peripheral nuclei were clearly resolved in all cases. For higher branching silicon centres (2B and 3B) hierarchical spectra with intensity ratios approximating binomial statistics were observed, *i.e.* characterizing the sequential shell populations; however the internal Ph-*Si* signal diminishes in relative intensity rapidly and was not observed after G(3).

GPC chromatography has been used to establish that all branch topologies exhibit a linear relationship of elution time *vs* molecular mass, with narrow peak width implying low polydispersity, *i.e.* complete reaction to close successive shells (generations, G(N)). Overall the dispersities of the samples analysed appear to be narrow, suggesting that the distribution is dominated by a single compound, and that the synthetic methodology used can be applied to extension from other core structures.

CHAPTER THREE

CORE MOLECULES WITHOUT AN INTERNAL INTEGRATION SIGNAL

The synthetic strategy for stepwise carbosilane dendrimer growth from a trifurcate core molecule was discussed in chapter two. It was established that the reaction chemistry is quantitative and that multinuclear NMR spectroscopy and GPC chromatography are valuable techniques for aiding characterization. To date workers in this area have looked only at spheroidal carbosilane dendrimers based on core molecules with either two or three branch points per generation.[27-32] The aim of this chapter is to show how different core molecules can be used to direct growth that parallels the bifunctional or trifunctional behaviour described in chapter two, and is tetrafunctional (spheroidal) or hexafunctional, (*i.e.* developed in two adjacent trifurcate domains). How the extent of branch point growth (1B, 2B or 3B) can be controlled by choice of chlorosilane is also considered, and the core molecules and building block silanes used in this manner are listed in Table 3.1.

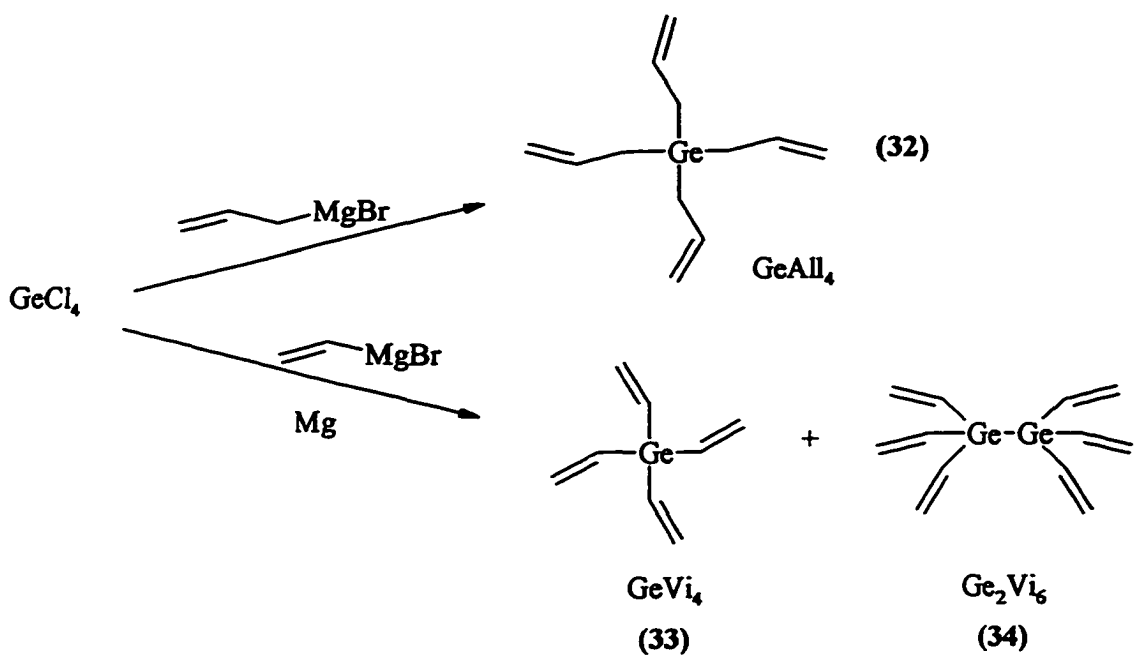
A series of dendrimers related to those derived from phenyl triallylsilane were synthesised using as a core structure, Scheme 3.1, hexavinyldigermane[67] (Ge_2Vi_6) **(34)**. The availability of this compound, which unusually can be obtained as a major product in tetravinylgermane[67] **(33)** ($GeVi_4$) synthesis, provides a 'masked' trifurcate unit which can be exposed by Ge-Ge bond cleavage and further modification; this will be demonstrated in chapter four.

Table 3.1 Carbosilane dendrimers synthesised using symmetrical core molecules

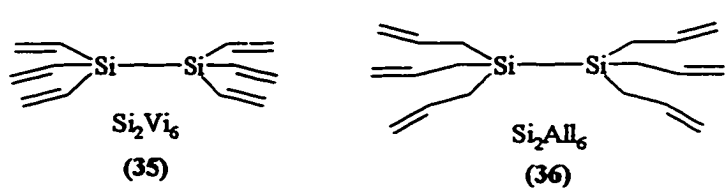
Core	Branching Silane	Nucleophile Used	Generation number reached	
$GeAll_4$	$HSiMe_2Cl$	AllylMgBr	G(1) to G(5)	
$GeAll_4$	$HSiMeCl_2$	AllylMgBr	G(1) to G(3)	
Ge_2Vi_6	$HSiMeCl_2$	AllylMgBr	G(1) to G(3)	
$SiAll_4$	$HSiMeCl_2$	AllylMgBr	G(1), G(2)	ref. 30
$GeVi_4$	$HSiMeCl_2$	AllylMgBr	G(1)	
$GeAll_4$	$HSiCl_3$	AllylMgBr	G(1) to G(5)	
Ge_2Vi_6	$HSiCl_3$	AllylMgBr	G(1) to G(5)	
$SiAll_4$	$HSiCl_3$	AllylMgBr	G(1), G(2)	ref. 28 and 32
$SiVi_4$	$HSiCl_3$	AllylMgBr and	G(1)Allyl and	
		VinylMgBr	G(1)Vinyl	ref. 29
$GeVi_4$	$HSiCl_3$	AllylMgBr	G(1)	
Si_2Vi_6	$HSiCl_3$	AllylMgBr	G(1), G(2)	
Si_2All_6	$HSiCl_3$	AllylMgBr	G(1), G(2)	

Tetraallylgermane[68] **(32)** may also be used as the central core, analogous to the corresponding silane chemistry of van Leuween and van der Made[28] (tetraallylsilane). This germanium centred molecule has been used as a model system for elaboration of the multinuclear NMR methodology developed in chapter two. The spheroidal dendrimers synthesised in this manner have no independent reference for integration of NMR signals, and hence completeness of shell expansions cannot be assessed in a similar manner to those dendrimers from chapter two. Starting from hexachlorodisilane, both hexavinyldisilane **(35)** (Si_2Vi_6) and hexaallyldisilane **(36)** (Si_2All_6) are accessible as hexafunctional analogues of

Ge_2Vi_6. Also, as a comparison to work by previous authors,[27-32] carbosilane dendrimers centred on tetrahedral silicon cores have been examined.



Scheme 3.1 Synthesis of germanium core molecules

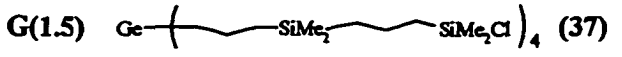


Disilane Core Molecules

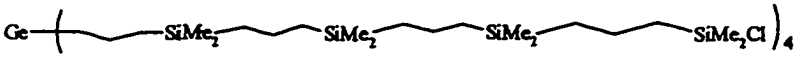
3.1 One-Directional Branching (1B)

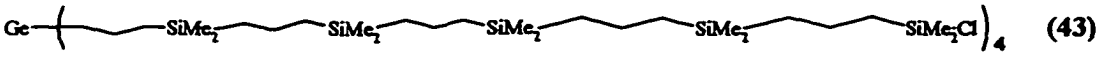
This series of molecules were synthesised as a comparison to the linear trifurcate models in chapter two. The core molecule, tetraallylgermane, was extended out to a fifth generation topology by iterative hydrosilylation ($HSiMe_2Cl$) and alkenylation reactions (allylmagnesium bromide). Shown below are the dimethylchlorosilyl intermediates formed from the hydrosilylation reactions.

G(0.5)  (35)

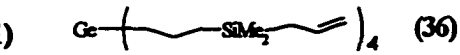
G(1.5)  (37)

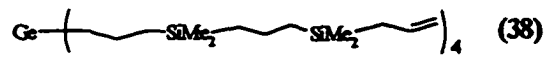
G(2.5)  (39)

G(3.5)  (41)

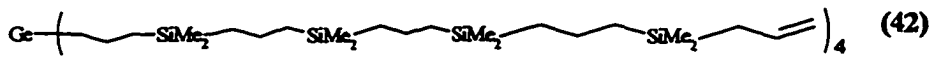
G(4.5)  (43)

Chlorosilyl terminated linear intermediates $Ge[(prSiMe_2)^N{}_1{:}Cl]_4$

G(1)  (36)

G(2)  (38)

G(3)  (40)

G(4)  (42)

G(5)  (44)

Allyl terminated linear carbosilanes $Ge[(prSiMe_2)^N_1:All]_4$

As in the previous chapter all of the dimethylchlorosilyl derivatives were isolated and characterized by multinuclear NMR (aliphatic resonances integrated relative to 24 $Si(CH_3)_2$ protons) and IR spectroscopy. In each case the spectra established that the reaction had gone to completion, with unsaturated groups no longer detected: allyl resonances in the ^1H NMR spectra were absent as was the large stretching absorption at 1630 cm^{-1} for the C=C in the IR spectrum. Selected spectral data for chlorosilyl compounds **(35, 37, 39, 41 and 43)** are highlighted in Table 3.2.

Table 3.2 Selected spectral data for linear Ge[(prSiMe$_2$)$^N_1$:Cl]$_4$ carbosilanes

^{1}H		CH_2	Si-$(CH_3)_2$Cl	Si-CH_3
δ ppm	G(N)	1.40~0.55	0.38	δ ppm
(35)	G(0.5)	(24±2) *24H*	(=24) *24H*	
(37)	G(1.5)	(48±5) *48H*	(=24) *24H*	-0.06 (24±2) *24H*
(39)	G(2.5)	(72±7) *72H*	(=24) *24H*	-0.06 (24±2) *24H*, -0.07 (24±2) *24H*
(41)	G(3.5)	(96±10) *96H*	(=24) *24H*	-0.05 (24±2) *24H*, -0.07 (48±5) *48H*
(43)	G(4.5)	(120±12) *120H*	(=24) *24H*	-0.04 (24±2) *24H*, -0.07 (72±7) *72H*

Integration (Experimental) *Calculated*

	^{13}C δ ppm		^{29}Si δ ppm	
G(N)	Si-$(CH_3)_2$Cl	Si-CH_3	Si-$(CH_3)_2$Cl	Si-CH_3
(35) G(0.5)	1.8		31.2	
(37) G(1.5)	1.8	-3.2	31.3	1.10
(39) G(2.5)	1.8	-3.17, -3.22	31.2	1.10 0.93
(41) G(3.5)	1.8	-3.2, -3.3	31.2	1.10, 0.93
(43) G(4.5)	1.8	-3.17, -3.23	31.2	1.10, 0.93

For the dimethylchlorosilyl series the Si(CH_3)$_2$ signals were set to 24 protons for the purposes of NMR integration, and proton populations in the remaining groups were measured relative to this value. In comparison with the trifurcate series investigated in chapter two,

where the methylsilyl signals were distinguishable up to a third generation in all multinuclear NMR spectra, these dimethylchlorosilyl compounds do not display separate peaks for interior groups ($prSiMe_2$) beyond the second generation G(1.5) (37).

Table 3.3 Selected spectral data for linear $Ge[(prSiMe_2)^N_1:All]_4$ carbosilanes

^1H		-CH=	$=CH_2$	$Si-CH_3$
δ ppm		5.75	4.80	δ ppm
(36)	G(1)	(=4) *4H*	(8±0.8) *8H*	-0.06 (24±2) *24H*
(38)	G(2)	(=4) *4H*	(8±0.8) *8H*	-0.04 (24±2) *24H*, -0.07 (24±2) *24H*
(40)	G(3)	(=4) *4H*	(8±0.8) *8H*	-0.03 (24±2) *24H*, -0.07 (48±5) *48H*
(42)	G(4)	(=4) *4H*	(8±0.8) *8H*	-0.04 (24±2) *24H*, -0.07 (72±7) *72H*
(44)	G(5)	(=4) *4H*	(8±0.8) *8H*	-0.04 (24±2) *24H*, -0.08 (96±10) *96H*
Integration (Experimental) *Calculated*				

^{13}C δ ppm	G(N)	$Si-CH_3$	^{29}Si δ ppm	$Si-CH_3$
(36)	G(1)	-3.6		0.72
(38)	G(2)	-3.2, -3.4		0.97, 0.76
(40)	G(3)	-3.2, -3.6		0.96, 0.75
(42)	G(4)	-3.2, -3.6		0.97, 0.76
(44)	G(5)	-3.2, -3.6		0.95, 0.73

Allyl terminated compounds, prepared using $GeAll_4$ as a central core, showed related proton integrations (Table 3.3) where the terminal four *β*-allyl protons were used as the integration reference. Details of the carbon and silicon chemical shifts for the silicon methyl resonances are also given. The observation of not more than two discrete resonances for

silicon-methyl nuclei in all NMR spectra (^{1}H, ^{13}C and ^{29}Si) is different to the situation found for the series derived from phenyl triallylsilane. Distinct signals are seen until the second generation, after which interior signals overlap. By contrast, in the trifurcate series of chapter two, this kind of overlap was not observed until the third generation at which interior groups gave rise to unresolved resonances observed as a single signal. As with the trifurcate compounds (chapter two), these molecules are of relatively low mass so reasonable mass spectroscopic data could be obtained, Table 3.4.

Table 3.4 Selected mass fragments for the linear $Ge[(prSiMe_2)^{N}_{1}:All]_4$ carbosilanes

$GeAll_4$ 1B	Calculated	Found
(36) G(1)	637	(EI): 637 (M^+), 581, 497, 397, 357, 297.
(38) G(2)	1037	(EI): 1022 (M^+ -Me), 997 (M^+ - allyl), 797, 558, 458.
(40) G(3)	1437	(EI): 1422 (M^+ - Me), 1398 (M^+ - allyl), 1097, 1055, 997.
(42) G(4)[a]	1837	(EI): 958, 858.
(44) G(5)	2237	(EI): 1698, 1159, 1058, 958, 858, 758.

[a]numerous attempts for analysis of this compound failed to give a higher mass ion

The fragmentation patterns are very similar to those observed with the trifurcate series with loss of methyl groups, allyl groups and dimethylallylsilyl groups (15, 41 and 100 amu respectively). GPC results are given in Table 3.5 where each sample gave a narrow peak, which implies that the product consists of one major compound.

Table 3.5 GPC data for $Ge[(prSiMe_2)^N_1:All]_4$ carbosilanes in $CHCl_3$ solution

	G(N)	M_w	$\log_{10}M_w$	Time (min)	Peak Width[a]
(36)	G(1)	637	2.804	11.40	± 0.11
(38)	G(2)	1037	3.015	11.05	± 0.12
(40)	G(3)	1437	3.157	10.80	± 0.12
(42)	G(4)	1837	3.264	10.60	± 0.12
(44)	G(5)	2237	3.349	10.35	± 0.13

[a] measured as the peak width at half height in minutes

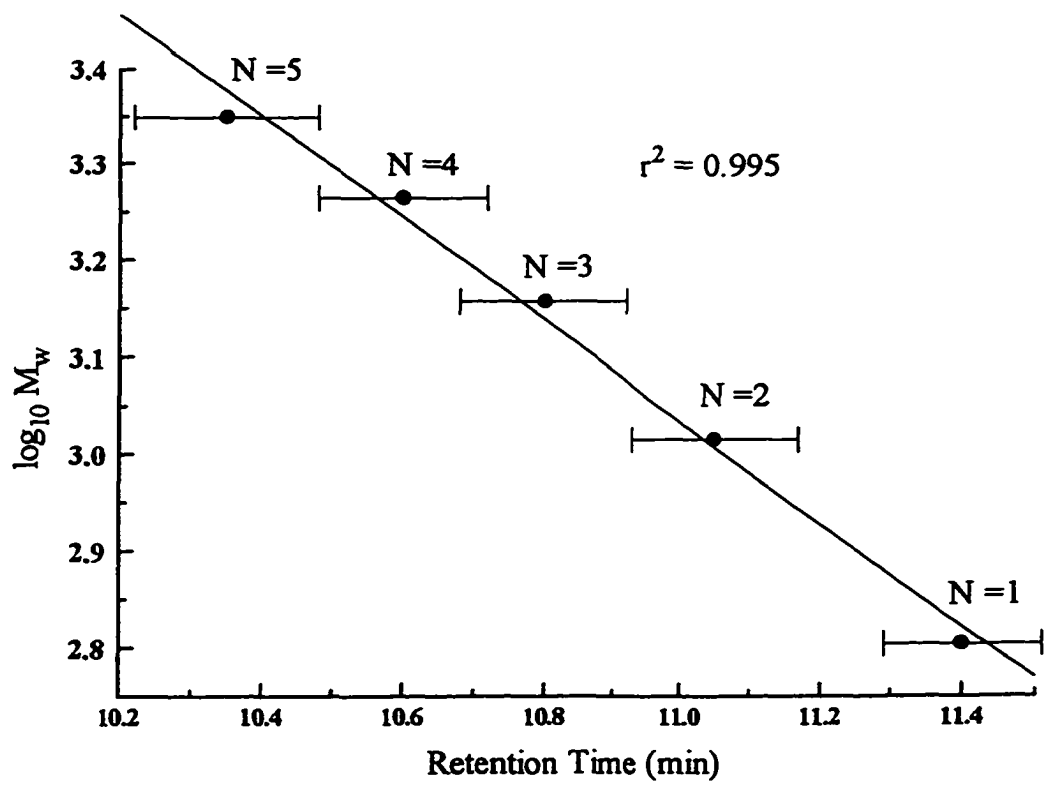
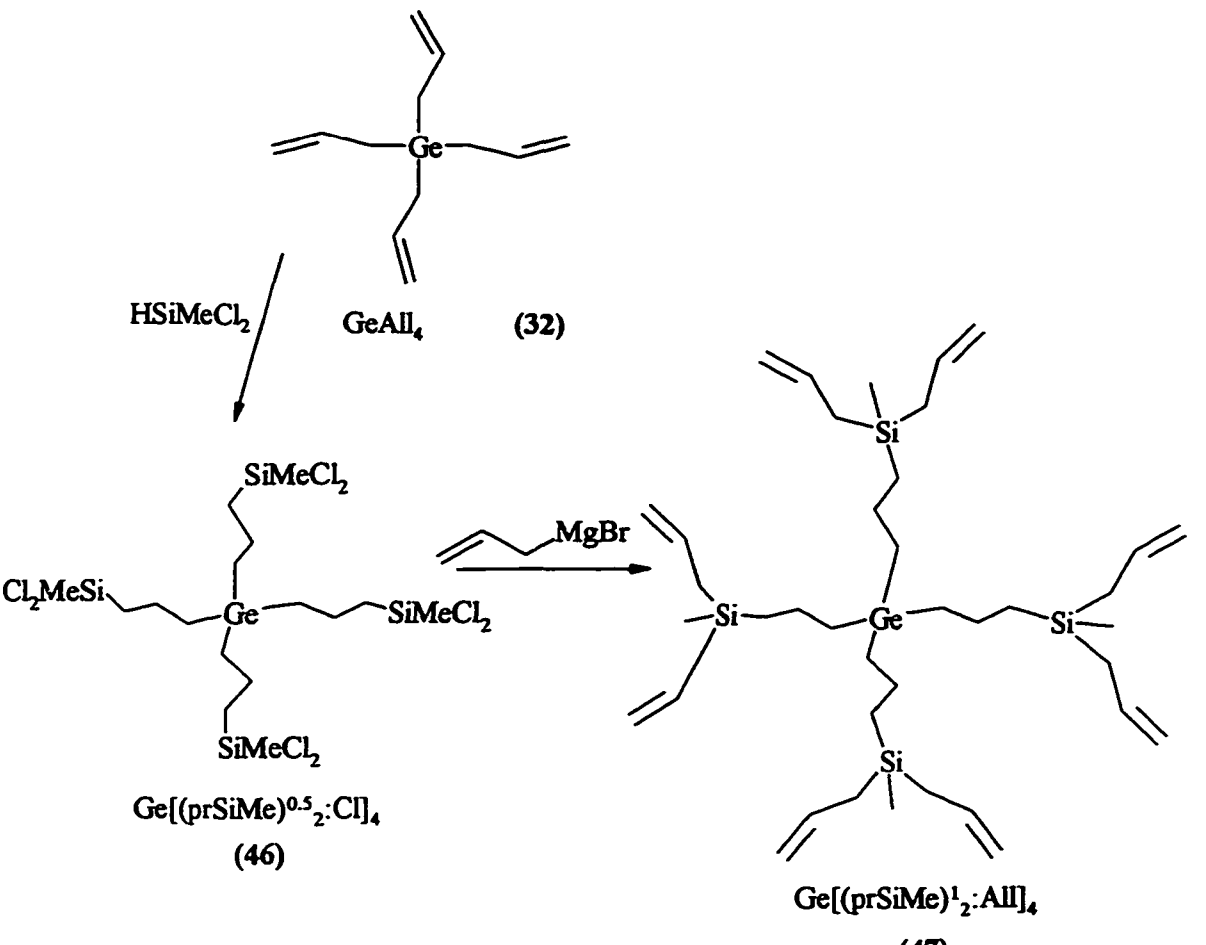


Figure 3.1 GPC plot of retention time *vs* $\log_{10}M_w$ for $Ge[(prSiMe_2)^N_1:All]_4$ dendrimers

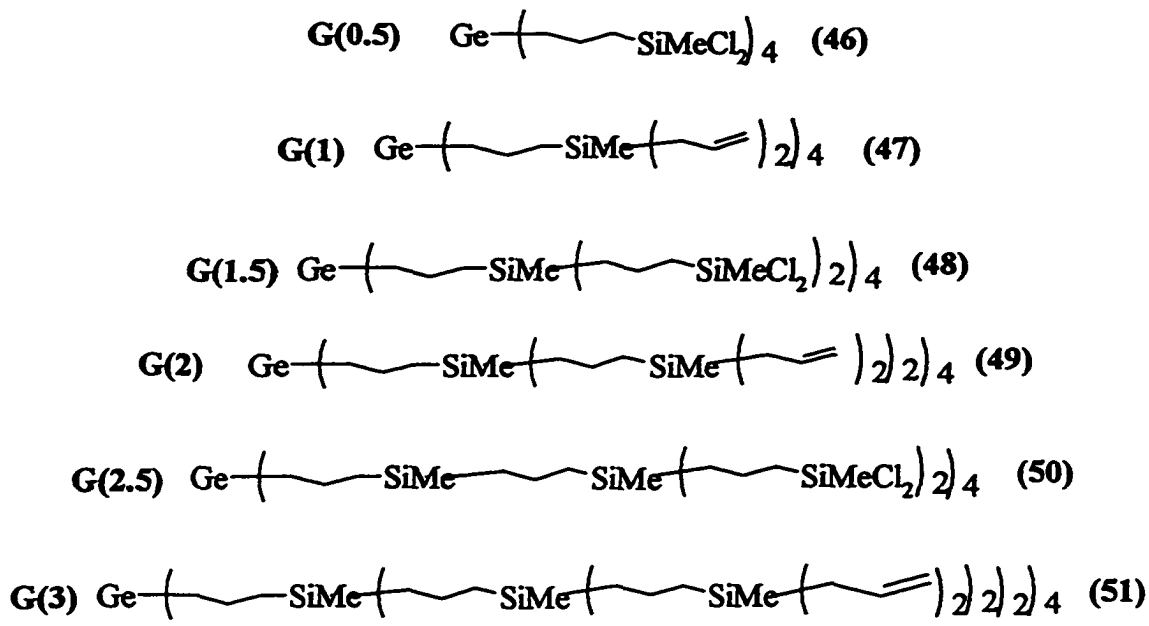
3.2 Two-Directional Branching (2B)

3.2.1 Spheroidal Core Molecules

Dendrimers with two-branch point (2B) silicon centres have also been synthesised using tetraallylgermane as a core molecule. Also, for comparison two other symmetrical cores, tetraallylsilane **(45)** ($SiAll_4$) and tetravinylgermane **(33)**, have been used.



Scheme 3.2 Synthesis of spheroidal germanium centred G(1) $Ge[(prSiMe)^1_2:All]_4$



Ge[(prSiMe)$^{N}_{2}$:Cl/All]$_4$ dendrimers

The preparative route for forming these carbosilane dendrimers is shown in Scheme 3.2 (preceding page), where there is no change to the synthetic methodology from that used previously. ^{1}H NMR and IR spectroscopy were again used to ensure complete hydrosilylation of the allylic groups. Multinuclear NMR data is reported in Table 3.6; data for the chlorosilyl intermediates can be found in the experimental section.

Table 3.6 Selected spectral data for spheroidal G(N)2B dendrimers

	=CH-	$-CH_2-$	CH_3
^1H δ ppm	5.80	4.85	
G(N)		$Ge[(prSiMe)^N{}_2:All]_4$	
(47) G(1)	(=8) *8H*	(16±1.6) *16H*	-0.03 (12±1.2) *12H*
^{13}C δ ppm			-5.76
(49) G(2)	(=16) *16H*	(32±3) *32H*	-0.03 (24±2.4) *24H* -0.06 (12±1.2) *12H*
^{13}C δ ppm			-5.34, -5.76
(51) G(3)	(=32) *32H*	(64±6) *64H*	-0.03 (48±4.8) *48H* -0.06 (24±2.4) *24H* -0.09 (12±1.2) *12H*
^{13}C δ ppm			-4.64, -5.34, -5.78
G(N)		$Si[(prSiMe)^N{}_2:All]_4$	
(59) G(1)	(=8) *8H*	(16±1.6) *16H*	-0.02 (12±1.2) *12H*
^{13}C δ ppm			-5.73
(61) G(2)	(=16) *16H*	(32±3) *32H*	-0.02 (24±2.4) *24H* -0.07 (12±1.2) *12H*
^{13}C δ ppm			-5.33, -5.73
G(N)		$Ge[(etSiMe)^N{}_2:All]_4$	
(63) G(1)	(=8) *8H*	(16±1.6) *16H*	-0.02 (12±1.2) *12H*
^{13}C δ ppm			-6.29

Integration (Experimental) *Calculated*

As with the 1B derivatives discussed earlier, the terminal β-allylic signals were set as a reference and the remaining peaks were integrated relative to this calculated number. These

2B compounds show multinuclear NMR characteristics that are similar to observations made earlier with the trifurcate series of dendrimers (chapter two); a slight deviation in the carbon chemical shift is observed for the first generation of the tetravinylgermane core. Further analysis of these germanium centred vinyl compounds is reported in the next section. Spectra below highlight the tetraallylgermane centred 2B molecules, Figures 3.2-3.5.

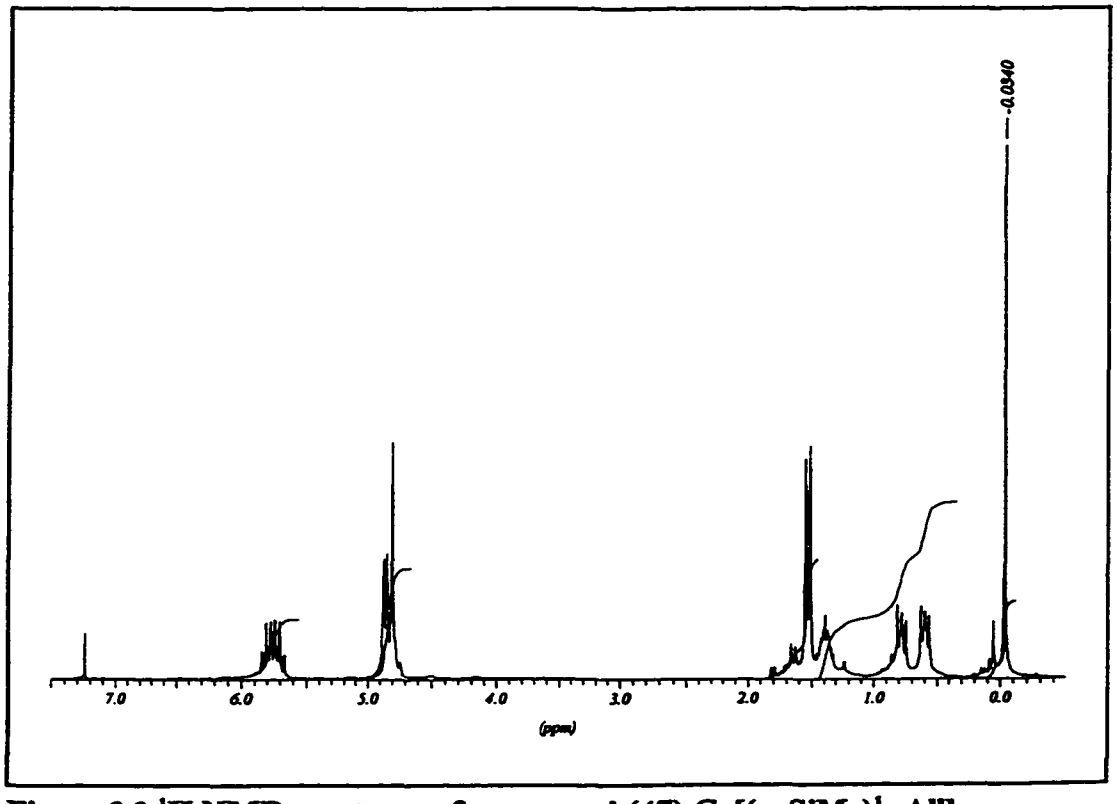


Figure 3.2 ^{1}H NMR spectrum of compound (47) Ge[(prSiMe)$^1_2$:All]$_4$

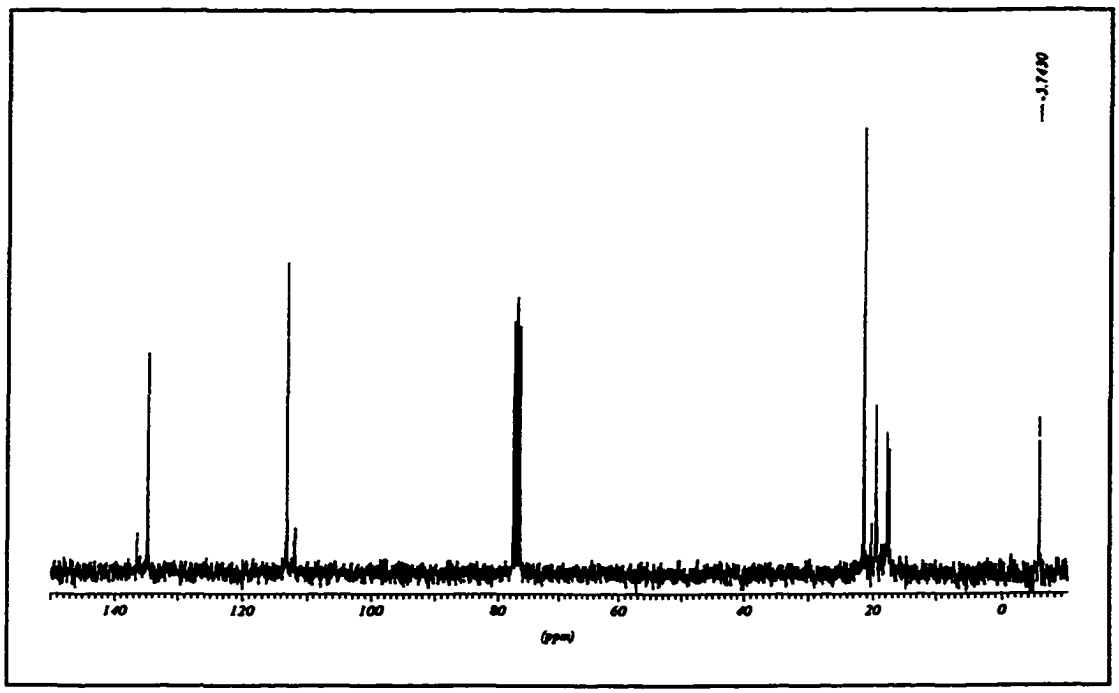


Figure 3.3 ^{13}C-{^{1}H} NMR spectrum of compound (47) Ge[(prSiMe)$^{1}_{2}$:All]$_4$

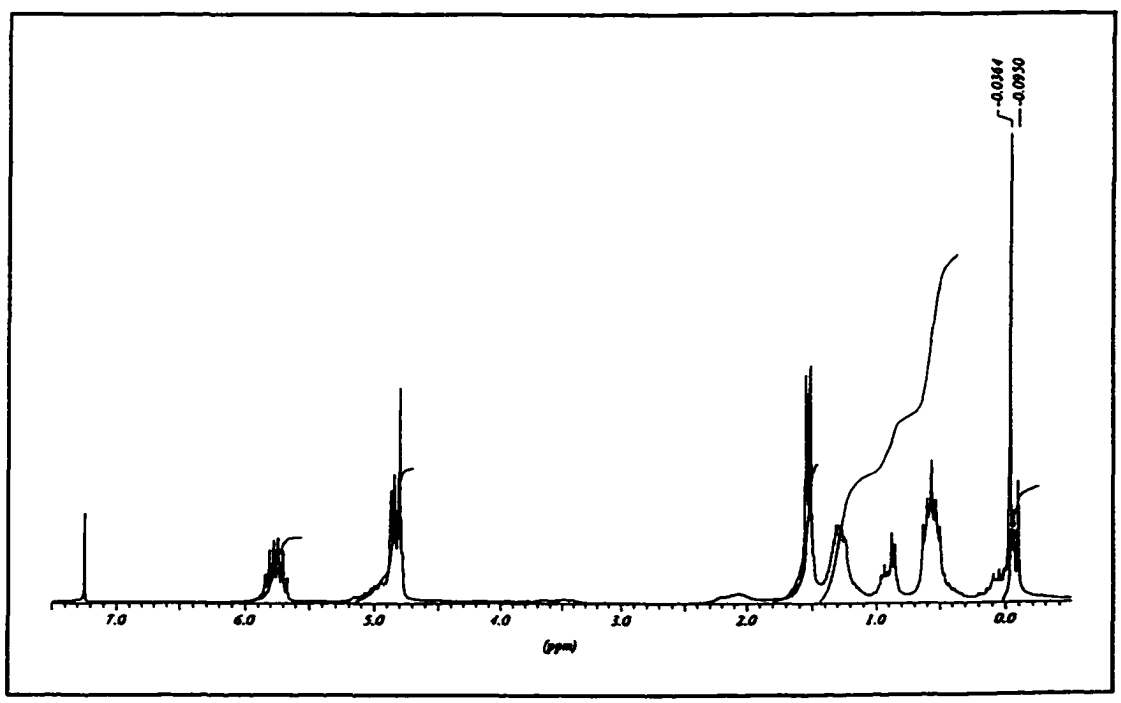


Figure 3.4 ^{1}H NMR spectrum of compound (49) Ge[(prSiMe)$^{2}_{2}$:All]$_4$

Similar to the trifurcate series (chapter two), a generational hierarchy exists in the ^{29}Si NMR spectra of the tetraallylgermane centred molecules. Distinct chemical environments for the first three generations are observed after which overlap of signals occurs for interior *Si*-Me groups, Table 3.7.

Table 3.7 ^{29}Si NMR Chemical Shifts of Spheroidal 2B Dendrimers

^{29}Si δ ppm	Internal	Si-CH_3
G(N)	Ge[(prSiMe)$^{N}_{2}$:All]$_4$	
(47) G(1)		0.23
(49) G(2)	0.72	0.24
(51) G(3)	1.02, 0.73	0.28
G(N)	Si[(prSiMe)$^{N}_{2}$:All]$_4$	
(59) G(1)	0.95	0.24
(61) G(2)	0.95, 0.70	0.24
G(N)	Ge[(etSiMe)$^{N}_{2}$:All]$_4$	
(63) G(1)		1.96

The ^{29}Si resonance of the vinyl germane compound **(63)** is observed further downfield relative to other molecules which have similar branch topology. This is attributed to the initial spacer unit (CH_2CH_2) in this system between the central germanium atom and the branch point silicon. This shorter linkage is probably deshielding the silicon nucleus at the

branch point, causing the signal to appear at a lower field than those compounds with the propyl ($CH_2CH_2CH_2$) spacer unit.

GPC chromatograms (Appendix B, page 306) were also recorded for the spheroidal germane derivatives in $CHCl_3$ solution. All compounds showed a major peak, implying that they are single compounds and not mixtures (Table 3.8), with a small amount (approximately 15%) eluting at a shorter retention time. The fractions that elute at shorter retention time are attributed to impurities that could not be removed from the major product fraction. A plot of retention time *vs* $\log_{10}M_w$ for the germanium centred molecules is shown in Figure 3.5. The linearity of this line implies that shell closure is complete and that each generation can be differentiated, similar to observations with the 2B trifurcate series (chapter two).

Table 3.9 GPC data for $Ge[(prSiMe)^N{}_2:All]_4$ carbosilane dendrimers in $CHCl_3$ solution

Compound	G(N)	M_w	$\log_{10}M_w$	Time (min)	Peak Width[a]
(47)	G(1)	741	2.869	11.30	± 0.15
(49)	G(2)	1749	3.243	11.00	± 0.15
(51)	G(3)	3765	3.576	10.60	± 0.15

[a] measured as the peak width at half height in minutes

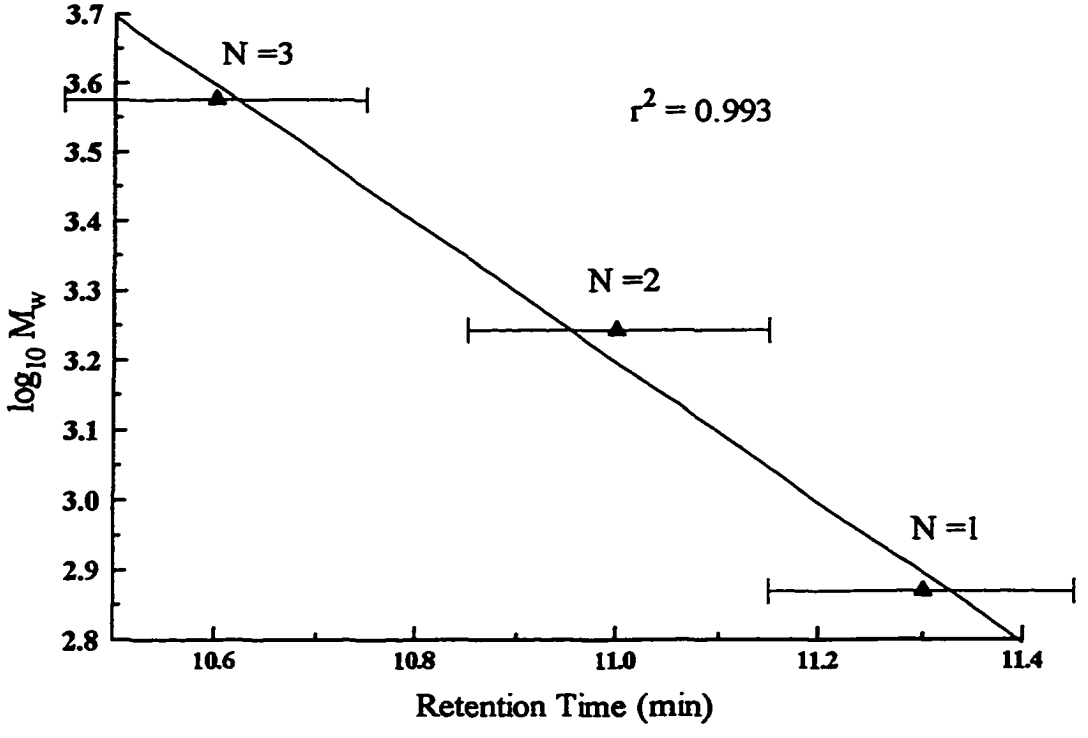
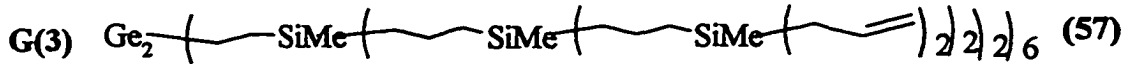


Figure 3.5 Plot of retention time *vs* $\log_{10}M_w$ for $Ge[(prSiMe)^N{}_2:All]_4$ dendrimers

3.2.1 Hexavinyldigermane Centred 2B Dendrimers

The hexavinyldigermane centred dendrimers that have been synthesised are shown on the following page, again using the established iterative hydrosilylation/alkenylation methodology.



$Ge_2[(etSiMe)^N{}_2:(prSiMe)^N{}_2:Cl/All]_6$ dendrimers synthesised

Selected spectral data for the allyl terminated compounds prepared *via* this route are highlighted in Table 3.9. Peripheral β-allyl resonances were used as the reference point for proton NMR integration as with the spheroidal germanes seen previously.

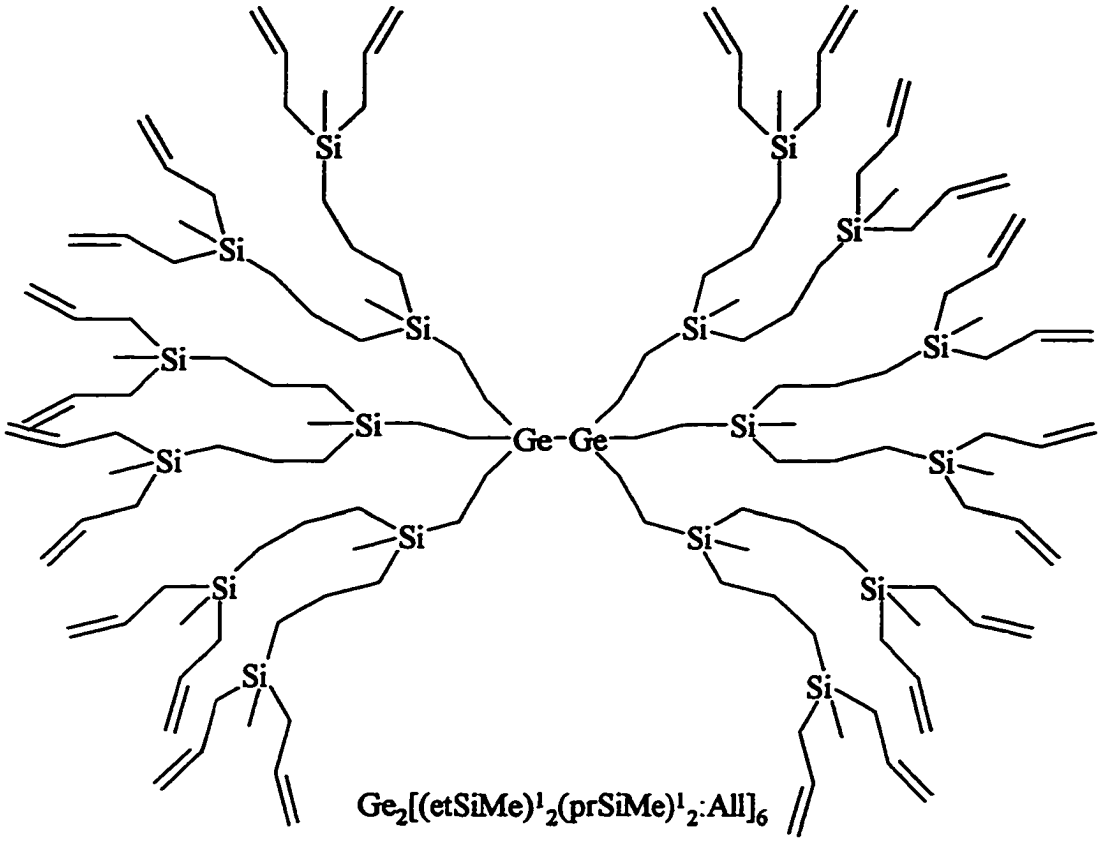
Table 3.9 Selected spectral data for $Ge_2[(etSiMe)^N{}_2(prSiMe)^N{}_2:All]_6$ dendrimers

^1H δ ppm	=CH	$=CH_2$	$Si-CH_3$
G(N)	5.75	4.80	δ ppm
(53) G(1)	(=12) *12H*	(24±2) *24H*	-0.02 (18±1.8) *18H*
(55) G(2)	(=24) *24H*	(48±5) *48H*	-0.03 (36±4) *36H* -0.07 (18±1.8) *18H*
(57) G(3)	(=48) *48H*	(96±9) *96H*	-0.03 (72±7) *72H* -0.05 (36±4) *36H* -0.07 (18±1.8) *18H*

Integration (Experimental) *Calculated*

G(N)	^{13}C δ ppm	$Si-CH_3$	^{29}Si δ ppm	$Si-CH_3$
(53) G(1)		-6.29		1.75
(55) G(2)		-5.70, -6.29		0.98, 0.23
(57) G(3)		-5.56, -5.70, -6.29		0.98, 0.23

For compound **(55)** the formula is written as $Ge_2[(etSiMe)^1{}_2:All]_6$, after this first generation the spacer units consist of propyl links and the formula becomes $Ge_2[(etSiMe)^1{}_2(prSiMe)^1{}_2:All]_6$ for **(55)** and $Ge_2[(etSiMe)^1{}_2(prSiMe)^2{}_2:All]_6$ for **(57)**. For the latter compound the formulation infers that after the initial ethylsilyl linkage, two more links are present both of which consist of propylsilyl units.



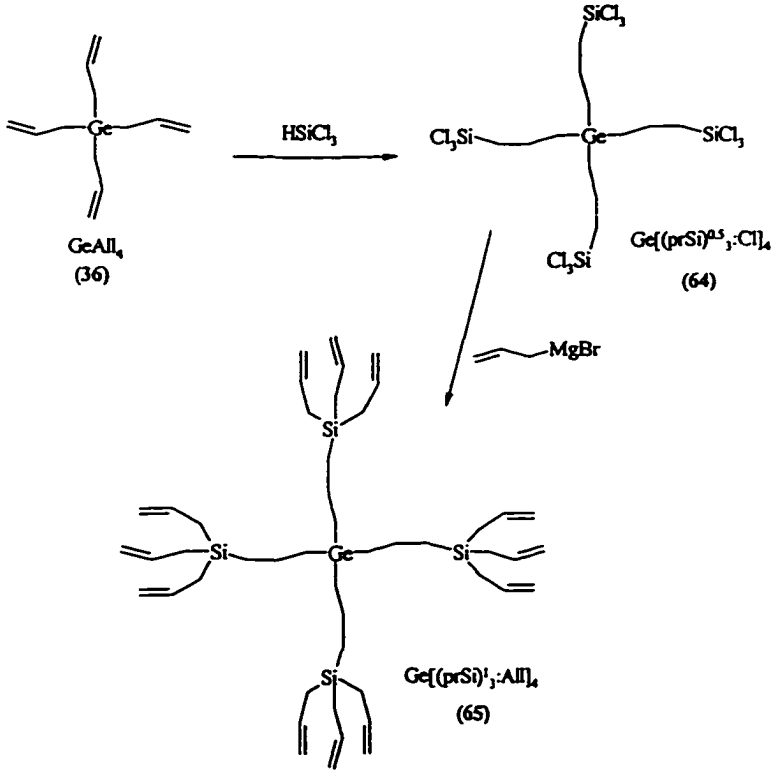
$Ge_2[(etSiMe)^1{}_2(prSiMe)^1{}_2:All]_6$

(55)

The relative proton integrations agree well for this 2B digermane series of compounds, there is little deviation from the calculated values. The proton chemical shift values show no difference from other compounds synthesised with an SiMe at the branch point. The ^{13}C NMR chemical shift values for these methylsilyl groups appear further upfield than in either the trifurcate (chapter two) or spheroidal analogues. This is attributed to the shorter linking unit (CH_2CH_2) for initial onset of dendritic growth compared to examples with a propyl spacer unit.

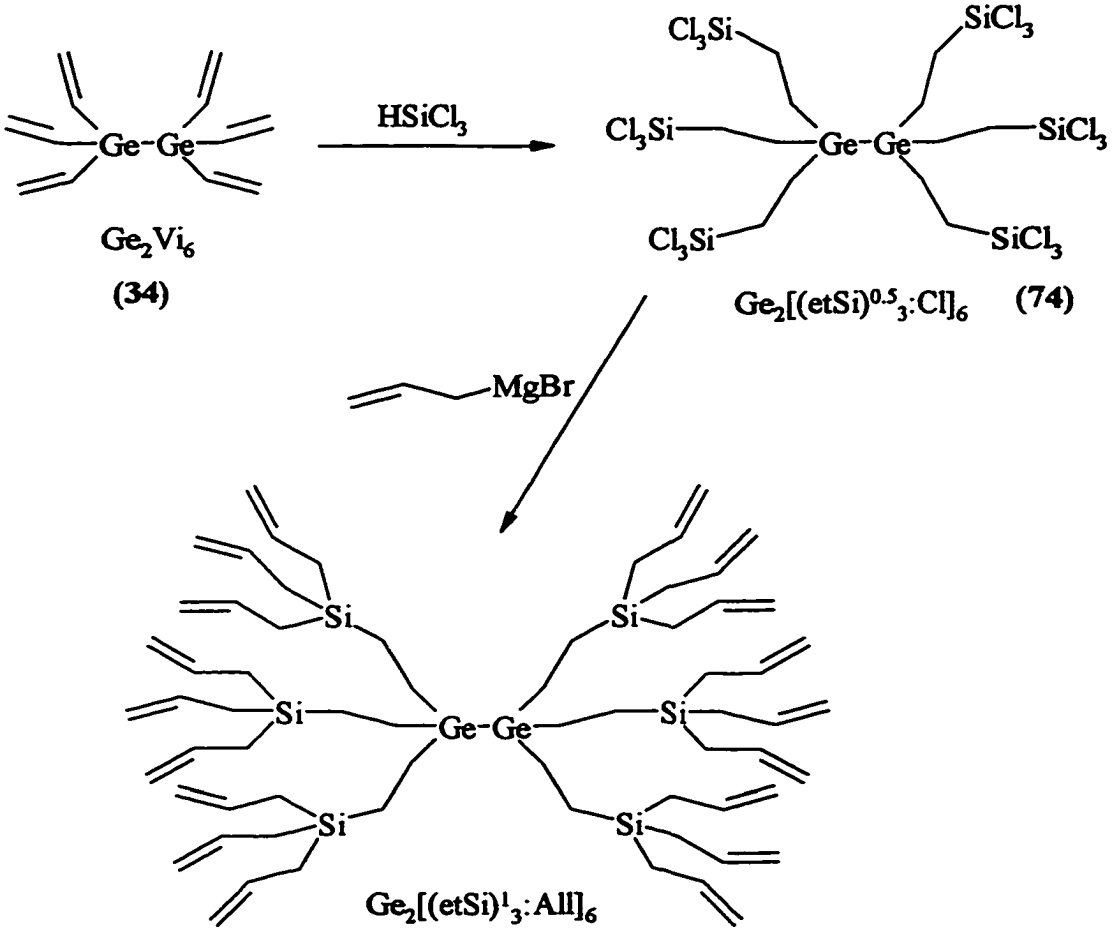
3.3 Three-Directional Branching (3B)

Carbosilane 3B dendrimers extended from phenyl triallylsilane have already been discussed in chapter two. The remainder of this chapter will examine the 3-directional branch site dendrimers based on different core molecules, and will relate the multinuclear NMR characteristics of these compounds to those of the trifurcate compounds. These tripropylsilyl (3B) branch points do not incorporate a unit that can be used for population analysis (end-group counting) by NMR integration.



3.3.1 Germanium based three branch point dendrimers

The synthetic methodology used for building each of these carbosilane dendrimers has been discussed previously. Use of trichlorosilane ($HSiCl_3$) during the hydrosilylation reaction gives branching in three different directions from the silicon centre. As seen earlier in this chapter, ^1H NMR and IR spectra were recorded on the intermediate trichlorosilyl derivatives; since no unsaturated resonances could be detected the reactions were judged to have gone to completion.

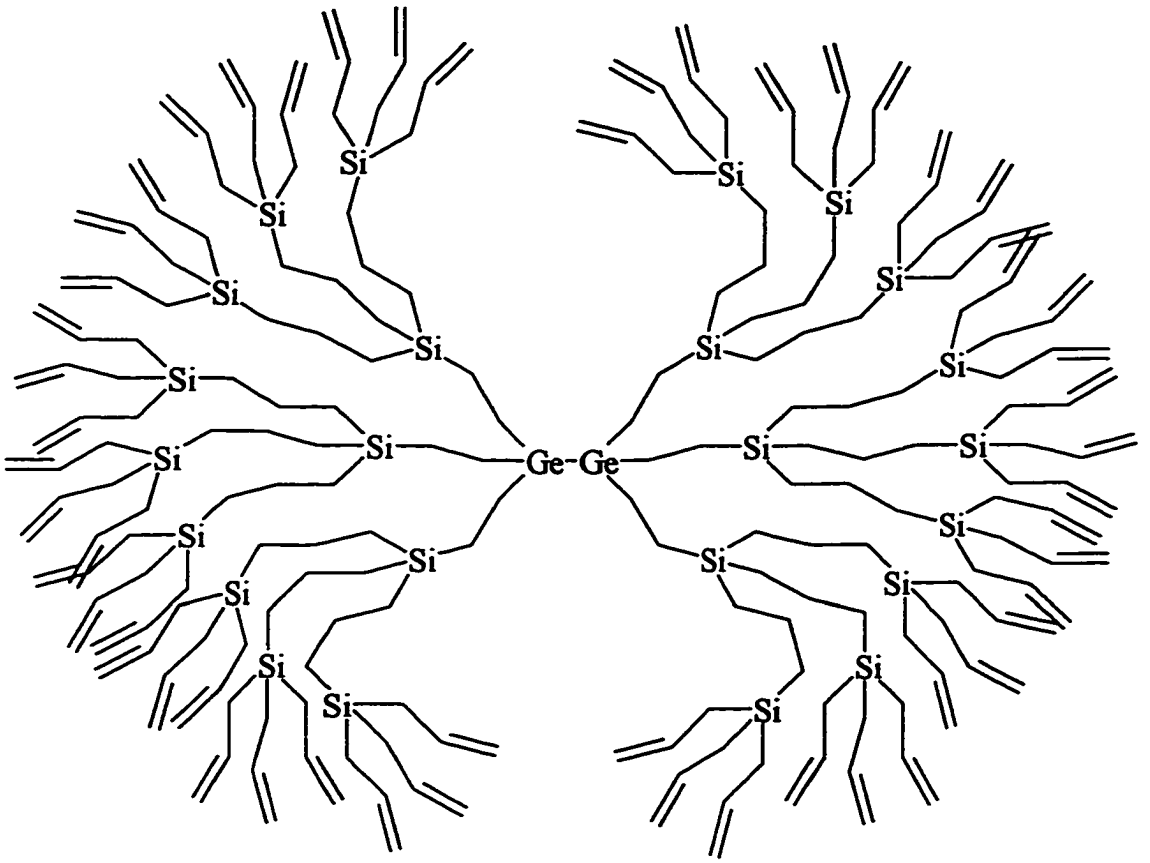


Ge_2Vi_6 (34)

$Ge_2[(etSi)^{0.5}{}_3{:}Cl]_6$ (74)

$Ge_2[(etSi)^1{}_3{:}All]_6$

(75)



$Ge_2[(etSi)^1_3:(prSi)^1_3:All]_6$ **(77)**

Some selected spectral data for the first five generations of the germanium centred dendrimers prepared in this manner are reported in Table 3.10, again peripheral β-allyl proton resonances were used as the reference point for proton NMR integrations. Also shown are some representative NMR spectra of the spheroidal germanium series.

Table 3.10 Selected spectral data for germanium centred G(N)3B dendrimers

^{1}H δ ppm		=CH	CH_2	^{29}Si δ ppm
G(N)		5.80	1.5-0.4	
	G(N)	$Ge[(prSi)^{N}_{3}:All]_4$		
(65)	G(1)	(=12) *12H*	(48±4.8) *48H*	-1.10
(67)	G(2)	(=36) *36H*	(168±17) *168H*	-0.37, -1.10
(69)	G(3)	(=108)*108H*	(528±53) *528H*	-0.37, -0.42, -1.10
(71)	G(4)	(=324) *324H*	(1608±161) *1608H*	0.14, -0.37, -0.42, -1.10
(73)	G(5)	(=972) *972H*	(4768±480) *4848H*	0.77, 0.14, -0.37, -0.42, -1.10

Integration (Experimental) *Calculated*

	G(N)	$Ge_2[(etSi)^{N}_{3}:(prSi)^{N}_{3}:All]_6$		
(75)	G(1)	(=18) *18H*	(60±6) *60H*	0.29
(77)	G(2)	(=54) *54H*	(240±24) *240H*	-0.37, -1.10
(79)	G(3)	(=162) *162H*	(754±75) *780H*	0.06, -0.37, -1.10
(81)	G(4)	(=486) *486H*	(2172±220) *2400H*	0.77, 0.14, -0.37, -1.10
(83)	G(5)	(=1458)*1458H*	(6446±650) *7260H*	0.77, 0.14, -0.37, -0.40, -1.10

Integration (Experimental) *Calculated*

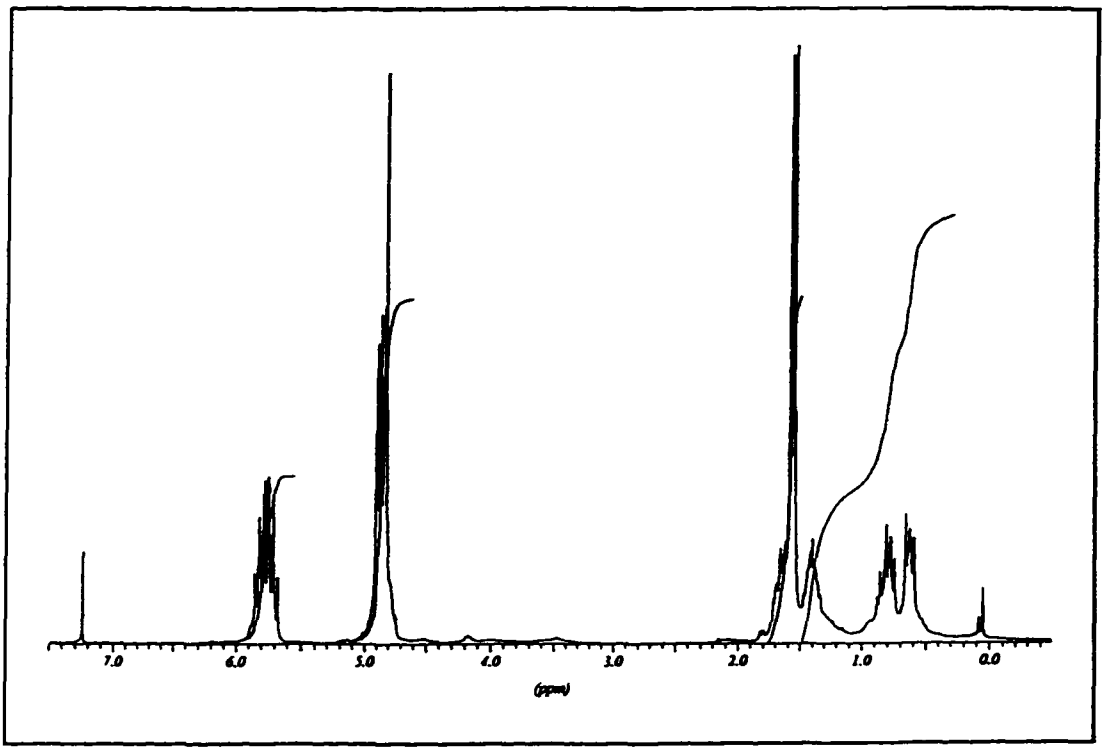


Figure 3.6 ^{1}H NMR spectrum of Ge[(prSi)$^{1}_{3}$:All]$_4$ (65)

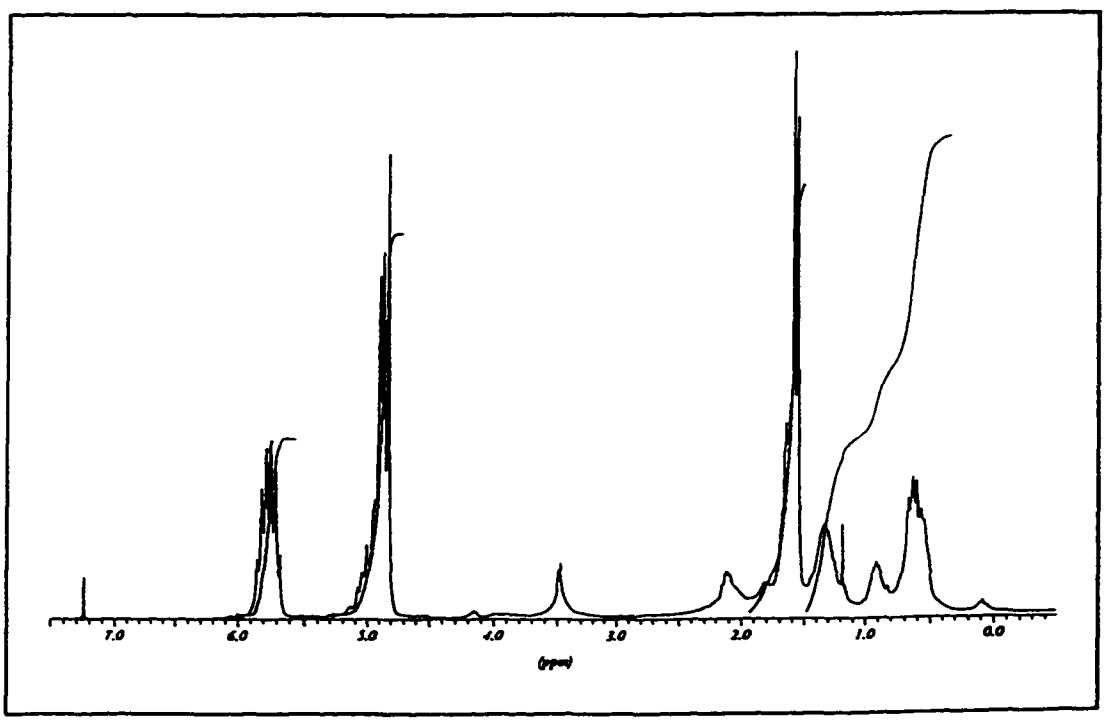


Figure 3.7 ^{1}H NMR spectrum of Ge[(prSi)$^{2}_{3}$:All]$_4$ (67)

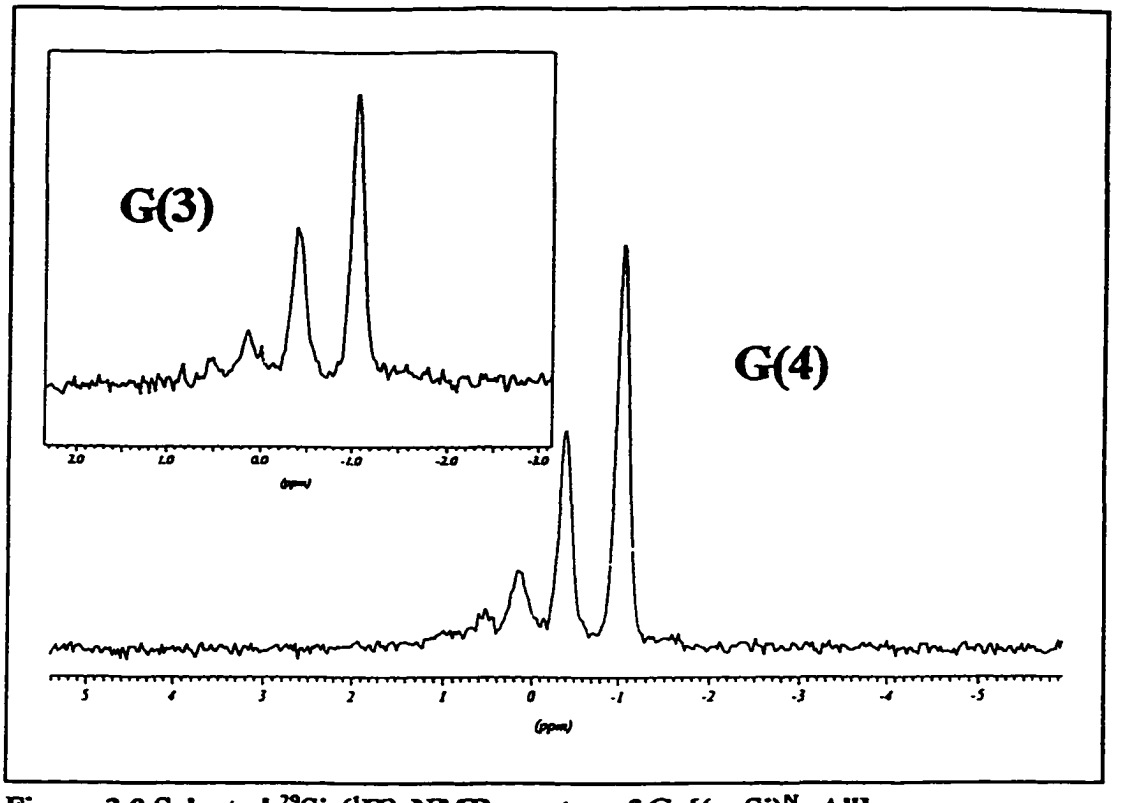


Figure 3.8 Selected ^{29}Si-{^{1}H} NMR spectra of $Ge[(prSi)^{N}_{3}:All]_{4}$

GPC chromatographs (Appendix B, page 306) of the tetraallylgermane series ($Ge(prSi)^{N}_{3}:All]_{4}$) were recorded in chloroform solution (calibrated against polystyrene standards). The retention times are reported in Table 3.11 and a plot of retention time *vs* the $\log_{10}M_{w}$ is shown in Figure 3.9. The first three generations analysed showed one major peak, and for the second and third generations there is a shorter retention time band that could not be removed. The fourth and fifth generations showed much broader chromatographs with a larger peak width at half height than previously observed. This could be attributed to a distribution of products that all have different masses which would arise from structurally incomplete shells and products with extra units added from coupling reactions of the

allylmagnesium bromide reagent, see page 27.[32]

Table 3.11 GPC data for Ge[(prSi)$^{N}_{3}$:All]$_4$ carbosilane dendrimers in $CHCl_3$

Compound	G(N)	M_w	$\log_{10}M_w$	Time (min)	Peak Width[a]
(65)	G(1)	845	2.927	10.90	± 0.12
(67)	G(2)	2669	3.426	9.15	± 0.18
(69)	G(3)	8141	3.911	8.00	± 0.15
(71)	G(4)	24557	4.390	6.95	± 0.60
(73)	G(5)	73805	4.868	5.80	± 0.60

[a] measured as the peak width at half height in minutes

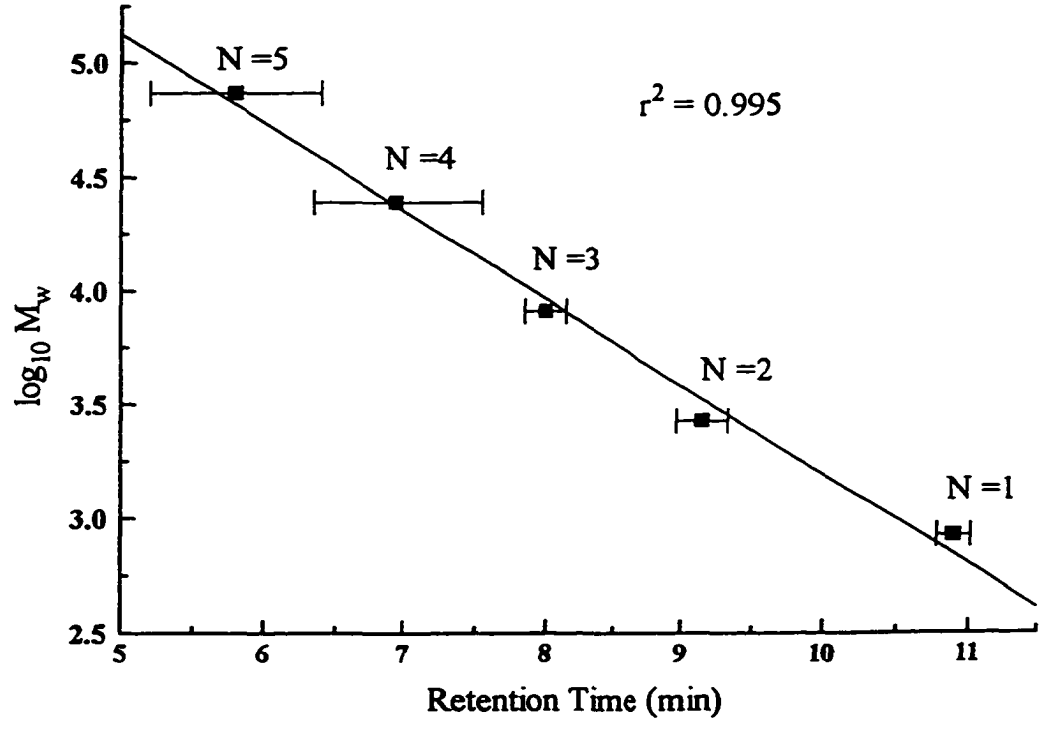


Figure 3.9 Plot of retention time *vs* $\log_{10}M_w$ for Ge[(prSi)$^{N}_{3}$:All]$_4$ dendrimers

Viscosity measurements on the first three generations for both $GeAll_4$ and Ge_2Vi_6 centred 3B dendrimer molecules were recorded in cyclohexane solution, Table 3.12. Other researchers have recorded the intrinsic viscosities of dendritic molecules[6, 27] and shown its use for calculating the hydrodynamic radius of the molecule (R_v). The viscosity of carbosilane dendrimers has been observed by Roovers[27] to reach a maximum at the fourth generation. This has been assigned as dense packing of the exterior of the dendrimer, which results in a lower viscosity after this generation number has been passed. Calculations of R_v for both series of compounds show that the digermanes have a larger radius compared to the spheroidal germanes. This is attributed to hexafunctional character building from a Ge-Ge bond which increases the radius of each generation in comparison to those with a tetraallylgermane core. $R_v = (3[\eta]M/10\pi N_A)^{1/3}$

Where $[\eta]$ is the intrisic viscosity, M the molecular mass and N_A is Avagadros constant

Table 3.12 Intrinsic viscosity data for germanium 3B carbosilane dendrimers

	G(N)	Nominal Mass	$[\eta]$ dLg^{-1}	R_v (Å)
		$Ge_2[(etSi)^N{}_3:(prSi)^N{}_3:All]_6$		
(75)	G(1)	1220	0.0120±0.005	6.14±0.1
(77)	G(2)	3956	0.0144±0.006	9.70±0.2
(79)	G(3)	12164	0.0208±0.009	15.9±0.4
		$Ge[(prSi)^N{}_3:All]_4$		
(65)	G(1)	845	0.0125±0.006	5.51±0.1
(67)	G(2)	2669	0.0182±0.008	9.13±0.3
(69)	G(3)	8141	0.0224±0.010	14.1±0.3

3.3.2 Other 3B Symmetrical Dendrimers

Two other research groups have used tetraallylsilane as a core molecule with trichlorosilane as the branch point silane and allylmagnesium bromide as the Grignard reagent.[28,32] The work summarised below (Table 3.13) repeats some of these results and all the data presented is in accord with these researchers findings; however neither of these two groups reported ^{29}Si chemical shift information. In both instances they only reported proton NMR data, mass spectroscopic results and elemental analyses.

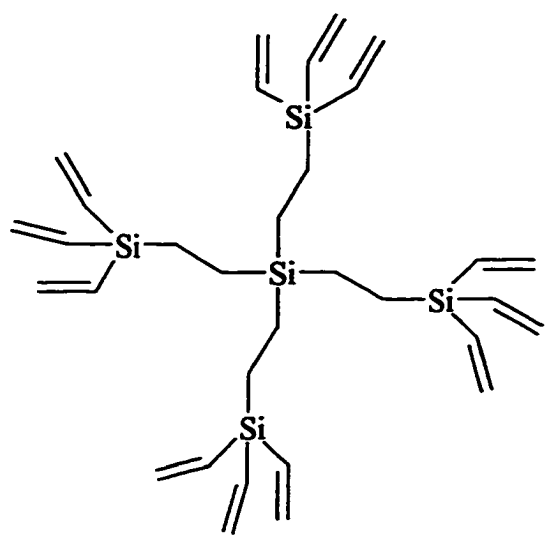
Table 3.13 Selected spectral data for spheroidal E[(pr/etSi)$^1_3$:All/Vi]$_4$ G(1)3B dendrimers

	^{1}H Integration		^{13}C δ ppm	^{29}Si δ ppm	
Compound	=CH-	CH_2	CH_2	Core	Term.
(85) Si[(prSi)$^1_3$:All]$_4$	(=12) *12H*	(24±0.5) *24H*	18.1, 16.5, 16.3	0.98	-1.10[28]
(87) Si[(etSi)$^1_3$:Vi]$_4$	(=12) *12H*	(16±0.4) *16H*	5.39, 3.89	10.07	-18.4[29]
(88) Si[(etSi)$^1_3$:All]$_4$	(=12) *12H*	(16±0.4) *16H*	4.24, 3.49	10.07	0.92
(90) Ge[(etSi)$^1_3$:All]$_4$	(=12) *12H*	(16±0.4) *16H*	5.27, 3.04		1.96

Integration (Experimental) *Calculated*

These first generation compounds were analysed by multinuclear NMR spectroscopy and the proton NMR data were found to be consistent with the formulations shown.

Interestingly there is a wide variety of silicon chemical shifts that appear to be dependant on the spacer unit and also on the nature of the peripheral group. When a saturated ethyl link is present between the core atom (*i.e.* Si or Ge) and the peripheral (*i.e.* allyl or vinyl) end groups the terminal silicon atom resonates at a lower frequency, δ -18.4 ppm for (87),[29] compared to those with propyl linkers as seen previously in this chapter. The central silicon signal is also influenced by the nature of the initial saturated link (CH_2CH_2 *vs* $CH_2CH_2CH_2$), the shorter spacer causes this signal to appear at a higher frequency (δ 10 ppm) than has been observed in the propyl examples. This downfield shift, as noted in section 3.2, page 106, is caused by desheilding of the silicon nucleus by the shorter linking unit.

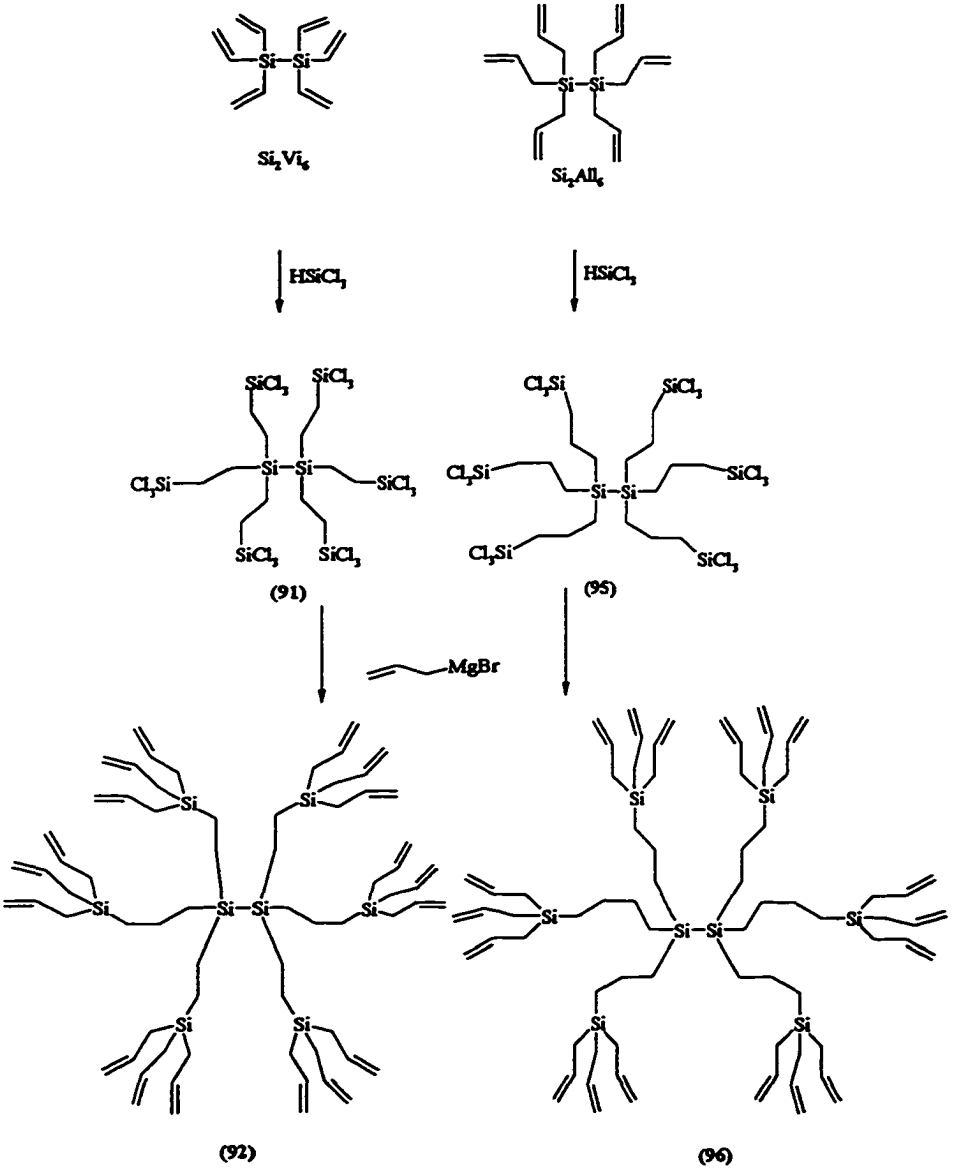


$Si[(etSi)^1_3:Vi]_4$

(87)

3.4 Other Core Molecules

Two other hexafunctional core molecules have been synthesised,[64] hexaallyldisilane (Si_2All_6) and hexavinyldisilane (Si_2Vi_6), and for both cases two generations of 3B branch site shells have been prepared. These two core molecules may be viewed in a similar manner to the digermane core, dendritic growth in two adjacent trifurcate domains, Scheme 3.3.



Scheme 3.3 Synthesis of disilane dendrimers $Si_2[(et/prSi)^1_3:All]_6$

As with the digermane centre there is the possibility for core substitution chemistry *via* Si-Si bond cleavage.[64] Chemical shift values observed in both ^{1}H and ^{29}Si NMR spectra, together with the relative proton integration, are reported for these allyl terminated compounds in Table 3.14.

Table 3.14 Selected NMR data for disilane dendrimers $Si_2[(et/prSi)^{N}_{3}$:All$]_6$

	=CH-	CH_2	^{29}Si δ ppm
Si_2Vi_6			
(92) G(1)	(=18) *18H*	(24±0.8) *24H*	0.75, -4.80_{core}
^{1}H δ ppm	5.75	0.6-0.3	
^{13}C δ ppm	134.4	4.89, 4.23	
(94) G(2)	(=54) *54H*	(132±4) *132H*	-0.40, -1.10, -4.98_{core}
^{1}H δ ppm	5.75	1.4-0.5	
^{13}C δ ppm	134.4	18.1, 16.7, 16.3	
		11.6, 0.98	
Si_2All_6			
(96) G(1)	(=18) *18H*	(36±1) *36H*	-1.10, -14.4_{core}
^{1}H δ ppm	5.75	1.4-0.5	
^{13}C δ ppm	134.3	18.5, 17.8, 17.3	
(98) G(2)	(=54) *54H*	(144±4) *144H*	-0.40, -1.10, -14.4_{core}
^{1}H δ ppm	5.75	1.4-0.5	
^{13}C δ ppm	134.3	18.5-17.8, 17.3	

Integration (Experimental) *Calculated*

The ^{29}Si chemical shifts of the *Si-Si* link are further upfield in comparison to data obtained from tetrahedral silane centres (spheroidal) and trifurcate centres. Once saturated the *Si-Si* signals resonate further downfield than in the original precursor molecules, *i.e.* Si_2All_6 δ -16.8 ppm and Si_2Vi_6 δ -35.0 ppm. This has also been observed in examples with phenylsilane as the central core (chapter two) and diphenylsilane at the core, and these saturated *Si-Si* resonances remain at the same frequency as dendritic growth begins. The vinyl derivative G(1) **(98)** shows a different initial chemical shift for the exterior silicon (see section 3.3, page 121), which relocates to an upfield position after the second generation has been isolated in a similar manner to the hexavinyldigermane series (2B or 3B).

3.5 Summary

For various spheroidal (or hexafunctional) carbosilane morphologies (1B, 2B or 3B), proton NMR spectroscopy has been shown by using selected signals (Si-*Me* or =C*H*) as a reference point for integration purposes to provide results analogous to those presented in chapter two. The advantage of using an NMR active heteroatom as the branch point in the dendrimer structure has been shown to lead to structural correlation between different topologies. Silicon NMR chemical shift data collected for these compounds have been used to demonstrate 'shell' hierarchy in dendrimeric molecules synthesised from high symmetry

core structures. In the 2B spheroidal series it is possible to use ^{1}H NMR integration of interior Si-*Me* signals *vs* periphery groups for end-group counting, but clearly this is not possible with the 3B analogues. A further interesting observation is that in the 2B spheroids, generational (hierarchical) dispersion is observable in Si-Me signals in both ^{1}H and ^{13}C NMR spectra.

Where there is no experimental evidence *via* proton NMR integration (3B dendrimers), the GPC chromatographs proved invaluable for a measure of polydispersity. The GPC data collected for various derivatives are analogous to those for the trifurcate series (chapter two); plots of retention time *vs* $\log_{10}M_w$ are linear which implies complete shell closure, *i.e.* that each reaction was completed as expected.

The ^{29}Si NMR chemical shift for first generation systems derived from vinyl-element cores shows a resonance shifted further downfield (δ 1.9 ppm) from those observed for analogous allyl based structures (δ -1.1 ppm). However, addition of a second 'layer' of silicon branches moves this resonance towards an upfield position, (*i.e.* similar chemical shift values to those reported in chapter two), as well as for propyl spaced spheroidal dendrimers.

CHAPTER FOUR

CORE AND PERIPHERAL GROUP MODIFICATION

As shown previously, divergent hyper branching, using the now well established iterative methodology, has been employed to extend dendritic structures for both trifurcate systems $PhSiD_3$ (D = carbosilane monodendron) and the related digermanes ($D_3Ge_2D_3$). This has led to the formation of various topologies that have been characterized by multinuclear NMR spectroscopy. In this chapter, substitution of the residual core functionality, by either Ph-Si bond scission[62] or by Ge-Ge cleavage,[72] is shown to provide a useful route to a range of new compounds with bifunctional characteristics.

The interest in forming dendrimer systems for new applications such as micelle mimics,[73] NMR imaging agents,[74] nano-antenna,[60] and drug delivery systems[75] has led to a large body of research devoted to exterior functionalisation,[3] *i.e.* substitution of peripheral groups at the outermost 'shell'. Exterior substitution of this type may also help to adapt the molecules for more facile characterization *via* conventional techniques. For example, as seen in work by Frey[32] *et al*, substitution of the exterior of carbosilane dendrimers by poly-ol functions has led to characterization by MALDI-TOF mass spectrometry. The latter technique has been shown by Tomalia,[3] as well as Frey, to be able to detect defects caused by missing groups in what would otherwise be assumed to be complete shells.

By contrast substitution of the non-dendritic group of a trifurcate system, see chapter two, has been explored in only a very few systems. Gossage[80] in this laboratory selectively replaced the phenyl core of an ethyl terminated model dendrimer ($Ph[(prSiMe_2)^1{}_3{:}CH_2CH_3]_3$) *via* triflate cleavage and substitution with an anthracenemethoxy group. Polyallylcarbosilane dendrimers that contain a pyrene group at the core atom have been examined by Muzafarov[76] *et al*; however, these were not prepared by the core substitution route described above.

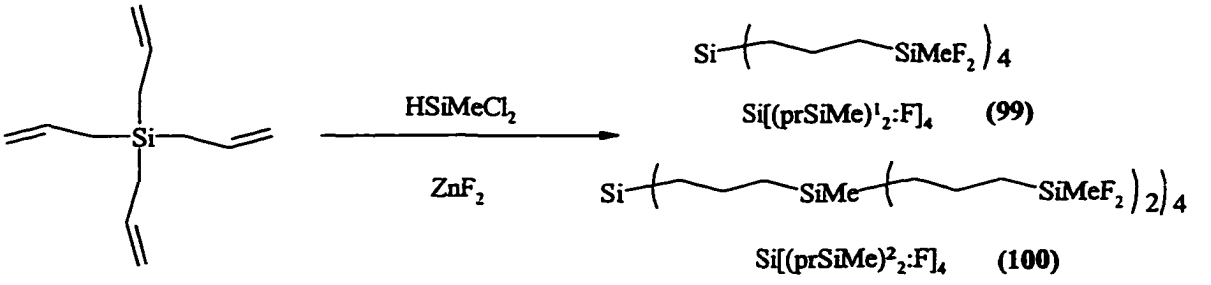
Two series of dendrimers introduced in chapters two and three of this thesis, $PhSiD_3$ and $D_3Ge_2D_3$, offer a choice of either interior or exterior substitution and this chapter will focus on both peripheral functionalisation for 'end-group' counting and surface behaviour,[63] and core substitution chemistry for bifunctional applications.

4.1 Peripheral Substitution

Carbosilane dendrimers can be transformed into structures that contain highly reactive peripheral Si-Cl bonds, *e.g.* formed as intermediates from hydrosilylation reactions. These chlorosilyl bonds can then undergo nucleophilic substitutions with a range of different peripheral groups. The development of allyl (or vinyl) exteriors has already been reported by others[27-32] and in this thesis (chapters two and three).

4.1.1 Fluorosilyl Peripheries

Using compounds previously investigated in chapter three, terminal chlorosilyl groups extended from a tetrahedral silane core can be converted by using zinc fluoride to quantitatively yield compounds **(99)** and **(100)**, as outlined in Scheme 4.1 . These two compounds have been analysed by multinuclear NMR spectroscopy as highlighted in Table 4.1.



Scheme 4.1 Synthesis of Si-F terminated dendrimers

Table 4.1 Selected NMR data for compounds (99) and (100) Si[(prSiMe)$^{N}_{2}$:F]$_4$

		^{1}H δ ppm	^{13}C δ ppm	^{29}Si δ ppm	^{19}F δ ppm
(99)	G(1)	1.45[a] (8±0.8) *8H*	17.9[b]		
		0.85(8±0.8) *8H*	16.2		
		0.59(8±0.8) *8H*	15.9	1.10 (Si_{core})	
		0.30[a] (=12) *12H*	-4.14[c]	3.40[d] (SiF_2)	-135.4
(100)	G(2)	1.45[a] (16±1.6) *16H*	17.9[b]		
		1.00-0.00 (72±7.2) *72H*	17.9-16.3	1.95 (Si_{core})	
		0.29[a] (24±2.4) *24H*	-4.09	1.26 ($Si\text{-}CH_3$)	
		-0.07 (=12) *12H*	-5.34[c]	3.45[d] (SiF_2)	-135.4

[a] $^{3}J_{HF} = 6.5$ Hz [b] $CH_2\ ^{2}J_{CF} = 14.3$ Hz [c] $CH_3\ ^{2}J_{CF} = 16.2$Hz [d] $^{1}J_{SiF} = 300$ Hz

Both of these fluorosilyl terminated compounds exhibit some interesting but predictable coupling patterns, see Table 4.1 and also in the NMR spectra shown as Figures 4.1-4.3. Coupling of the fluorine to the silicon centre gives a coupling constant of 300 Hz which is comparable to other known Si-F compounds,[65] with the other smaller splitting patterns arising due to the SiF_2 coupling to adjacent carbons and protons.

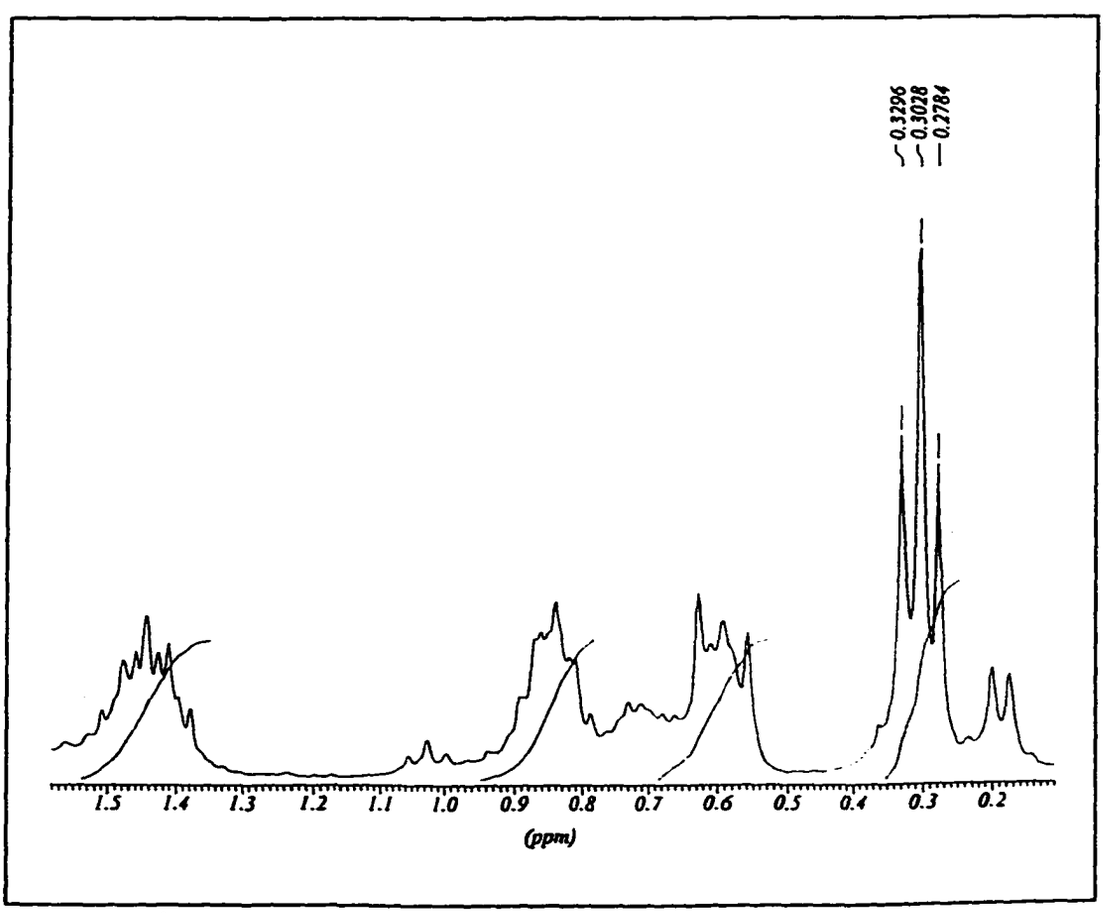


Figure 4.1 ^{1}H NMR spectrum of Si[(prSiMe)$^1_2$:F]$_4$ compound (99)

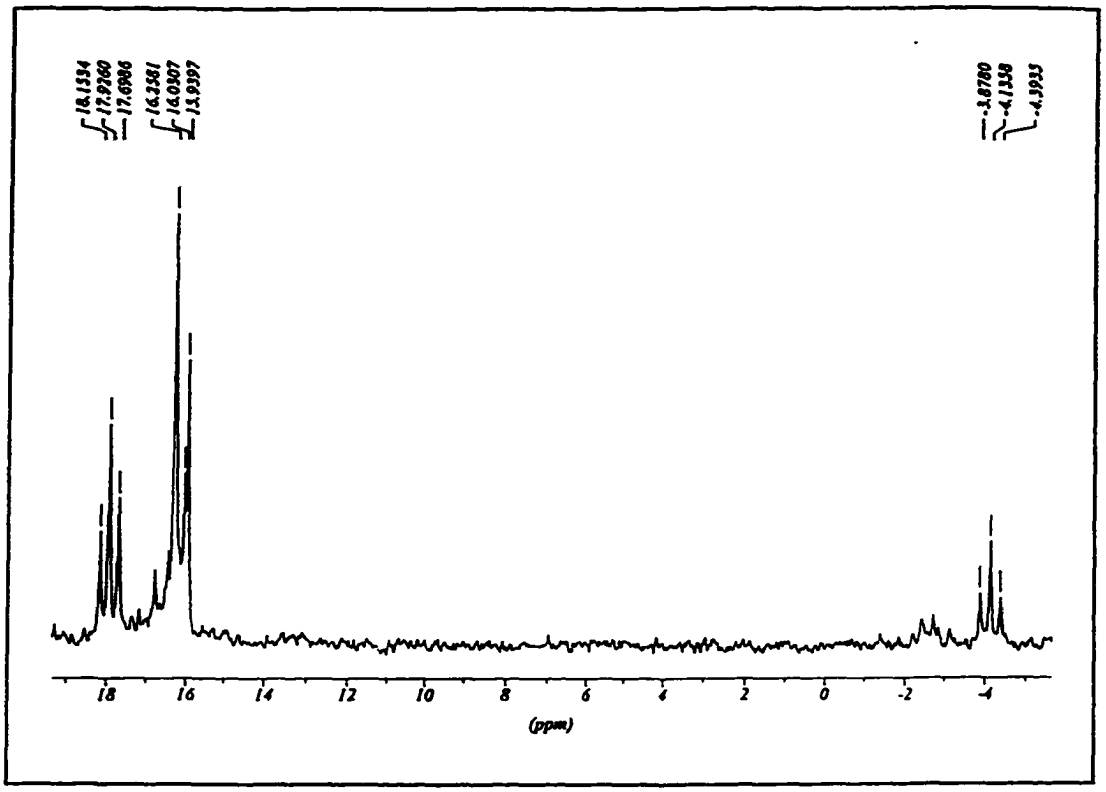


Figure 4.2 ^{13}C-{^{1}H} NMR spectrum of Si[(prSiMe)$^{1}_{2}$:F]$_4$ compound (99)

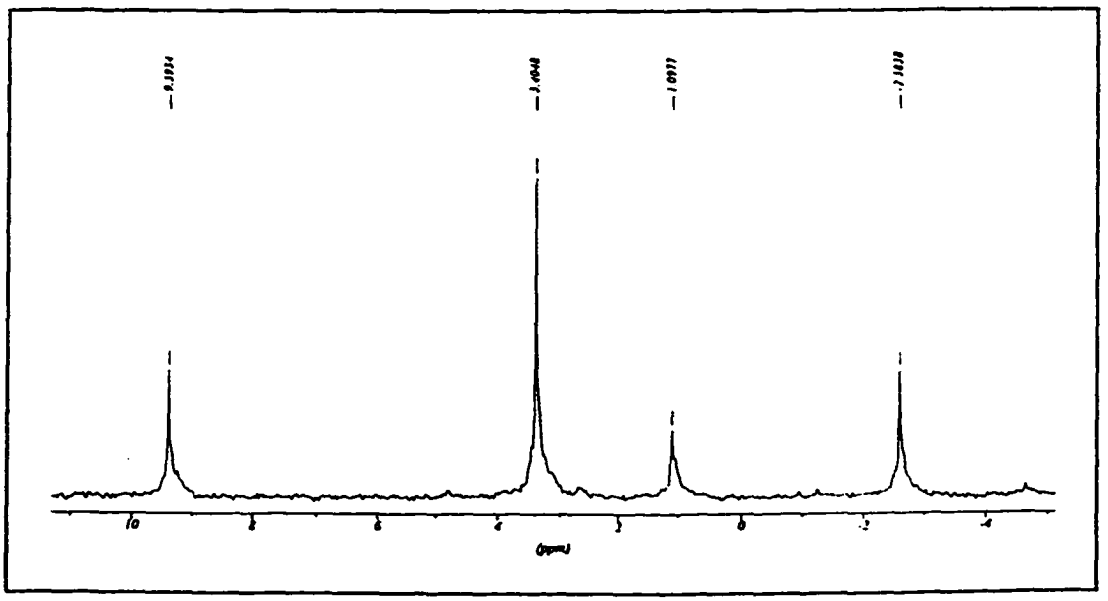
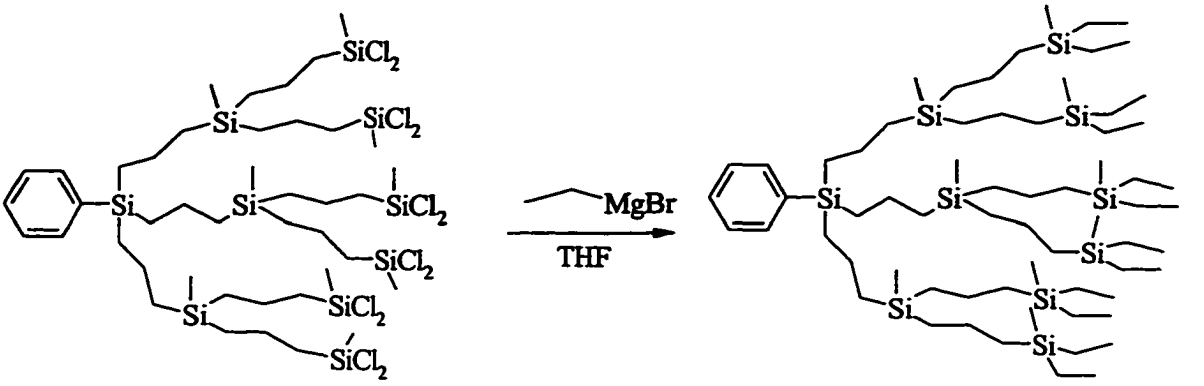


Figure 4.3 ^{29}Si-{^{1}H} NMR spectrum of Si[(prSiMe)$^{1}_{2}$:F]$_4$ compound (99)

The core silicon resonates at a position further downfield in the second generation than in the first generation, as does the internal *Si*-Me signal (*vs* other spheroidal 2B compounds referred to in chapter three) which is probably an effect of the more electronegative fluorine atoms at the periphery. Both of these fluorine terminated compounds have been adsorbed onto either an iodine monolayer on Pt or a platinum surface and studied by LEED spectroscopy by Mr Scott Furman of this university in an effort to try to ascertain the size of these molecules by forming a monolayer of the dendrimer onto the surface.[63]

4.1.2 Ethyl Terminated Dendrimers

Substitution of the dendrimer periphery with ethyl groups was accomplished using similar methodology to that established in chapters two and three to introduce alkenyl group exteriors, *i.e.* nucleophilic Grignard displacement of Si-Cl. This saturated exterior is not useful for further dendrimer growth but its use as a protecting group will be important later in this chapter. The synthesis of a second generation trifurcate system is seen in Scheme 4.2; the ^{1}H NMR spectrum (Figure 4.4) also shows some residual THF that could not be removed from this compound and selected spectroscopic data are listed in Table 4.2.



$PhSi[(prSiMe)^2_2:Cl]_3$ (14)

$PhSi[(prSiMe)^2_2:Et]_3$ (101)

Scheme 4.2 Synthesis of an ethyl terminated dendrimer

Table 4.2 Selected spectroscopic data for compound (101) $PhSi[(prSiMe)^2_2:Et]_3$

	Ph	CH_2	Si-CH_3
^1H δ ppm	7.5-7.3 (=5) *5H*	1.5-0.4 (124±12) *114H*	0.04--0.12 (33±3) *27H*
^{13}C δ ppm	134.0, 128.5	19.4-17.5	-4.33, -5.01, -6.09
	127.6	7.46 (CH_3) 5.66 (CH_2)	
^{29}Si δ ppm	4.85 (SiEt)	0.97 (Si-CH_3)	-4.08 (Ph-Si)
MS (EI)	1219 (M^+), 1190 (M-Et), 1165 (M-Et_2), 1150, 1142, 1113.....		

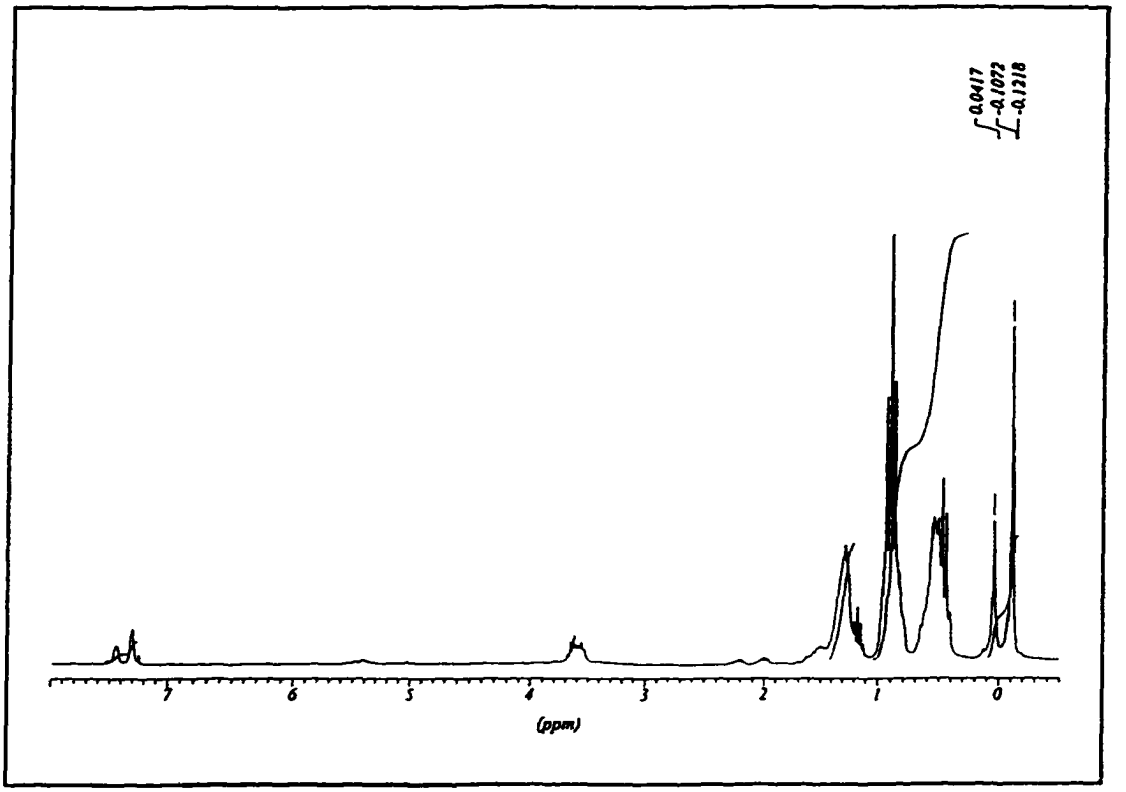


Figure 4.4 ^{1}H NMR spectrum of compound (101) $PhSi[(prSiMe)^{2}_{2}:Et]_{3}$

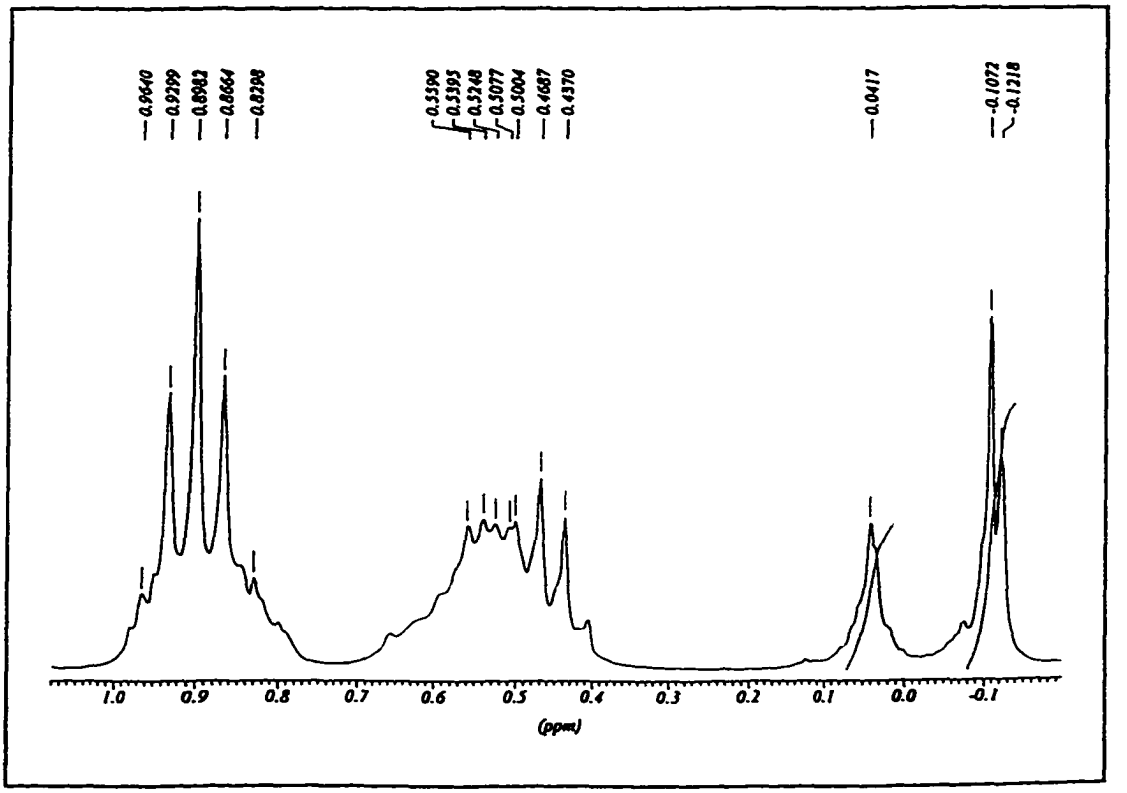
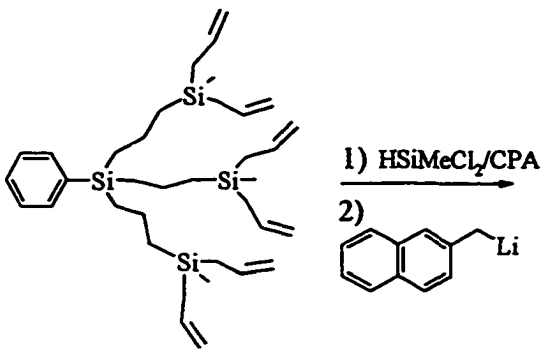


Figure 4.4a Enlargement of Figure 4.4, upfield region

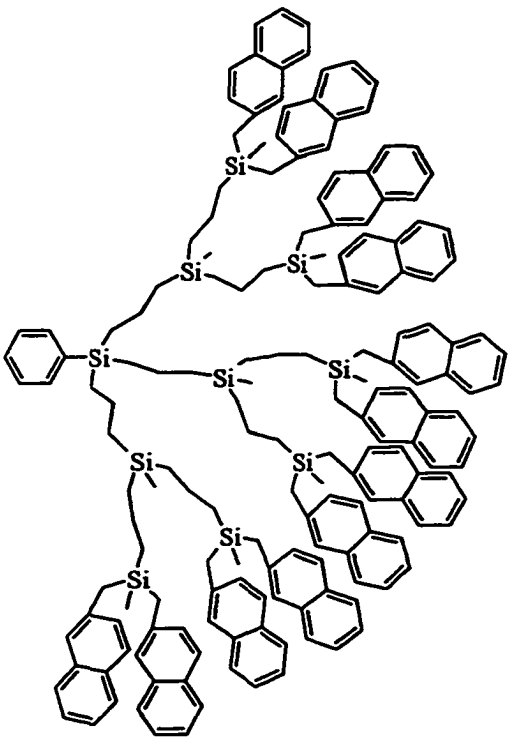
Analysis of the proton NMR spectrum indicates the presence of ethylsilyl groups; the triplet and quartet (δ 0.90 and 0.45 ppm respectively, $^{3}J_{HH}$ = 8Hz) that appear due to the ethyl resonance are at similar chemical shifts to those observed for tetraethyl silane.[65] This is attributed to the silicon centre being electropositive and so the methylene protons appear further upfield than the methyl protons (in comparison to compounds with ethyl groups attached to a carbon centre). The exterior silicon methyl resonances which are found further downfield than corresponding interior methyls in allyl terminated dendrimers (chapter two), are instead to low field of the interior Si-*Me* signals in the new poly-ethyl systems; here the exterior groups (δ -0.11, -0.12 ppm) appear as two signals, possibly due to chain entanglement. The resonances are further upfield than the inner Si-*Me* signal (at δ 0.04 ppm) and integrate in a 1:2 ratio as calculated for interior *vs* exterior methyl groups (9:18). The carbon NMR spectrum also shows the methylene and methyl carbons reversed in frequency as determined by ^{13}C-{^{1}H} DEPT spectroscopy: these features are typical for group 14 ethyl signals (Si, Ge and Sn). The silicon NMR shows three peaks at positions anticipated for ethyl, methyl and phenyl substituted silicon atoms.[65] Mass spectroscopy showed a weak molecular ion at 1219 amu, with successive loss of methyl, ethyl and various alkyl fragments also observed.

4.1.3 2-Methylnaphthalene Terminated Dendrimers

Formation of methylnaphthyl terminated dendrimers was accomplished by reaction of the chlorosilyl group with the appropriate organolithium reagent as shown in Scheme 4.3. The lithium salt formed from 2-methylnaphthalene is deep red in solution (hexanes) and after slow addition of the chlorosilyl dendrimer this colour slowly turns yellow. The product was isolated as an oil which appeared to have some residual hexanes incorporated into the interior of the molecule which could not be removed. This affects the alkyl integration in the proton NMR spectrum reported in Table 4.3, but the integration of peripheral naphthyl groups to interior methyl signals is as expected.



$PhSiAll_3$ G(1)2B
(13)



$PhSi[(prSiMe)^2_2:2\text{-}CH_2(C_{10}H_7)]_3$ (102)

Scheme 4.3 Synthesis of a 2-methylnaphthyl terminated dendrimer

Table 4.3 Selected spectroscopic data for compound (102)

$PhSi[(prSiMe)^2_2:2\text{-}CH_2(C_{10}H_7)]_3$

	Naphthyl/Ph	NaphthylCH_2	CH_2	Si-CH_3
^1H δ ppm	7.8-7.3	2.53	1.6-0.4	-0.05, -0.07
	(89±9) *89H*	(23±2) *24H*	(90±9)*54H*	(=27) *27H*
^{13}C δ ppm	135.3-124.9	26.7, 26.2	21.7-16.1	-5.07 ppm
^{29}Si δ ppm	2.67, 2.38 (Si-CH_2Naph)		1.77, 1.14 (Si-CH_3)	-3.90 (Ph-Si)
MS (EI)	1643, 1559, 1480, 1450, 1302, 1159, 1017.			

The ^1H NMR spectrum of this naphthyl terminated compound, shown in Figure 4.5, clearly shows the peripheral naphthyl groups (δ 8.0-7.3 ppm) but the phenyl resonance is obscured by the larger population of naphthyl aromatic signals. The methylene link to the peripheral silicon methyl group is observed (δ 2.53 ppm) as a singlet, which importantly offers another integration signal for end group counting (*i.e.* $C_{10}H_7$:$SiCH_2$:$SiCH_3$); in the ^{13}C NMR (Figure 4.6) the same group appears at δ 26.7 and 26.2 ppm (δ 21.7 ppm in the starting material). The silicon methyl resonances reported in the proton NMR are in similar positions to those observed in dendrimers with alkenyl end groups (*i.e.* chapters two and three), with the exterior *Si*-Me signal observed further downfield than the interior resonances; only the terminal methylsilyl group is resolved in the ^{13}C NMR spectrum.

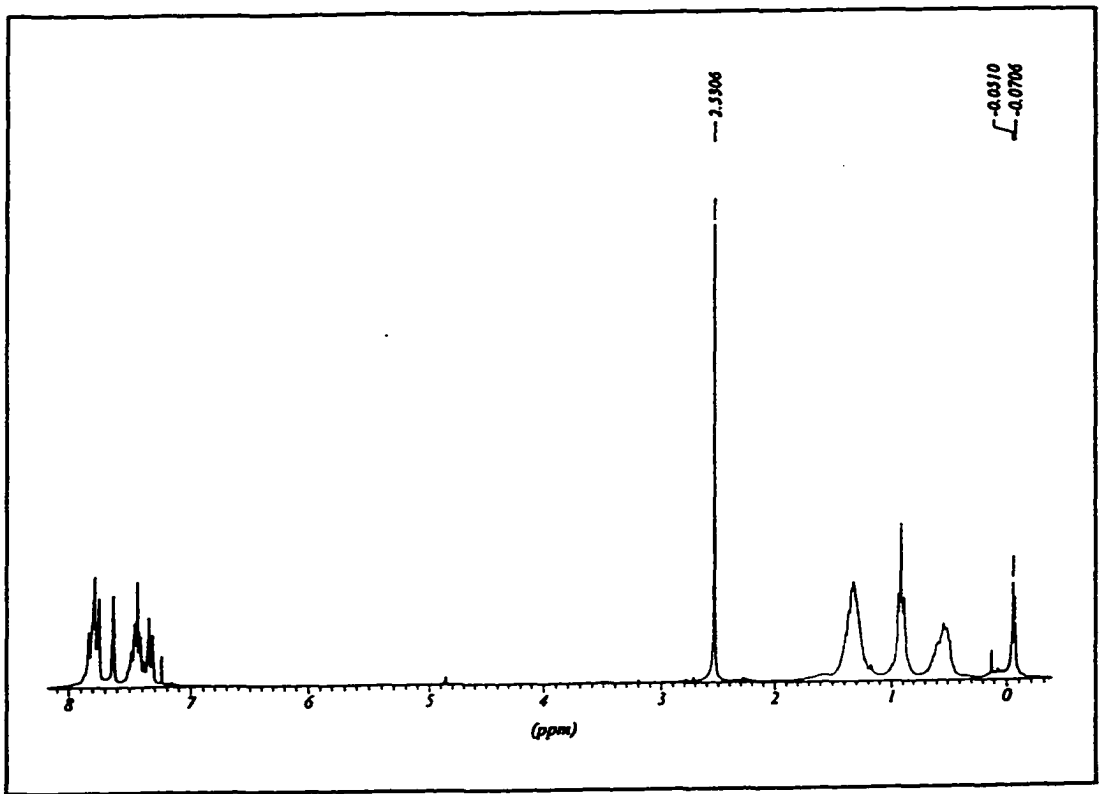


Figure 4.5 ^{1}H NMR spectrum $PhSi[(prSiMe)^{2}_{2}:2\text{-}CH_{2}(C_{10}H_{7})]_{3}$ (102)

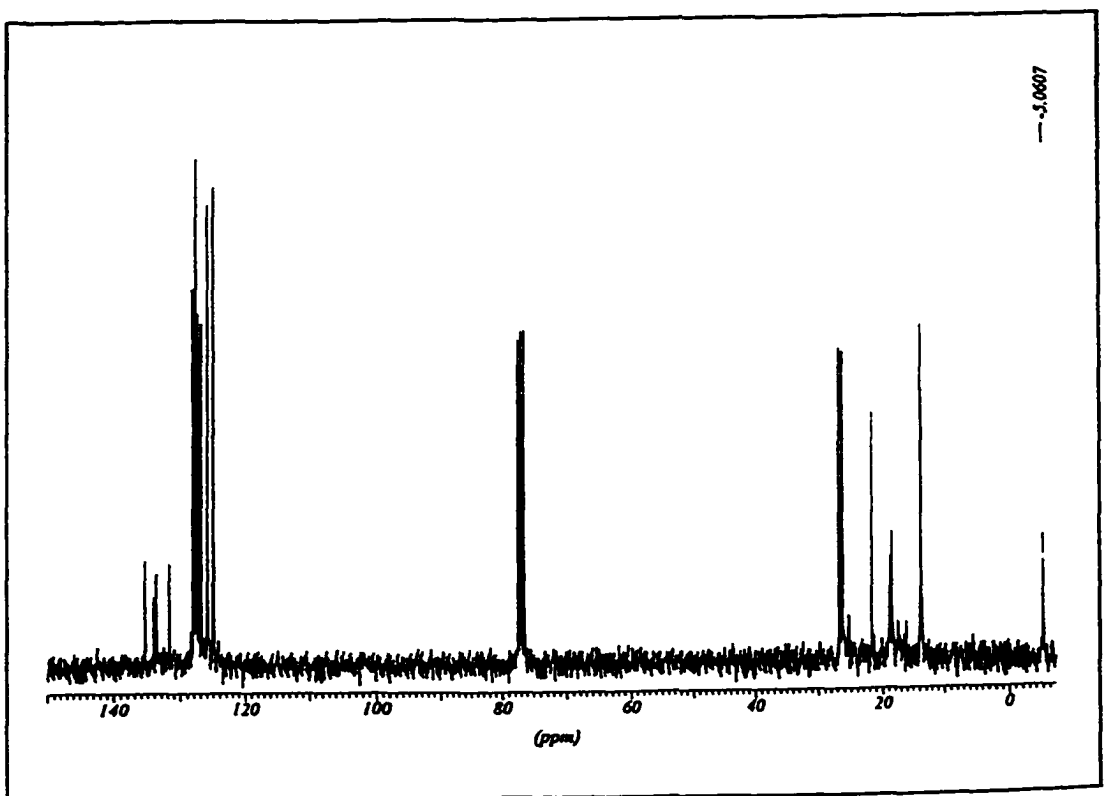


Figure 4.6 ^{13}C-{^{1}H} NMR spectrum of $PhSi[(prSiMe)^{2}_{2}:2\text{-}CH_{2}(C_{10}H_{7})]_{3}$ (102)

The silicon NMR spectrum (Figure 4.7) shows the peripheral silicon as a sharp resonance at δ 2.38 ppm, the interior silicon methyls at δ 1.77 and 1.14 ppm, and the silicon phenyl at δ -3.90 ppm. The interior *Si*-Me signals are observed as separate peaks, as was seen previously in other second generation dendrimers (chapters two and three) where chain entanglement was suggested as a possible cause. Here, steric constraints imposed by the methylnaphthyl groups may be inhibiting free rotation of the interior methylsilyl groups. Mass spectroscopy of the poly-naphthyl compound did not yield a molecular ion but did show patterns which are interpreted as fragmentation resulting from loss of methyl (15 amu), propyl (42 amu) and naphthyl (120 amu) groups. The UV-visible spectrum of the naphthyl terminated compound shows a strong absorptions at 227 nm ($\varepsilon = 1.8 \times 10^5$) and 275 nm ($\varepsilon = 4.5 \times 10^4$), both of which are assigned as 2-methylnaphthalene π-π^* transitions.

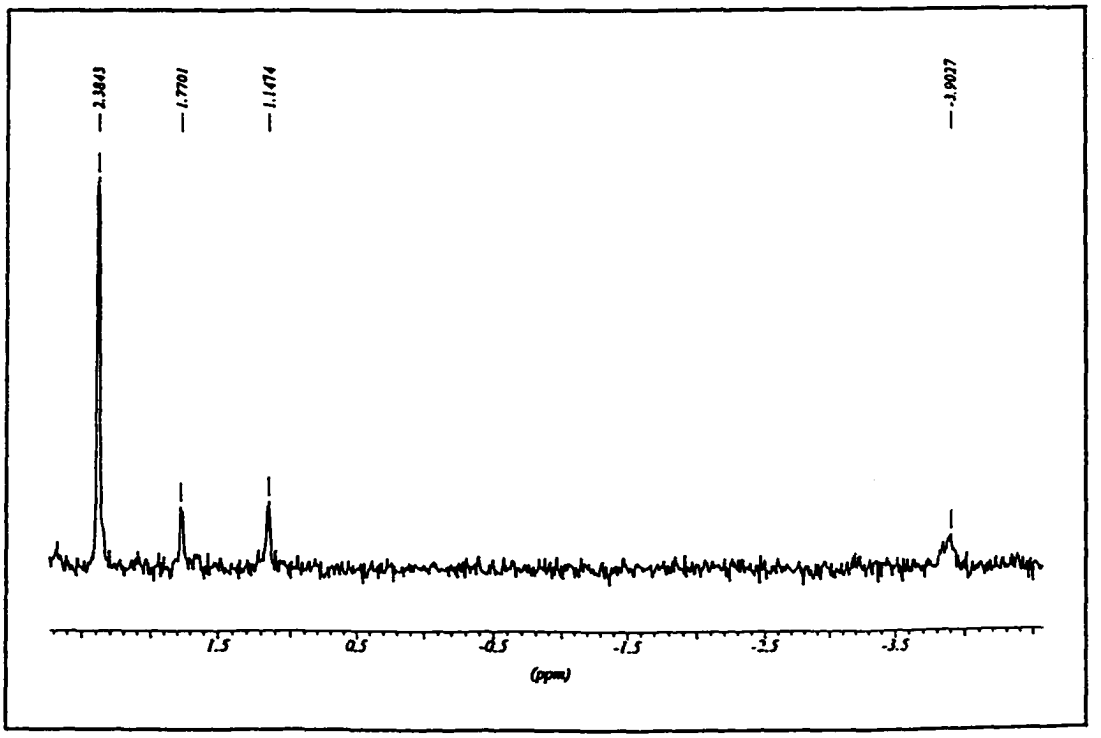
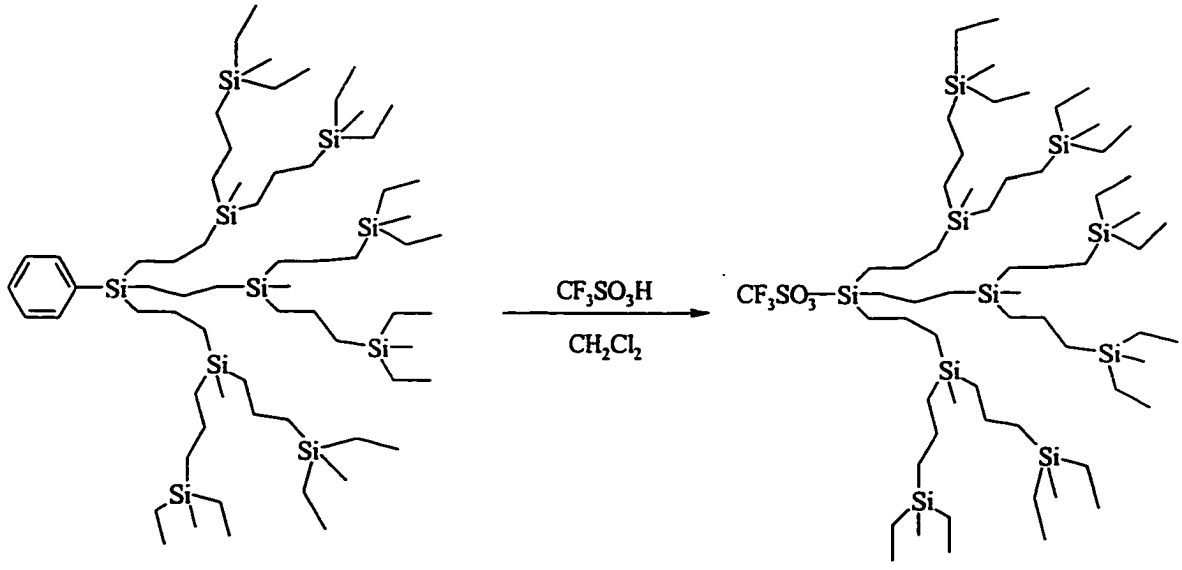


Figure 4.7 ^{29}Si-{^{1}H} NMR spectrum of PhSi[(prSiMe)$^2_2$:2-CH$_2$(C$_{10}$H$_7$)]$_3$ (102)

4.2 Core Substitution

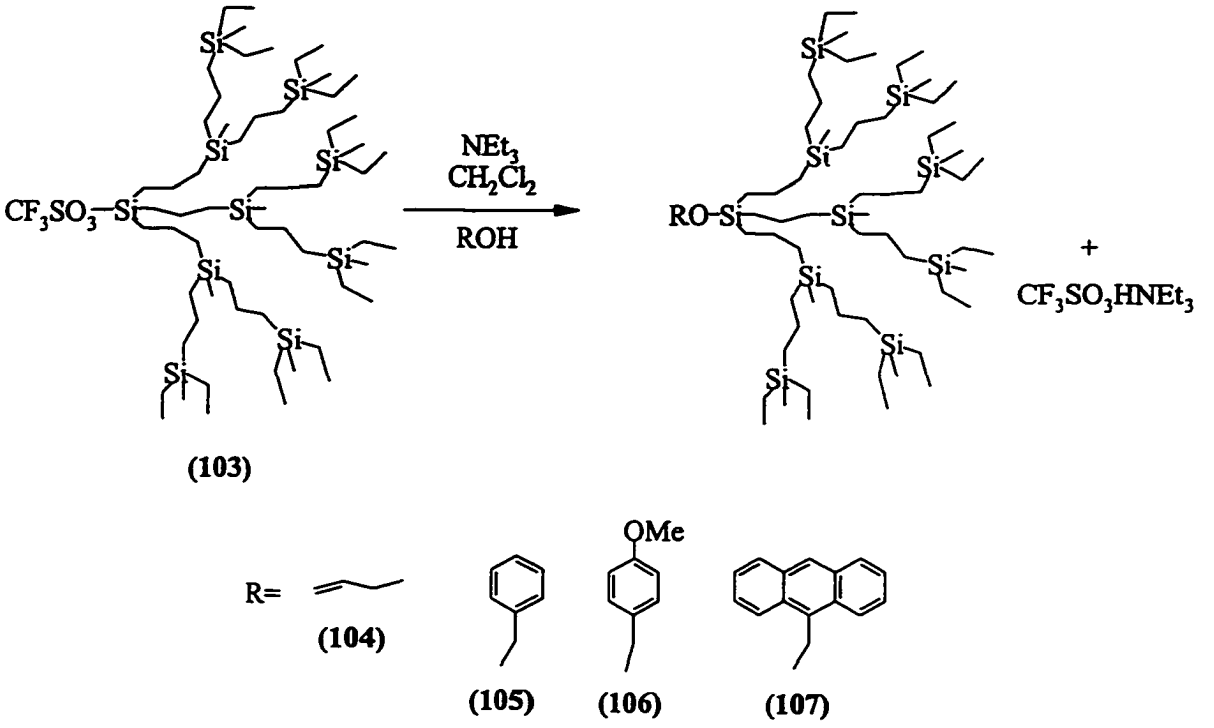
This section will focus on the modification of a trifurcate dendrimer using trifluoromethanesulphonic acid, (CF_3SO_3H) triflic acid, to selectively cleave the Ph-Si bond.[62] This step yields a triflate salt, which can then be further reacted with a range of alcohols, forming a silylether linkage at the core, and at the same time reforming triflic acid. It will be shown that the reaction is general for trifurcate systems which do not contain peripheral alkenyl groups, and also that the subsequent substitution with alcohols are quantitative. The phenyl-silicon bond cleavage reaction, using compound **(101)** with peripheral ethyl groups, is shown in Scheme 4.4. Reactions of the intermediate triflate product, compound **(103)**, with various alcohols has been investigated (Scheme 4.5), with external base being used to remove triflic acid as it reforms.



$PhSi[(prSiMe)^2_2:Et]_3$
(101)

$TfOSi[(prSiMe)^2_2:Et]_3$
(103)

Scheme 4.4 Phenyl group cleavage with triflic acid



(103)

(104)

(105) (106) (107)

Scheme 4.5 Core substitution with alcohols

Table 4.4 Selected spectroscopic data for compound (103) TfOSi[(prSiMe)^2$_2$:Et]$_3$

^{1}H δ ppm	CH_3, CH_2 1.5-0.4 (119±12) *114H*			Si-CH_3 -0.06--0.11 (=27) *27H*	
^{13}C δ ppm	CF_3	CH_2	CH_3	CH_2	Si-CH_3
	119.0[a]	17.9-16.8	7.4	5.12	-3.4, -6.1
^{29}Si δ ppm	43.5 (TfO*Si*)	5.02 (*Si*Et_2)		1.32 (*Si*Me)	
^{19}F δ ppm	-79.7 (TfOSi)				

[a] $^1J_{CF}$ = 320 Hz

The intermediate triflate salt was analysed by multinuclear NMR spectroscopy, shown in Table 4.4 and Figures 4.8-4.10. As previously described for the example of peripheral substitution with methylnaphthalene groups, the core cleavage reaction with triflic acid can be monitored visually. The trifurcate dendrimer solution in dichloromethane is colourless, slow addition of the triflic acid in CH_2Cl_2 resulted in a deep brown solution after one hour at room temperature and removal of solvent under vacuum yielded a dark oil. The lack of the phenyl resonance in the proton NMR (δ 7.5-7.3) confirms that this core group has been removed (Figure 4.8), *i.e.* that triflic acid is selective for cleavage of a phenyl silicon bond in this ethyl terminated trifurcate dendrimer, and ^{1}H NMR integration suggests that no other silicon carbon bonds have been cleaved. There is also the presence of the some THF (δ 4.2 ppm) solvent remaining trapped in the sample from the ethyl Grignard synthesis. The ^{13}C NMR shows a weak quartet at δ 119.0 ppm implying the presence of the triflate group, with a coupling constant of 320 Hz due to coupling of the carbon with the fluorine atoms. The ^{29}Si NMR spectrum has no resonance at δ -4.0 ppm for the Ph-*Si* signal (Table 4.2) but there is the presence of a new resonance at δ 43.5 ppm assigned as the TfO*Si* group.[65] The instability of this compound did not allow for further characterization.

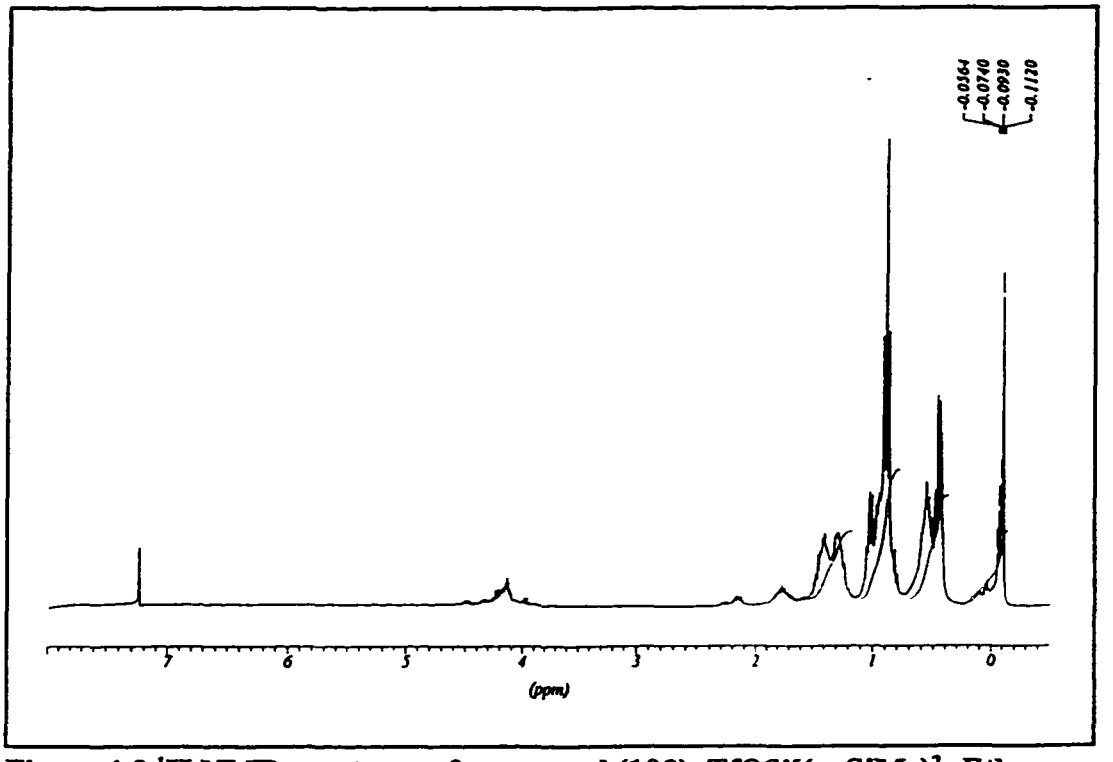


Figure 4.8 ^{1}H NMR spectrum of compound (103) $TfOSi[(prSiMe)^{2}_{2}:Et]_{3}$

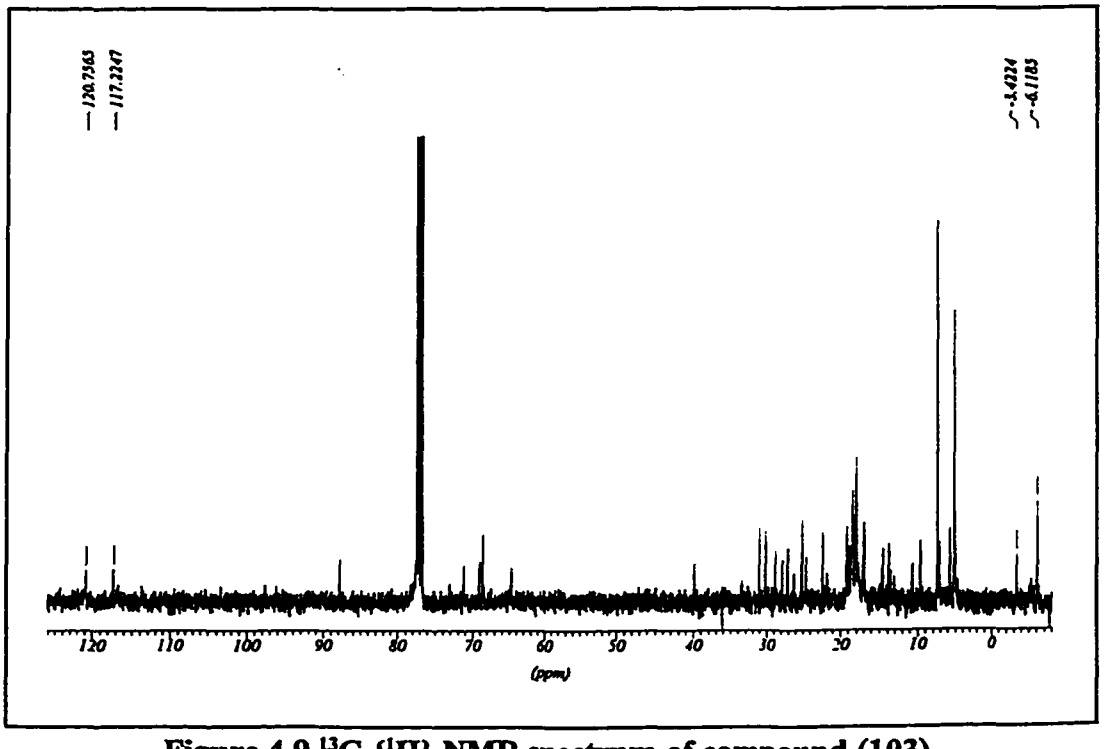


Figure 4.9 ^{13}C-{^{1}H} NMR spectrum of compound (103) $TfOSi[(prSiMe)^{2}_{2}:Et]_{3}$

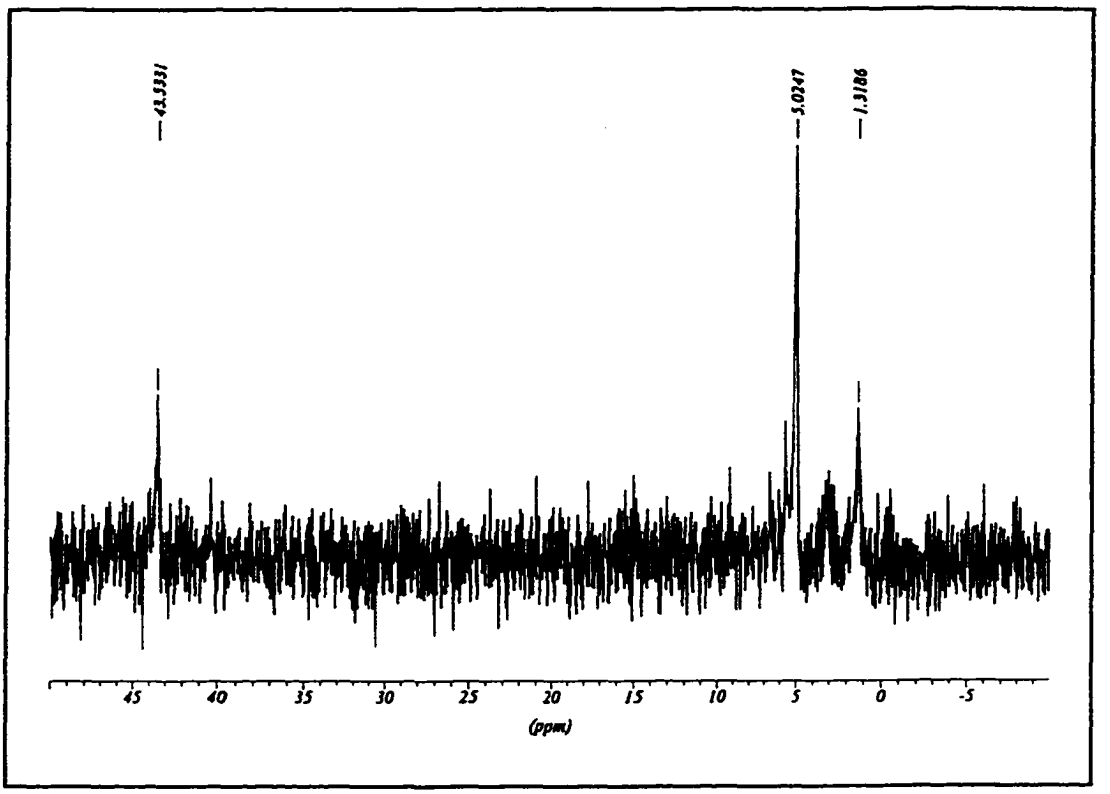


Figure 4.10 $^{29}Si\{^1H\}$ NMR spectrum of compound (103) $TfOSi[(prSiMe)^2_2:Et]_3$

The triflate product was then redissolved into dichloromethane and divided into four equal amounts. To each of these solutions a different alcohol dissolved in CH_2Cl_2 was slowly added (Scheme 4.5), with a base (Et_3N) present to neutralise the triflic acid that is reformed. This resulted in the loss of the dark colouration with formation of a yellow or colourless solution. These reactions were stirred overnight at room temperature, all solvent was removed and each product was dissolved into hexanes. These products were then washed with a slightly acidic solution (ammonium chloride), dried with magnesium sulphate and any remaining volatiles were removed under vacuum. Multinuclear NMR spectra were recorded on each reaction product and are reported in Table 4.5.

Table 4.5 Selected spectroscopic data for ROSi[(prSiMe)^2]$_2$:Et]$_3$ compounds

	^{1}H δ ppm	^{13}C δ ppm	^{29}Si δ ppm
(104)	5.9 (=1) *1H*	113.0	17.4 (OSi)
	1.5-0.4 (132±13) *114H*	19.0-18.0 CH_2	4.88 (SiEt)
	0.04--0.12 (30±3) *27H*	7.4, 5.2 Ethyl	1.05 (SiMe)
R = Allyl		-4.2, -4.9, -6.0 CH_3	
MS	1204, 1190 (M^+ - Me), 1175 (- Me), 1163 (M^+ - allyl)		
(105)	7.4-7.3 (=5) *5H*	128.6-127.0	17.3 (OSi)
	1.5-0.4 (152±15) *114H*	19.0-18.0 CH_2	4.85 (SiEt)
	-0.01--0.10 (30±3) *27H*	7.4, 5.2 Ethyl	0.97 (SiMe)
R = Benzyl		-6.0 CH_3	
MS	1250, 1234 (M^+ - Me), 1221 (M^+ - Et), 1206 (- Me), 1143 (M^+ - BenzylO)		
(106)	7.36, 6.95 (=4) *4H*	128.6, 113.9	17.3 (OSi)
	1.5-0.4 (96±10) *114H*	19.0-18.0 CH_2	4.90 (SiEt)
	0.00--0.12 (26±3) *27H*	7.4, 5.2 Ethyl	1.00 (SiMe)
R = *p*-MeOBenzyl		-4.9, -6.0 CH_3	
MS	1276, 1262 (M^+ - Me), 1249 (M^+ - Et), 1140 (M+ - *p*MeOBenzylO)		
(107)	8.5-7.4(=9) *9H*	131.5-124.0	17.4 (OSi)
	1.5-0.4 (118±12) *114H*	19.0-18.0 CH_2	4.97 (SiEt)
	-0.02--0.10 (26±3) *27H*	7.4, 5.2 Ethyl	1.07 (SiMe)
R = 9-CH_2Anthracene		-5.07 CH_3	
MS	1348, 1333 (M^+ - Me), 1319 (M^+ - Et), 1141 (M^+ - AnthraceneCH_2O)		

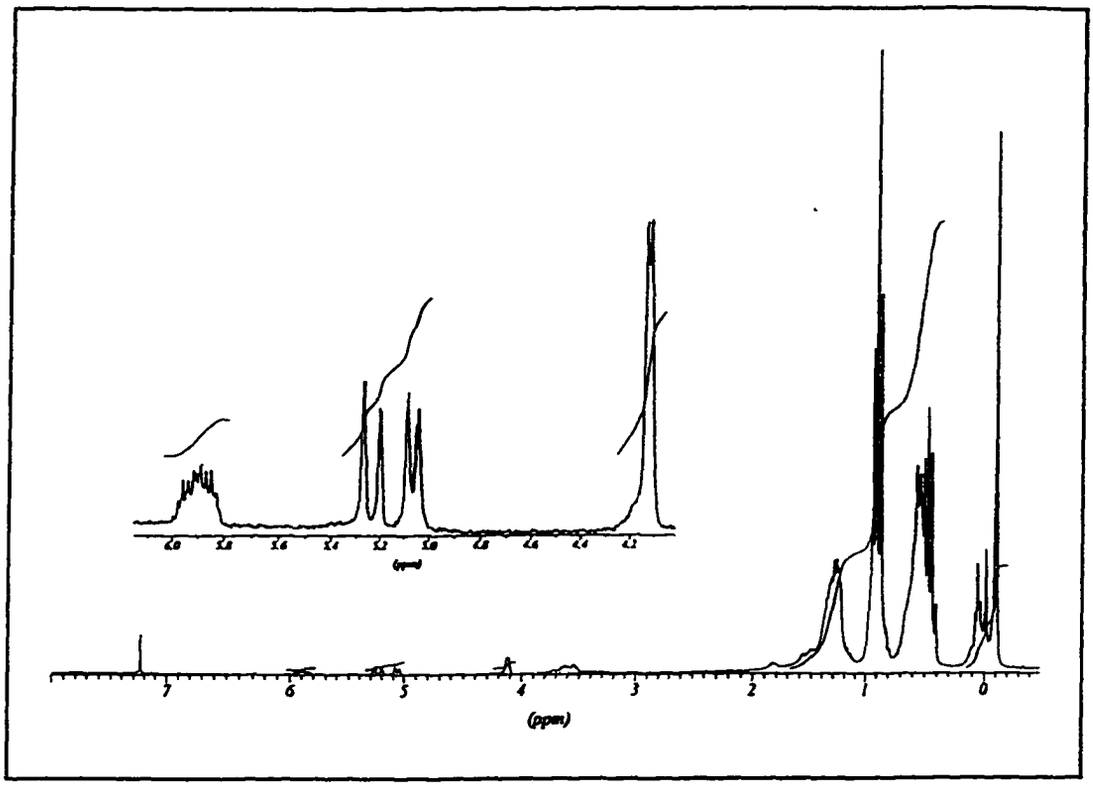


Figure 4.11 ^{1}H NMR spectrum of allylOSi[(prSiMe)$^2_2$:Et]$_3$ (104)

The proton spectrum shown in Figure 4.11 was recorded for the product, compound (104), isolated from the reaction between allyl alcohol and the triflate intermediate. The allyl resonance, which is hard to distinguish on the full scale proton spectrum owing to the large population of terminal ethyl and silylmethyl groups, is shown in the enlargement to aid in the interpretation. This shows the allyl ether substituted core, where integration of the β-allyl proton relative to the Si-*Me* signals is in close agreement to the calculated values, further spectral data being provided in Table 4.5. The most convincing evidence for triflate displacement is found in the silicon NMR where a resonance at δ 17.3 ppm, attributed to the O-*Si*, is in an analogous position to other known silyl ethers.[65, 80]

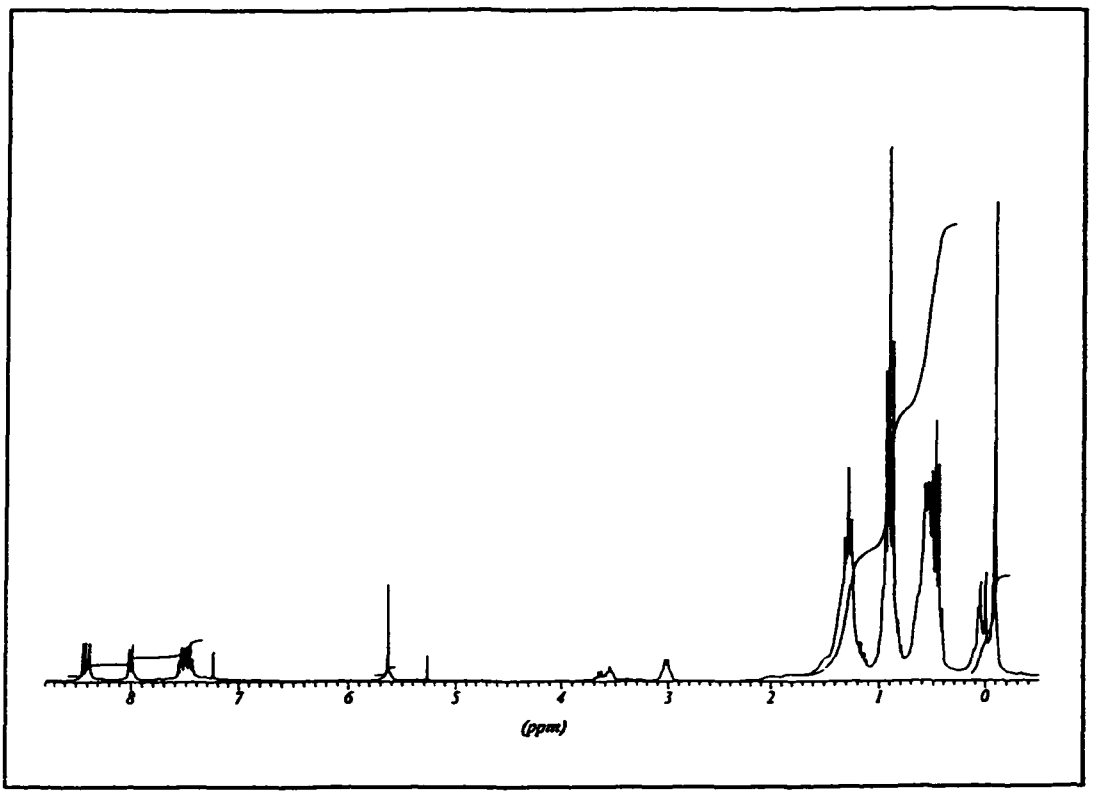
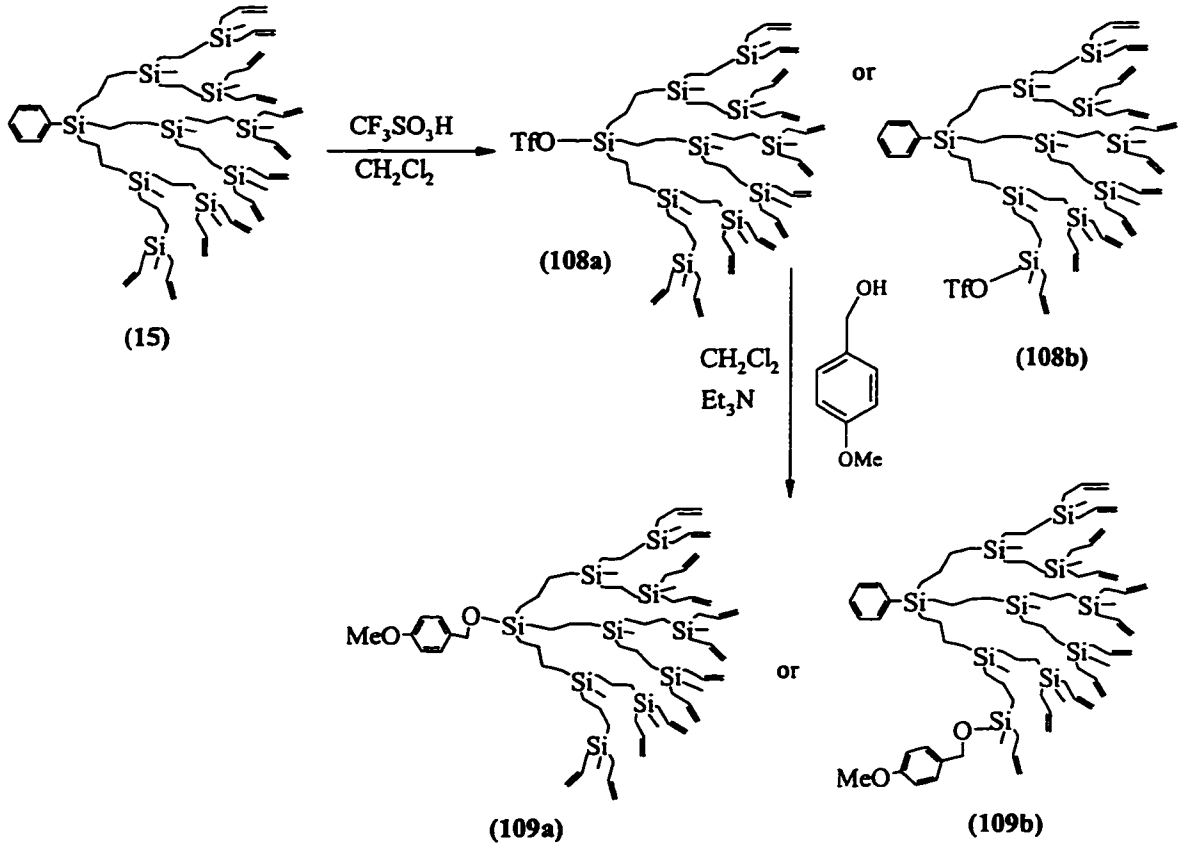


Figure 4.12 ^{1}H NMR spectrum of 9-$C_{14}H_9CH_2OSi[(prSiMe)^2_2:Et]_3$ (107)

The product from the reaction between the triflate salt and 9-anthracenemethanol was isolated and the proton NMR spectrum is shown in Figure 4.12. This spectrum shows the chemically distinct anthracene resonances (δ 8.5-7.4 ppm), the methoxy protons as a singlet (δ 5.63 ppm) and the silylmethyl peaks (δ 0.0–0.1 ppm). There is also some solvent remaining inside this compound at δ ~3.5 ppm which is believed to be the THF from the original $PhSi[(prSiMe)^2_2:Et]_3$ compound (101). The silyl ether signal appears at δ 17.3 ppm in the ^{29}Si NMR spectrum with a similar observation for other reaction products, Table 4.5, and the ethyl resonances are still clearly visible in all NMR spectra (^{1}H, ^{13}C and ^{29}Si).

In order to establish that the presence of alkenyl groups will interfere with the Ph-Si bond cleavage, a test reaction was performed as is shown in Scheme 4.6, where triflic acid

was added to a second generation trifurcate dendrimer (see chapter two). After stirring at room temperature for one hour, the solvent was removed and a proton NMR spectrum was recorded and then the reaction mixture was slowly added to a solution of *p*-methoxybenzylalcohol.



Scheme 4.6 Triflic acid substitution of allyl terminated trifurcate dendrimer

The ^{1}H NMR spectrum of the intermediate material showed the presence of a phenyl resonance (δ 7.5-7.3 ppm) which indicates that this product still contains a Ph-Si bond, *i.e.* compound **(108b)**. The product isolated after addition of *p*-methoxybenzylalcohol would

be either **(109a)**, **(109b)** or a mixture in which both allyl and phenyl bonds had been substituted in the same molecule. Proton (Figure 4.13) and silicon NMR spectra (Figure 4.14) were recorded and showed strong evidence that one of the allyl-silicon bonds had been substituted, rather than Ph-Si bond cleavage as seen previously. The presence of a phenyl resonance (δ 7.5-7.3 ppm; *Ph*-Si) as well as the signal from a *p*-methoxybenzyl group (δ 7.3, 6.9; dd) in the proton NMR spectrum, together with the observation of a Ph-*Si* peak (δ -3.9 ppm) in the silicon spectrum strongly indicate that the product formed is **(109b)**, see Table 4.6.

This chemistry indicates that the cleavage reaction by triflic acid is not selective for a Ph-Si group when Si-allyl bonds are also present in the same molecule; therefore the peripheral allyl groups present in dendrimers investigated in chapter two must be converted to aliphatic silyl moieties before core substitution can be attempted.

Table 4.6 Selected spectroscopic data for compound (109b)

$PhSi[(prSiMe)^2_2$:All/p-MeObenzyl$]_3$

	^{1}H δ ppm	^{13}C δ ppm	^{29}Si δ ppm
(109b)	7.5-6.8 (10±1) *9H*	134.8-127.6	17.4 (OSi)*
	5.80 (10±1) *1IH*	113.0	0.97 (SiMe)
	1.5-0.4 (126±13) *78H*	19.0-18.0 CH_2	0.68, 0.28 (SiMe)
	0.00--0.07 (=27) *27H*		-3.91 (Ph-Si)
R = *p*-MeOBenzyl		-5.32, -5.71 CH_3	

* weak signal

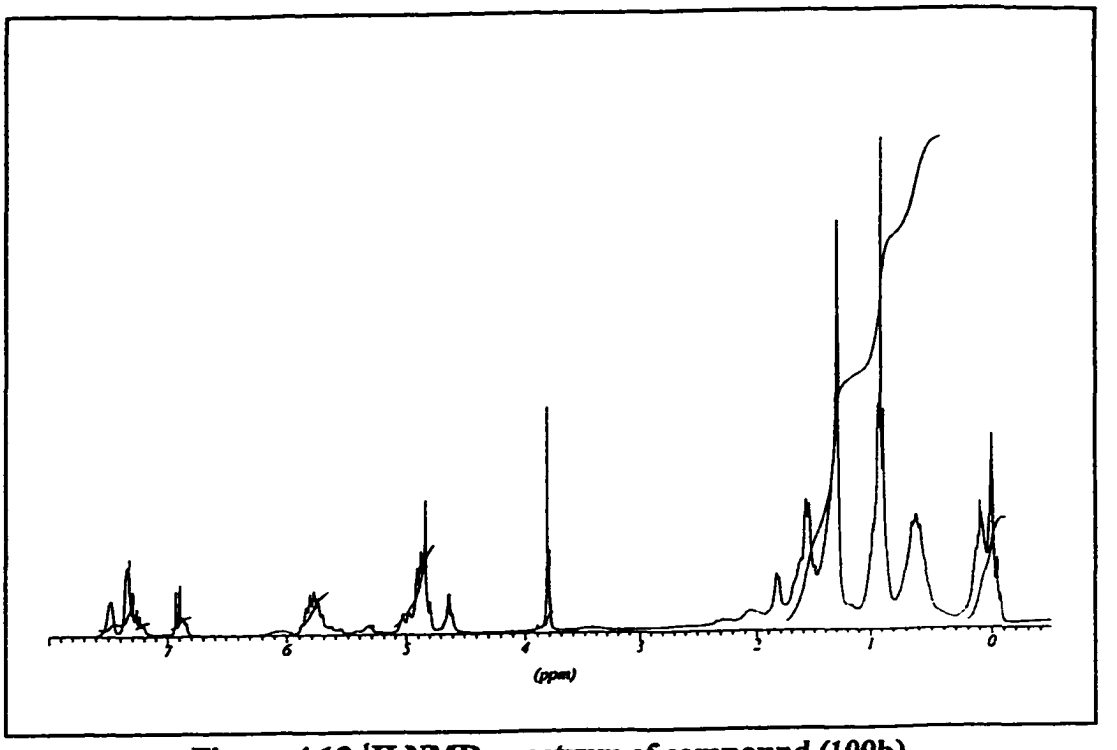


Figure 4.13 ^{1}H NMR spectrum of compound (109b)
PhSi[(prSiMe)$^{2}_{2}$:All/p-MeObenzyl]$_3$

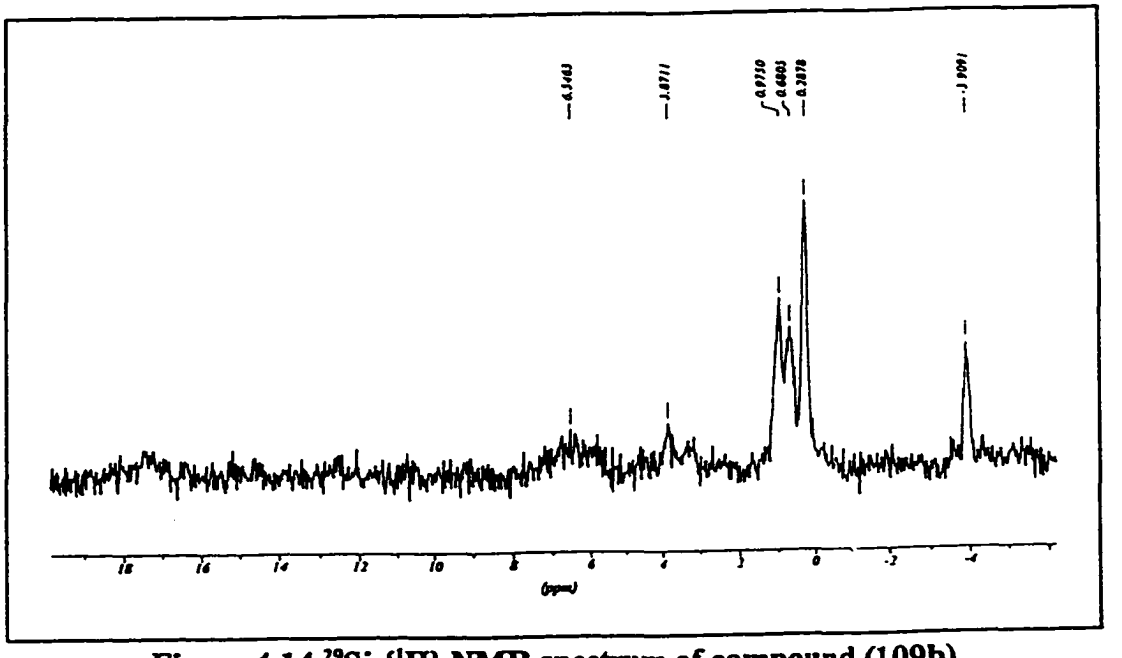


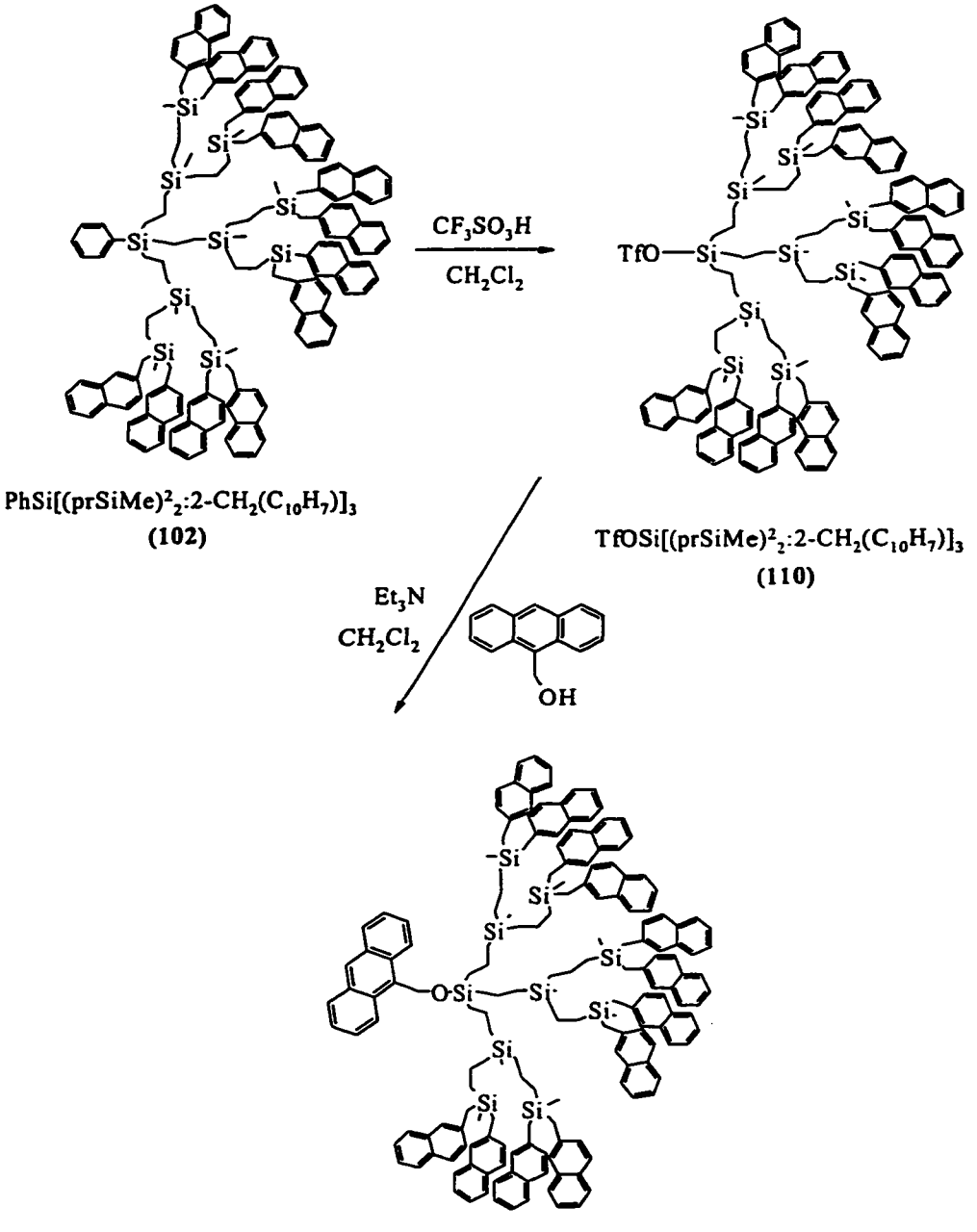
Figure 4.14 ^{29}Si-{^{1}H} NMR spectrum of compound (109b)
PhSi[(prSiMe)$^{2}_{2}$:All/p-MeObenzyl]$_3$

4.3 Combination of Interior and Exterior Functionalization

The construction of nano-antennae has been of interest for some time; many reviews are available and extensive study of polymeric antennas in organic solvents has been carried out.[76] Intramolecular energy transfer was demonstrated by Schnepp and Levy[77] in an anthracene-naphthalene system in which the two chromophores were joined by saturated carbon chains of differing length. A review on 'Light-Harvesting' polymers by Guillet[61] states that "a typical antenna polymer consists of a long chain of monomer units containing sequences of naphthalene or other chromophoric groups and small amounts of an attached trap such as anthracene." If this idea is applied to dendrimeric systems this trap could be at the centre (core) of a dendritic structure; substituents capable of absorbing light would be connected to the periphery which, by a process of intramolecular migration, transfers the energy toward the electron 'sink' at the centre of the molecule. Work of this nature has been attempted by Moore *et al*[78] where rigidly assembled phenyl acetylene units have been studied for energy transfer properties; Fox and Stewart[61b] have also used dendritic polybenzyl ethers that contain chromophore capping groups to study quenching effects by placing suitable donors at the dendron focal point. Calculations of energy migration in dendrimers have recently been published by Kopelman *et al.*[79]

In the light of the above, it should be possible to study energy transfer processes in polycarbosilane dendrimers by the attachment of chromophoric groups at both the core and peripheral positions. A suitable approach would be to take the methylnaphthyl terminated compound **(102)**, synthesised earlier in this chapter (Table 4.3), and use the triflic acid

substitution reaction discussed in the previous section to replace the Ph-Si core with an anthracene group, see Scheme 4.7.



$PhSi[(prSiMe)^2_2:2\text{-}CH_2(C_{10}H_7)]_3$
(102)

$TfOSi[(prSiMe)^2_2:2\text{-}CH_2(C_{10}H_7)]_3$
(110)

$9\text{-}C_{14}H_9CH_2OSi[(prSiMe)^2_2:2\text{-}CH_2(C_{10}H_7)]_3$
(111)

Scheme 4.7 Core substitution with 9-methoxyanthracene

Table 4.7 Selected spectroscopic data for compound (110)

$TfOSi[(prSiMe)^2_2:2\text{-}CH_2(C_{10}H_7)]_3$

	^1H δ ppm	^{13}C δ ppm	^{29}Si δ ppm
(110)	8.0-7.3 (81±8) *84H*	135.4-124.9	43.2, 42.6 (OSi)
	2.51 (28±3) *24H*	26.7, 26.2	
	1.5-0.4 (226±23) *54H*	19.0-18.0 CH_2	2.47 (SiMeNaph)
	0.05–0.07 (=27) *27H* -5.09 CH_3		1.32, 1.17 (SiMe)

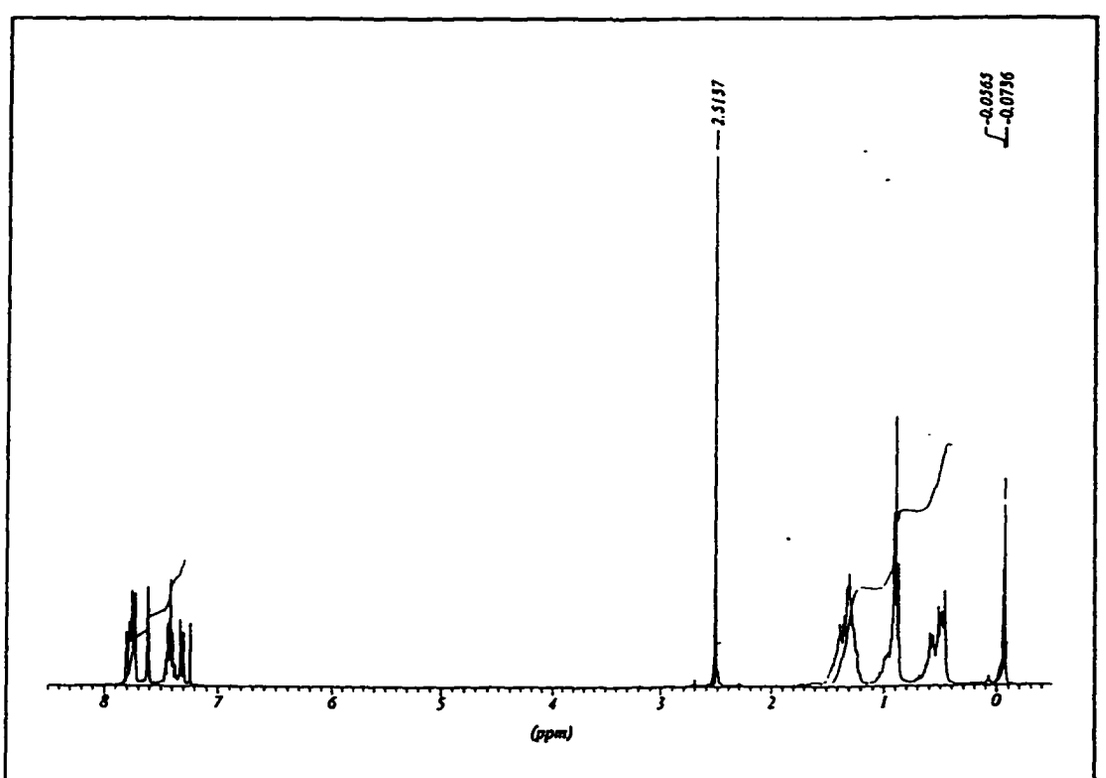


Figure 4.15 ^1H NMR spectrum of compound (110)
$TfOSi[(prSiMe)^2_2:2\text{-}CH_2(C_{10}H_7)]_3$

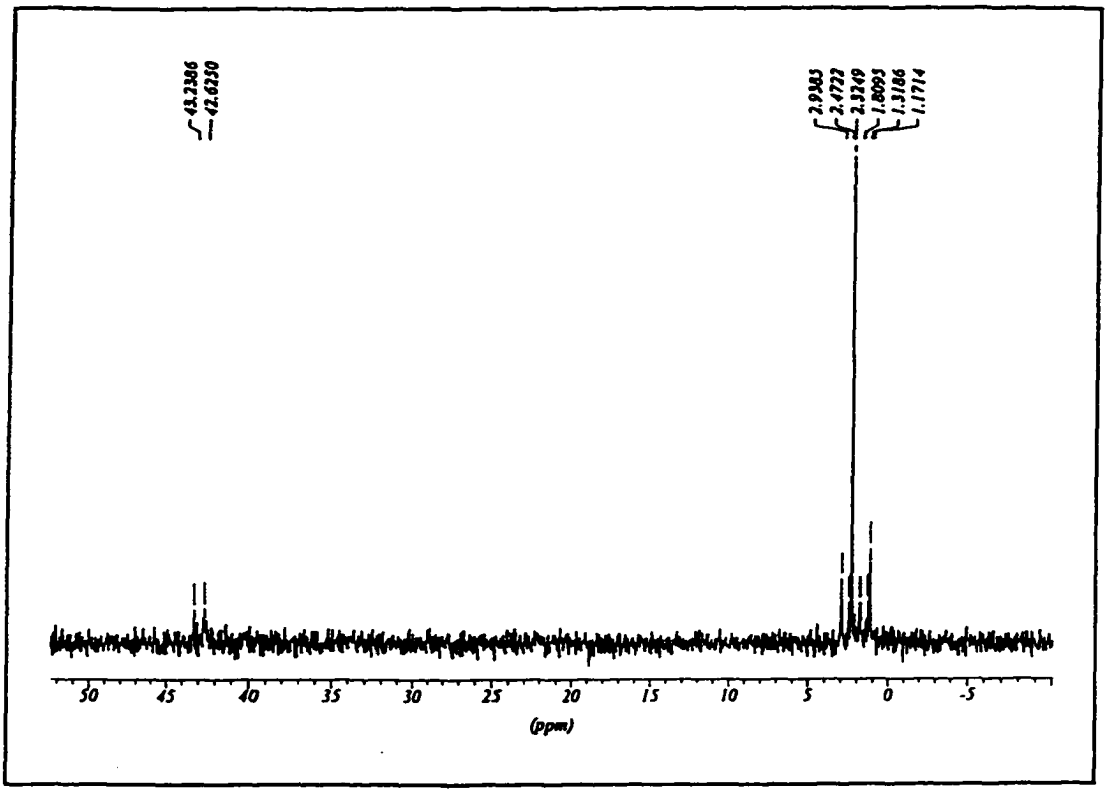


Figure 4.16 ^{29}Si-{^{1}H} NMR spectrum of compound (110) TfOSi[(prSiMe)$^{2}_{2}$:2-CH$_2$($C_{10}H_7$)]$_3$

Although the alkyl resonances integrate in excess of the calculated value (relative to the Si-Me signals), the spectral data for the isolated triflate salt (Table 4.7) implies that the cleavage reaction occurred. The strongest evidence that the Ph-Si is no longer present comes from the ^{29}Si NMR spectrum (Figure 4.16) in which there is no core silicon resonance (δ -4.0 ppm as in the precursor); instead signals are observed at δ 43.2 and 42.6 ppm, indicative of a silicon triflate.[65] The two signals probably arise from an increased steric hindrance within the interior of this molecule from the very bulky peripheral naphthyl groups. The triflate compound was redissolved into dichloromethane and to this solution a solution of 9-anthracenemethanol was slowly added in the presence of an auxiliary base (triethylamine). After stirring for 1 hour the solution turned from deep brown to green and slowly to yellow,[80]

and the resulting solution was stirred at room temperature overnight before solvent was removed and an orange oil was isolated. The product has been analysed by multinuclear NMR spectroscopy and the results are reported in Table 4.8.

Table 4.8 Selected spectroscopic data for compound (111)

9-$C_{14}H_9CH_2OSi[(prSiMe)^2_2$:2-$CH_2(C_{10}H_7)]_3$

	^{1}H δ ppm	^{13}C δ ppm	^{29}Si δ ppm
(111)	8.5-7.3 (91±9) *93H*	135.4-124.9	18.4 (OSi)
	5.63 (2±0.2) *2H*		
	2.51 (22±2) *24H*	26.7, 26.2	2.96 (SiMeNaph)
	1.5-0.4 (182±18) *54H*	19.0-18.0 CH_2	2.35 (SiMeNaph)
	0.05--0.07 (=27) *27H*	-5.09 CH_3	1.73, 1.12 (SiMe)
MS	No high mass material data could be collected for this compound using EI methods		

Both the ^{1}H and ^{29}Si NMR spectra (Figures 4.17 and 4.18 respectively) show that there is strong evidence to suggest that core substitution was achieved without cleavage of any naphthyl groups from the periphery. The appearance of the CH_2O signal (δ 5.63 ppm) in the proton NMR together with the O-*Si* resonance (δ 18.4 ppm) in the silicon NMR spectrum imply that a silicon ether link has been formed. These observations are in agreement with silyl ether resonances reported earlier in this chapter and by previous workers in this laboratory.[80]

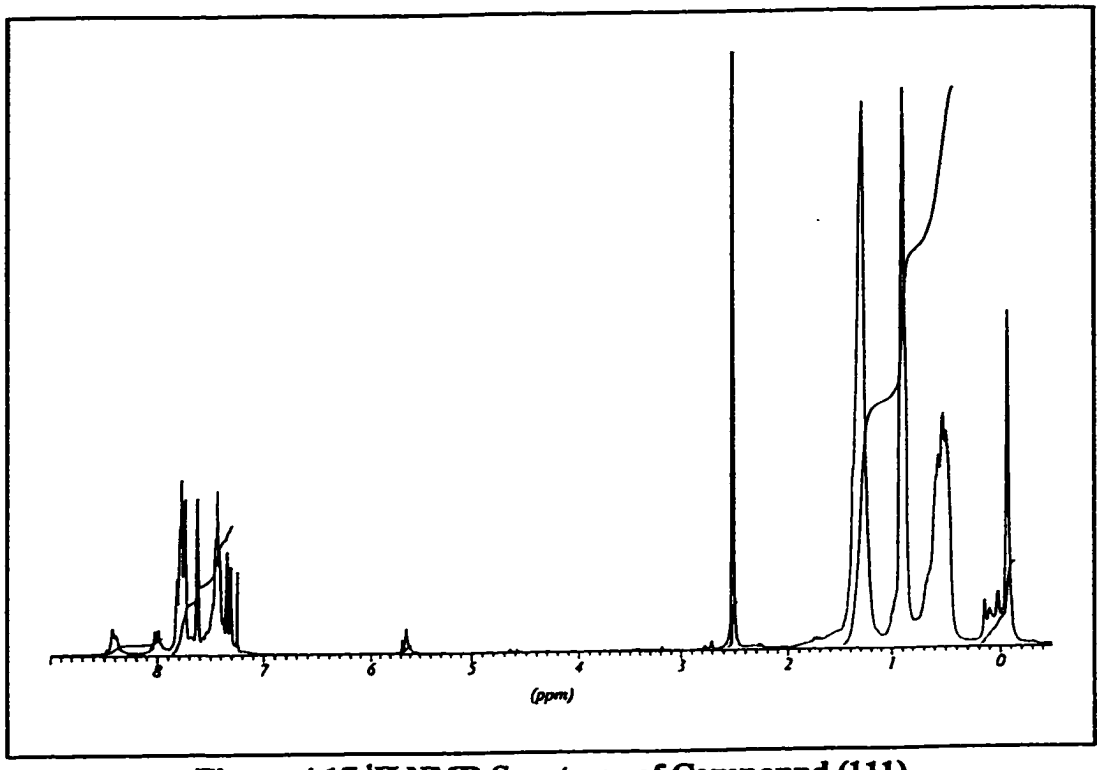


Figure 4.17 ^{1}H NMR Spectrum of Compound (111)
$9\text{-}C_{14}H_9CH_2OSi[(prSiMe)^2{}_2\text{:}2\text{-}CH_2(C_{10}H_7)]_3$

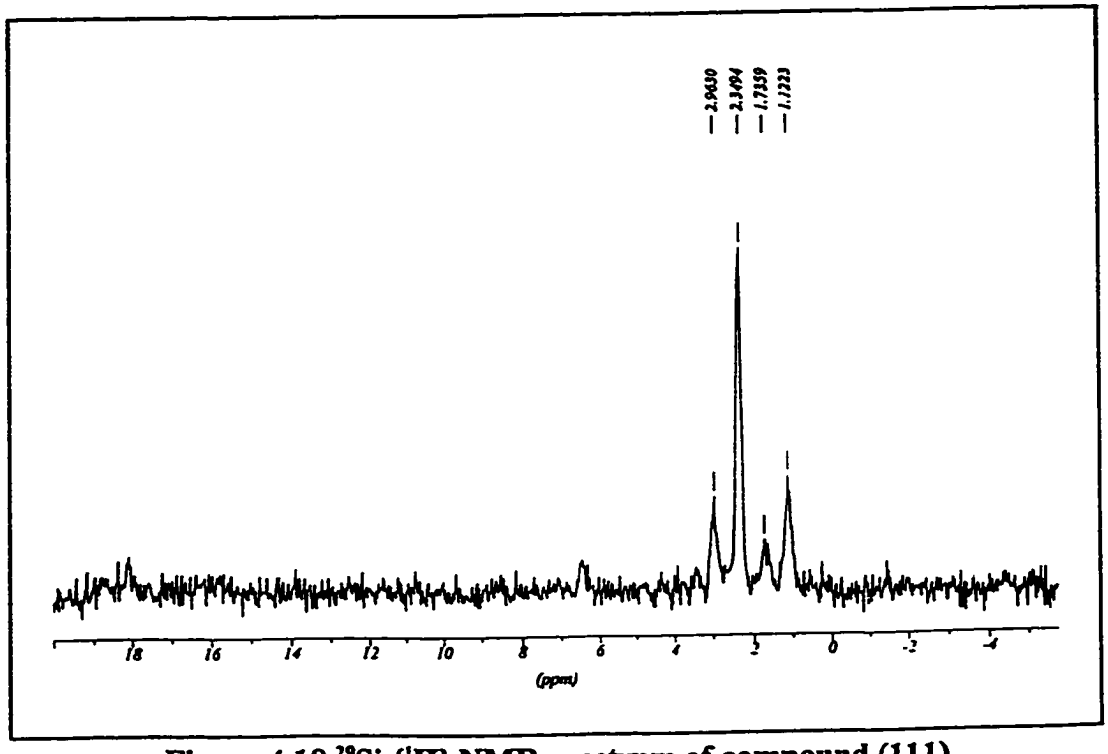


Figure 4.18 $^{29}Si\text{-}\{^{1}H\}$ NMR spectrum of compound (111)
$9\text{-}C_{14}H_9CH_2OSi[(prSiMe)^2{}_2\text{:}2\text{-}CH_2(C_{10}H_7)]_3$

UV-visible spectra have been recorded for three of these dendrimer compounds that contain a chromophore group(s) in the structure, Table 4.9. One has no internal anthracene moiety (**102**), another has no terminal methylnaphthyl groups (**107**), and the final compound studied has both the internal anthracene and external methylnaphthalene moieties (**111**). These examples were chosen to compare the properties of compounds containing only one of the chromophores *vs* that where both anthracene and methylnaphthalene groups are present. The table shows that with anthracene and methylnaphthalene groups in the same molecule, the UV-visible spectrum appears as a superimposition of the two individual spectra.

Table 4.9 UV-visible data for compounds with anthracene and methylnaphthalene groups attached (102), (107) and (111)

	λ nm (ε L mol^{-1} cm^{-1})
(102) PhSi[(prSiMe)$^2_2$:2-$CH_2(C_{10}H_7)$]$_3$	228 (1.8 x10^5), 276 (4.5 x10^4)
(107) 9-$C_{14}H_9CH_2OSi$[(prSiMe)$^2_2$:Et]$_3$	255 (1.2 x10^5), 346 (5.5 x10^3), 364 (7.9 x 10^3), 384 (7.1 x10^3)
(109) 9-$C_{14}H_9CH_2OSi$[(prSiMe)$^2_2$:2-$CH_2(C_{10}H_7)$]$_3$	227 (1.3 x10^5), 256 (8.7 x10^4), 276 (1.7 x10^4), 346 (4.4 x10^3), 364 (6.0 x10^3), 384 (5.4 x10^3)

The experiment that would be required to verify if intramolecular energy transfer is occurring involves fluorescence spectroscopy. Solutions would need to be prepared where

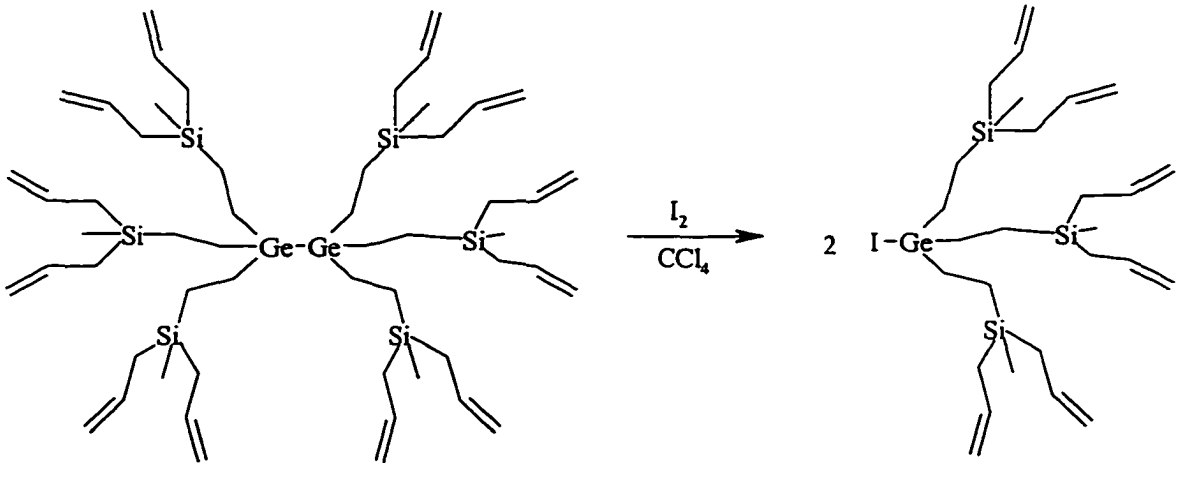
the intensity at the absorption maximum for the methylnaphthalene group (λ = 228 nm) would be identical for both compounds **(102)** and **(111)**. By scanning the emission spectrum at an excitation wavelength at which the methylnaphthalene is excited and where the anthracene component does not strongly absorb (*i.e.* λ = 275 nm) a quantitative measure of energy transfer can be obtained.

Rudimentary fluorescence measurements have been taken for all three compounds **(102)**, **(107)** and **(111)**. The results can be summarised in the following manner, based on emission spectra recorded at varying excitation wavelengths for almost equimolar solutions. The fluorescence spectrum of the compound with only terminal methylnaphthalene groups present showed a strong band (λ_{ex} = 275 nm) assigned as methylnaphthalene emission. That of the compound that only contained the anthracene group was recorded, and under similar conditions showed a weak anthracene emission only. Similar measurements using the anthracene-methylnaphthalene compound **(111)** at the same excitation wavelength (275 nm) showed an emission band for the methylnaphthalene moiety, together with a feature at approximately 320 nm assigned to the anthracene unit, which appeared to be stronger by a factor of approximately 2 than that for compound **(107)**.

These preliminary results suggest that intramolecular energy transfer may be occurring between the two chromophore groups within the structure of **(111)** and a much more rigorous series of experiments will be needed to prove that intramolecular energy transfer is taking place.[76]

4.4 Digermane Substitution

Oxidative cleavage of the Ge-Ge bond by iodine, as reported in 1957 by Seyferth,[72] may lead to a derivitised trifurcate monodendron; reactions of the latter include. 1). Reduction of the Ge-I bond to a germanium hydride using $LiAlH_4$; 2). Substitution of the Ge-I bond by alkylation with an organolithium reagent. The hydride may be viewed as an intermediate 'monodendron' unit for the first convergent approach for carbosilane dendrimer synthesis. Either of these two options leads to a modified core group that can then be further modified to give a variety of different peripheral or core functionalities, some of which are analogous to those reported with the above trifurcate series.

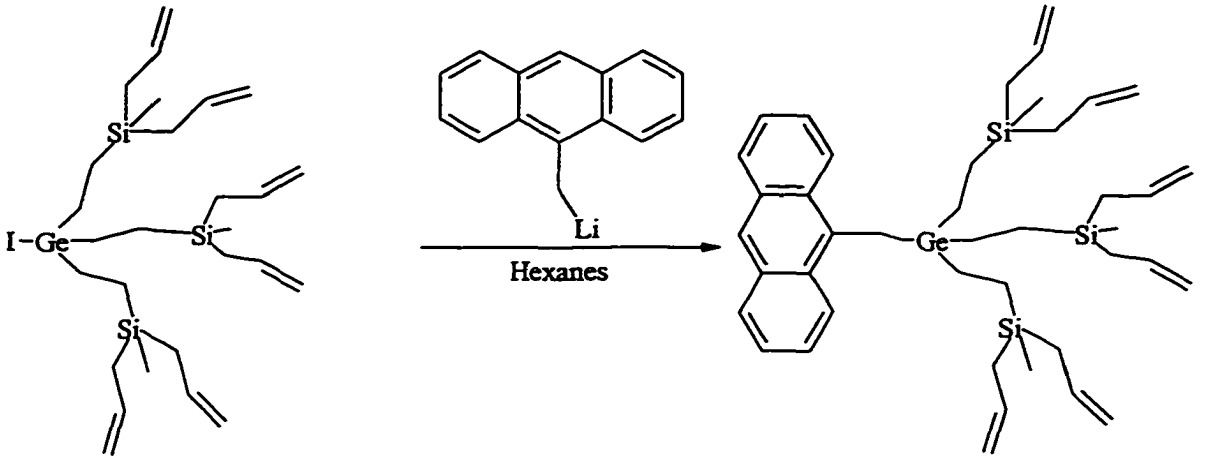


$Ge_2[(etSiMe)^1{}_2{:}All]_6$

$IGe[(etSiMe)^1{}_2{:}All]_3$

(112)

Scheme 4.8 Digermane G(1) cleavage with iodine



$IGe[(etSiMe)^{1}_{2}:All]_3$ (112)

9-Anthracene$CH_2Ge[(etSiMe)^{1}_{2}:All]_3$ (113)

Scheme 4.9 Iodogermane core substitution with 9-methylanthracene

Modification of this digermane cleavage reaction, reported by Seyferth, has been investigated using a first generation dendrimer and has led to compound **(112)**. Further reaction of this iodogermane intermediate with the organolithium salt of 9-methylanthracene produced compound **(113)** in near quantitative yield, Scheme 4.9. Multinuclear NMR data were recorded for compounds **(112)** and **(113)**. Only selected data are given in Table 4.10 as the most interesting observations are seen in the proton NMR and the silicon NMR.

Table 4.10 Selected spectroscopic data for compounds (112) IGe[(etSiMe)$^1_2$:All]$_3$ and (113) 9-anthraceneGe[(etSiMe)$^1_2$:All]$_3$

Compound	^{1}H (δ ppm)	^{13}C (δ ppm)	^{29}Si (δ ppm)
(112)	1.25 (6±0.6) *6H*	11.1 (CH_2)	1.90
	0.65 (6±0.6) *6H*	7.7 (CH_2)	
	-0.07 (=12) *12H*	-6.2 (Si-Me)	
(113)	3.58 (2±0.2) *2H*	20.8 (Ge-CH_2)	2.30
	1.20 (6±0.6) *6H*	10.2 (CH_2)	
	0.75 (6±0.6) *6H*	6.1 (CH_2)	
	-0.07 (=12) *12H*	-6.2 (Si-Me)	

Upon Ge-Ge bond cleavage a downfield shift is observed for the methylene proton and carbon resonances, and there is also a slight downfield shift in the ^{29}Si NMR signal (δ 1.75 ppm for Ge_2[(etSiMe)$^1_2$:All]$_6$ see page 106) . Mass spectroscopy of this iodogermane compound was consistent with the proposed formulation, especially with the loss of both peripheral allyl groups (41 amu) and loss of iodine (127 amu). After reaction with the organolithium salt a new triplet occurs at δ 3.58 ppm, attributable to the methylene attached to the Ge and anthracene. The product is not very clean, possibly due to incorporation of hexanes solvent into the dendritic backbone, and it appears to have decomposed more readily than with other systems studied in this chapter. However it does have some similar characteristics to those of the trifurcate systems mentioned above; the UV-visible data for this compound shows similar absorptions to the anthracenyl trifurcate compounds reported previously in this chapter, compounds **(107)** and **(111)**.

4.5 Summary

This chapter has shown that by reaction of terminal chlorosilyl groups with a range of different nucleophilic substrates a variety of compounds can be produced; these are anticipated to exhibit useful properties and may also be examined by multinuclear NMR spectroscopy (*i.e.* see chapters two and three). Fluorosilyl exteriors have been synthesised and characterized specifically for attempts at monolayer surface adsorption although results are still at a preliminary stage.[63] Other peripheral functions have included naphthyl or ethyl moieties, with the latter compound being used for model Ph-Si cleavage reactions with triflic acid: a general reaction route using trifluoromethanesulphonic acid (triflic acid) in dichloromethane has been shown to selectively cleave the phenyl silicon bond forming a silyl triflate. Subsequent substitution with a range of alcohols (*i.e.* R'OH: R' = allyl, benzyl, *p*-MeObenzyl, anthracenylmethoxy), forms a silyl ether bond at modified trifurcate cores. Using an allyl terminated trifurcate dendrimer (from chapter two) it has been shown that reaction with triflic acid cleaves the terminal alykenyl group rather than the core phenyl silicon bond. This route, although not advantageous for work presented in this thesis, could also be used as an alternative method of functionalising both the interior and exterior of a dendrimer in 'one-pot'. A digermane dendrimer has also been modified at the core, using the known oxidative cleavage with iodine (*i.e.* Ge-Ge to Ge-I), and subsequent nucleophilic reaction with an anthracenyl reagent. Thus, either initial trifurcate ($PhSiD_3$) or the masked analogues ($D_3Ge_2D_3$) have been shown to be modified at the core or at the periphery by a range of different functional groups.

CHAPTER FIVE

HYPERBRANCHED MATERIALS

Efforts have recently been focussed on the synthesis of 'dendrimer' molecules in a 'one-pot' approach.[19-21,40-42,68] This is in relation to the study of dendrimer molecules, which due to their regular shape and anticipated difference in rheological properties compared with classical linear polymers,[3-6] have attracted much attention. The purpose of this chapter is to draw comparisons between pure dendrimer molecules and those that can be attained in a 'rapid-assembly' manner, defined from here on as "hyperbranched materials". Dendrimer molecules are defined by the iterative reaction procedure used in their synthesis; repetition of a terminal unit emanating from a central core molecule.[1-3] A very similar argument can be used for hyperbranched materials since they are repetitive monomer units with or without a core molecule present. However, dendrimers have well defined internal connectivity, each branch point being identical, while hyperbranched molecules do not necessarily have such a regularly defined pattern. Obvious advantages can be imagined for a rapid synthesis of highly branched, perfectly symmetrical materials (dendrimers). Ease of synthesis and large scale production could help to draw this new class of materials into wider commercial use.[3a]

The different properties between hyperbranched, rapidly assembled, materials and those derived from an ideally symmetrical branching type of synthesis (dendrimers) have

been discussed by Fréchet[69] *et al* and by Hult[19a] *et al.* Flory predicted, and then demonstrated, that a polycondensation reaction between an AB_x monomer, $x \geq 2$, would lead to a highly branched polymer.[18] Thus the need for simpler and more economical materials, leading towards the idealised dendritic architecture, has been the driving force behind the recent research advances in hyperbranched polymers. Of the comparisons that may be drawn between hyperbranched and dendritic materials, not all are applicable to carbosilane molecules. Most of the systems studied to date are based on polyaromatic connectivity; for those that contain silicon the products analysed by Mathias[21] *et al* poly(siloxysilanes) are the best examples.

The following general observations have been made by Fréchet.[69] Thermal properties (such as T_g and decomposition temperature) of dendrimers and hyperbranched polymers are independent of the shape or architecture of the compound, they are only influenced by the nature of the chain end groups. High solubility of polyaromatic hyperbranched and dendritic molecules has also been mentioned, compared with linear analogues, by Fréchet. However, polycarbosilanes do not appear to have the problem of insolubility, probably because of the large number of aliphatic residues present within the materials which increases the solubility in organic solvents. With molecules of the same apparent mass, dendrimers have a smaller hydrodynamic volume than with those of their linear or hyperbranched counterparts, attributable to the inherent density obtained with regularly branched materials. Viscosity measurements of dendrimers reach a plateau at a critical mass, since the volume increases as a cubic function ($V = 4/3\pi r^3$), whilst the mass is dependant on the generation branching

number ($M_w \sim 2^{G-1}$ or $M_w \sim 3^{G-1}$) so that it increases exponentially.[69] Hyperbranched polymers do not have a defined, identical architecture and therefore always show a linear increase in viscosity with mass, although this increase is less incremental than for linear polymers. The difference in intrinsic viscosity behaviour for linear, hyperbranched and dendritic molecules (taken from Reference 69) is shown in Figure 5.1.

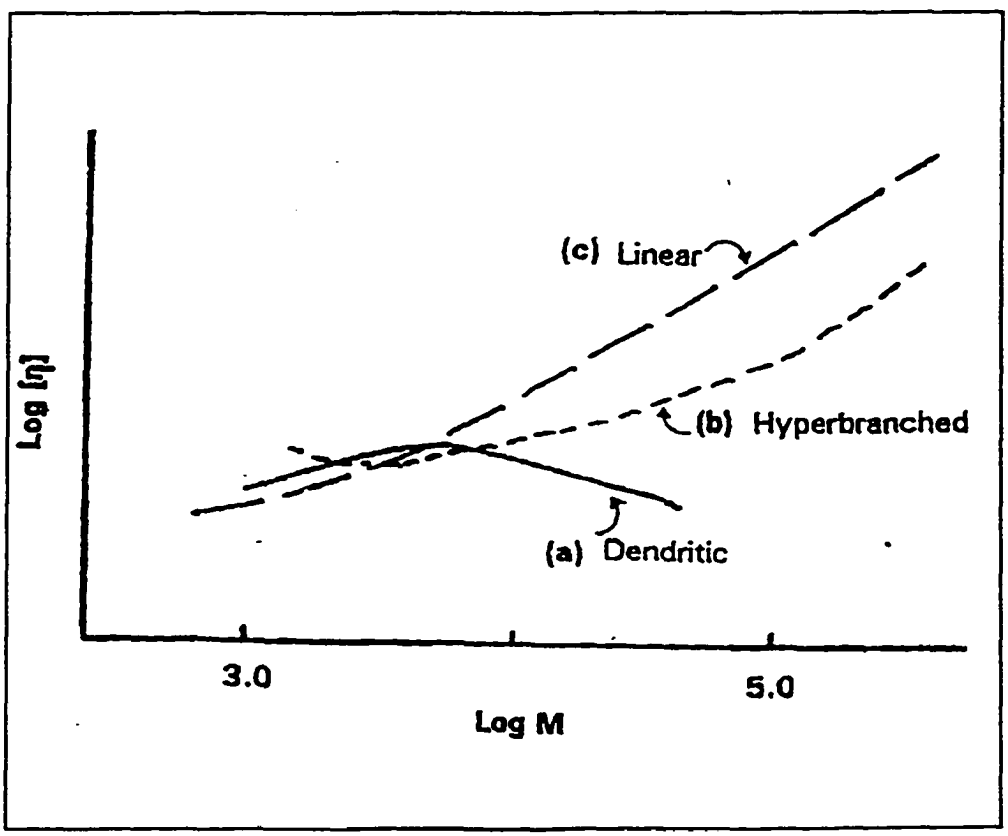
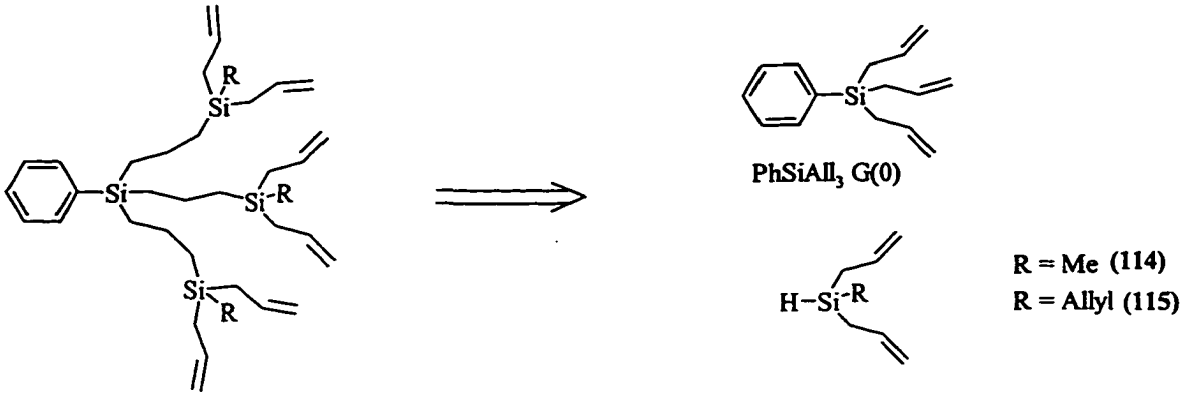


Figure 5.1 Comparison of intrinsic viscosity *vs* molecular weight relationship for three different polymer architectures from ref. 69

5.1 Synthetic Strategy

The synthetic approach is to attempt to perform both the hydrosilylation and alkenylation steps in one reaction vessel (*i.e.* in 'one-pot') which can be illustrated in a retro synthetic analysis. The substructures built into the dendritic framework are identified as both a monomer unit and core component which would have to be used for a rapid synthesis approach. A model G(1) compound with three branches per silicon (3B) is shown in Scheme 5.1; this identifies the core as phenyltriallylsilane and the monomer units could be either diallylmethylsilane **(114)** or triallylsilane **(115)**.



Scheme 5.1 Retro synthetic analysis for a rapid synthesis approach

The plan is to use triallylsilane as an AB_3 monomer, where A = H-Si and B = allyl group, and the core group as the focal point of attachment. Two synthetic tactics may be employed; addition of the core with the stoichiometric amount of monomer in 'one-pot', or by slow addition of this repeating unit to the core molecule. The latter is a more 'controlled' procedure where the purpose is to overcome the statistical distribution in which the monomer is more likely to react with itself before reacting with the core. Both approaches have been

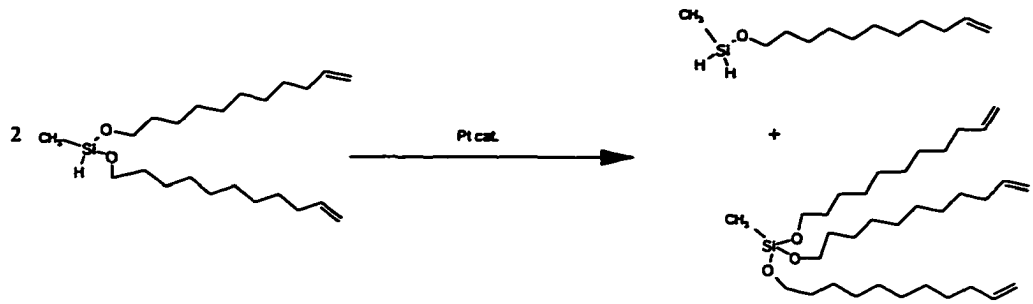
attempted by various workers with varying degrees of success.[19a,d] For either case above, the purity of the monomer unit is critical; impure starting materials give many unwanted side products as previously seen in polymer syntheses undertaken in a 'one-pot' manner.[70] Also of significance is the choice of catalyst used in a rapid synthesis; Muzafarov *et al*[71] studied various active hydrosilylation catalysts and a summary of the results is presented in Table 5.1.

Table 5.1 Hydrosilylation Reaction Conditions for $H(CH_3)Si[O(CH_2)_9CH=CH_2]_2$[71]

Catalyst	Reaction Mixture	Results
PC 072[a]	Bulk	Cross linked, after 25 min
H_2PtCl_6[b]	Bulk	Cross linked, after 15 min
H_2PtCl_6[b]	30% monomer in hexane	Soluble polymer, after 90 min viscous, clear liquid
$Co_2(CO)_8$[c]	Bulk	Soluble polymer, after 25 h viscous, clear liquid

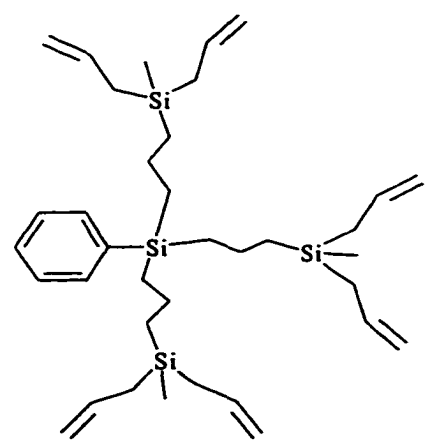
[a] Pt-divinyltetramethyldisiloxane complex, 3-3.5 wt % Pt in xylene. [b] 0.05 g/mL in THF. [c] 1×10^{-3} mol of Co/L in hexane.

The more active catalysts give highly cross-linked materials and a proposal[71] to explain these results is illustrated in Scheme 5.2, where an unwanted rearrangement of the monomer unit occurs however, dilution into hexanes suppresses this gelation. More selective catalysts, such as the Co dimer, seem to further suppress gelation, which is attributed to the stability of the product towards further reaction with the catalyst.[33]

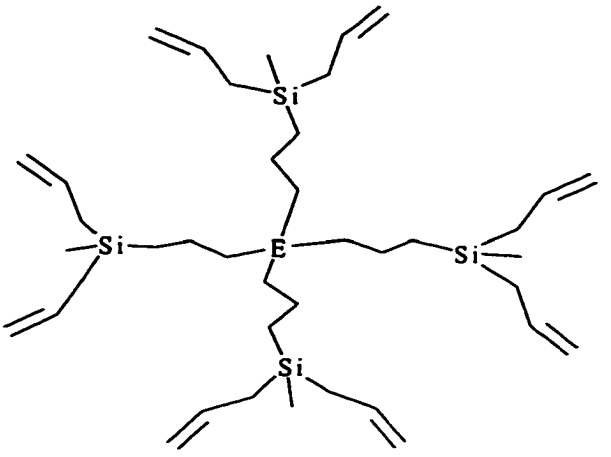


Scheme 5.2 Rearrangement process from ref. 71

For a rapid synthesis reaction, the simplest case that could be looked at is where only one new layer ('shell') is added to the periphery. When using a trifurcate core group, analysis of the result should be straightforward, since the product will contain an internal integration device (or even with a bifurcate system); however, for the spheroidal or hexafunctional structures this is not as simple. The problems associated with NMR studies of materials that contain three identical groups per silicon atom and no integration reference have been analysed in chapter three; this problem may be overcome if the chosen core molecule has been pre-synthesised as a first generation two-branch point molecule, G(1)2B such as those illustrated on the following page (see also pages 58 and 106).



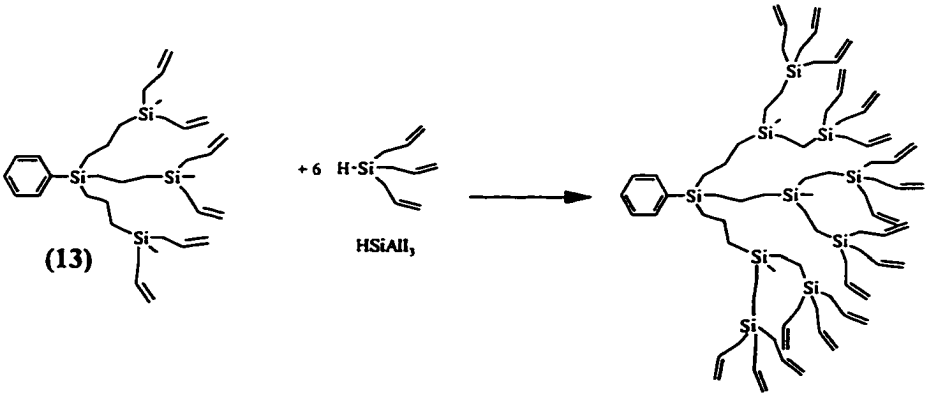
PhSi[(prSiMe)$^{1}_{2}$:All]$_3$ (13)



E[(pr/etSiMe)$^{l}_{2}$:All]$_4$ E = Si or Ge

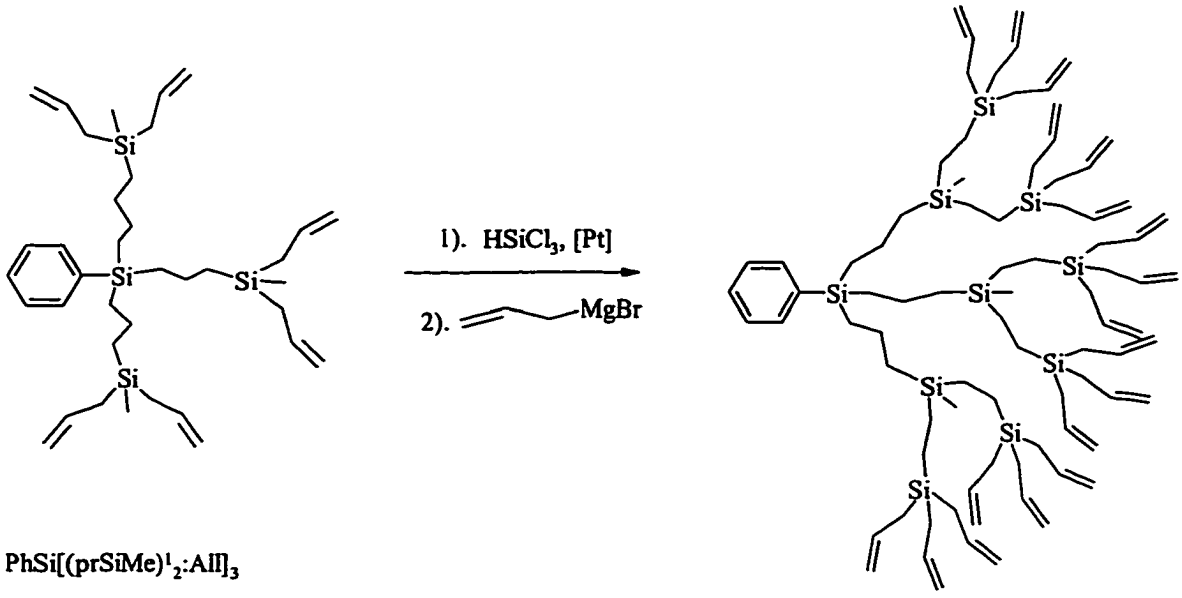
(47), (59) or (63)

In either example shown **(13)**, **(47)**, **(59)**, and **(63)** there are pre-positioned silicon methyl groups present, *i.e.* a 'hypercore', which can act as the integration reference for proton NMR spectroscopy. Thus, the simplest case of hyperbranched polymers can now be studied with all systems; spheroid, trifurcate and bifurcate cores, with the aim of controlling the growth of the next generation to one more discrete shell. These materials are designated as 'hybrid' molecules since the branch point multiplicity changes from 2 to 3. A specific possibility is shown below using one of these hypercores **(13)**; this is an idealised case where all the terminal allyl groups have reacted identically with the triallylsilane monomer, Scheme 5.3.



Scheme 5.3 Idealised addition of triallylsilane to PhSi[(prSiMe)$^{l}_{2}$:All]$_3$ hypercore

These hyperbranched materials can be characterized using multinuclear NMR (^{1}H, ^{13}C and ^{29}Si) spectroscopy, and comparisons will be made to the compounds synthesised in a stepwise manner from the same hypercores, Scheme 5.4. The use of GPC is now crucial for identification of different polymeric materials present in any mixtures produced from a rapid synthesis; differing masses and the degree of polydispersity may be detected although the overall architecture of a hyperbranched polymer will remain unknown.



$PhSi[(prSiMe)^{1}_{2}:All]_{3}$

$PhSi[(prSiMe)^{1}_{2}(prSi)^{2}_{3}:All]_{3}$

Scheme 5.4 Stepwise formation of a hybrid dendrimer system

Listed are the different hypercore molecules that have been used in the one-shell expansion experiments described in this thesis; these have been synthesised *via* step-wise methodology and are fully characterized (see chapters two and three).

Core Molecules

(13) PhSi[(prSiMe)$^1_2$:All]$_3$ G(1)2B **(59)** Si[(prSiMe)$^1_2$:All]$_4$ G(1)2B

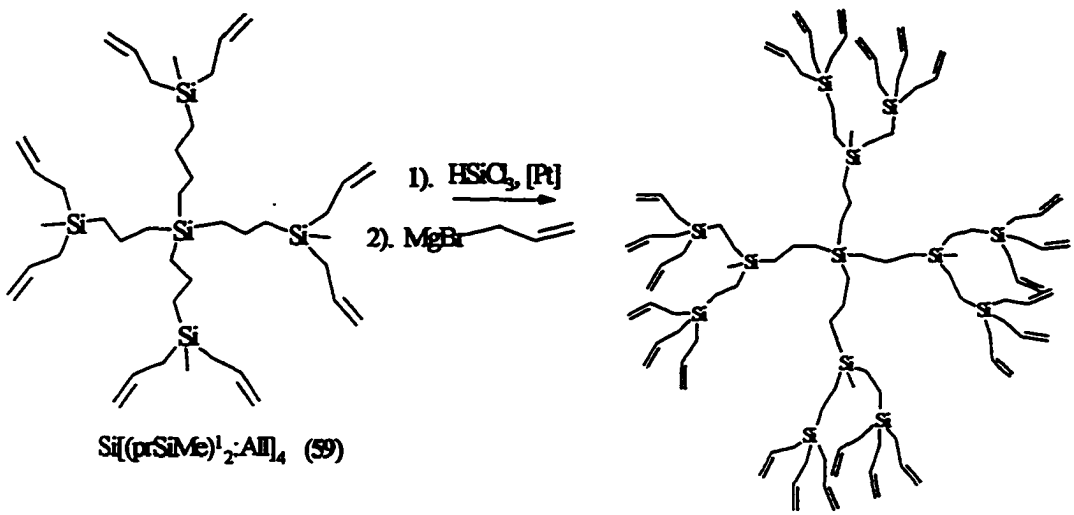
(47) Ge[(prSiMe)$^1_2$:All]$_4$ G(1)2B **(63)** Ge[(etSiMe)$^1_2$:All]$_4$ G(1)2B

(53) Ge$_2$[(etSiMe)$^1_2$:All]$_6$ G(1)2B **(61)** Si[(prSiMe)$^2_2$:All]$_4$ G(2)2B

(15) PhSi[(prSiMe)$^2_2$:All]$_3$ G(2)2B

5.2 Stepwise synthesis

The target molecules for this chemistry have been prepared independently *via* a controlled stepwise reaction sequence (*i.e.* chapters two and three) from a trifurcate hypercore molecule, Scheme 5.4, resulting in a change in the branch point topography from two branches per silicon atom to three (2B to 3B). The reaction sequence used from a first generation tetrahedral core molecule is shown in Scheme 5.5, where the four internal methyl groups may be used as integration signals in the hybrid product.



Scheme 5.5 Stepwise synthesis of spheroidal hybrid dendrimer (117) $Si[(prSiMe)^1_2:(prSi)^2_3:All]_4$

The first stage addition of trichlorosilane led to a trichlorosilyl intermediate $Si[(prSiMe)^1_2(prSi)^2_3:Cl_3]_4$ **(116)**. Data are shown in Table 5.2, with the internal methyl signal assigned a peak intensity proportional to twelve protons (using WIN-NMR software) and the remaining hydrogens being integrated relative to this. All NMR features are as expected.

Table 5.2 Selected spectral data for compound (116) $Si[(prSiMe)^1_2(prSi)^2_3:Cl_3]_4$

^{1}H δ ppm (Int)	1.8-0.4 m (72±) *72H* 0.05 s (=12) *12H* (CH_3)
^{13}C δ ppm	28.4, 24.3, 22.4, 17.3 16.9, 16.5 -5.28 (Si-CH_3)
^{29}Si δ ppm	12.20 (Si-Cl_3) 1.66 (Si-Me) 0.95 (Si_{core})
IR cm^{-1}	2910 (C-H) 1255 (Si-C) 570 (Si-Cl)

Subsequent reaction with an excess of allyl magnesium bromide produced a thick colourless oil (117). It would be predicted (from results in chapter three, *i.e.* compound (61)) that in the ^{1}H NMR, the methyl resonance would be one sharp peak (δ -0.04 ppm) but in fact some very interesting differences from this are observed. Five Si-Me resonances appear in the ^{1}H NMR spectrum of the product (Figure 5.1) integrating to the calculated ratio, apparently experiencing distinguishable environments that are not averaged in solution. This may be attributed to either steric crowding of the interior methyl proton environments because of addition of bulkier triallylsilyl groups in the exterior shell, or to an increase in chain entanglements caused by the addition of these larger peripheral groups.

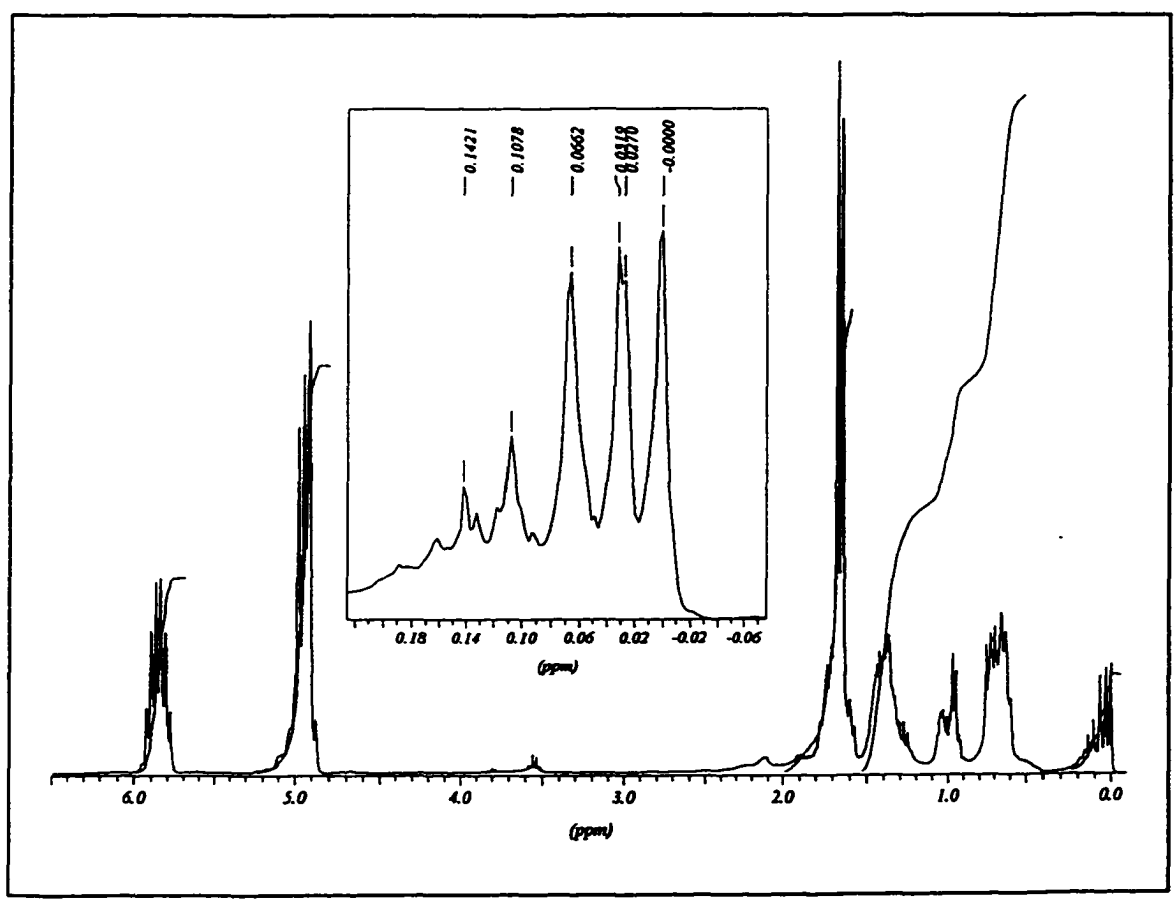


Figure 5.2a ^{1}H NMR spectrum of compound (117) Si[(prSiMe)$^1_2$(prSi)$^2_3$:All]$_4$

The ^{13}C NMR spectrum of this compound (117) also shows multiple methylsilyl signals, with the strongest resonance occurring at δ -5.03 ppm accompanied by three weak lines. This also suggests that interior positions are not free to behave ideally in solution (compared to single topology branch sites in chapters two and three) and therefore appear less intense. It appears that the interior methyl groups of the second generation using any outer branching system show some degree of inequivalence.

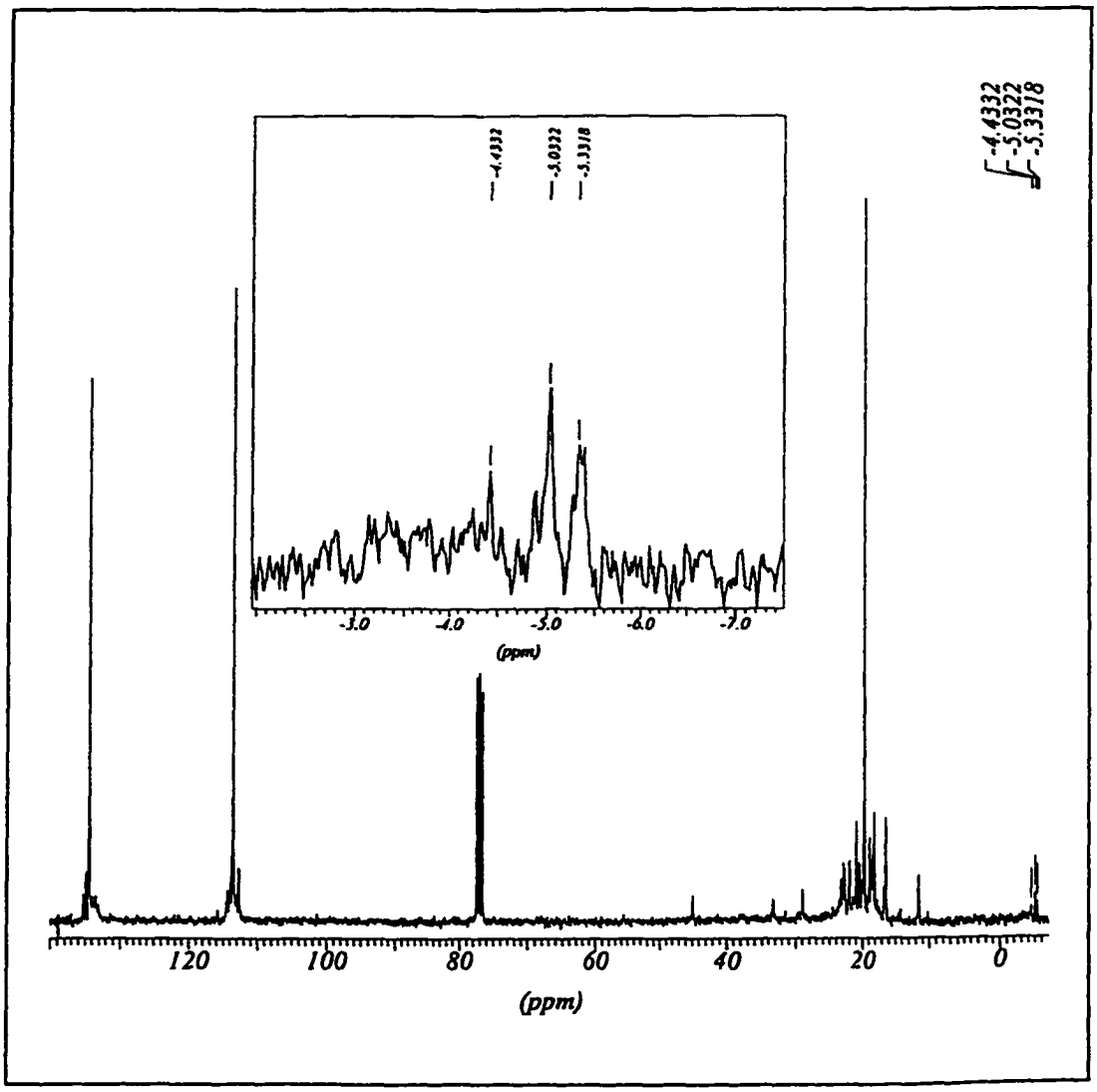


Figure 5.2 ^{13}C NMR of compound (117) $Si[(prSiMe)^1_2(prSi)^2_3:All]_4$

The ^{29}Si NMR shows a very weak signal for the silicon attached to the methyl groups (Figure 5.3). The core silicon is observed at δ 1.12 ppm as expected from the precursor, while the exterior triallylsilyl silicon (δ -1.10 ppm) is comparable to other derivatives with this terminal group (chapters two and three). Another peak at δ 0.32 ppm is assigned as a chain entangled terminal allylsilane resonance and the Si-Me resonance (δ 0.68 ppm) is not well resolved compared to the sharp peak seen at δ 0.23 ppm seen in the precursor.

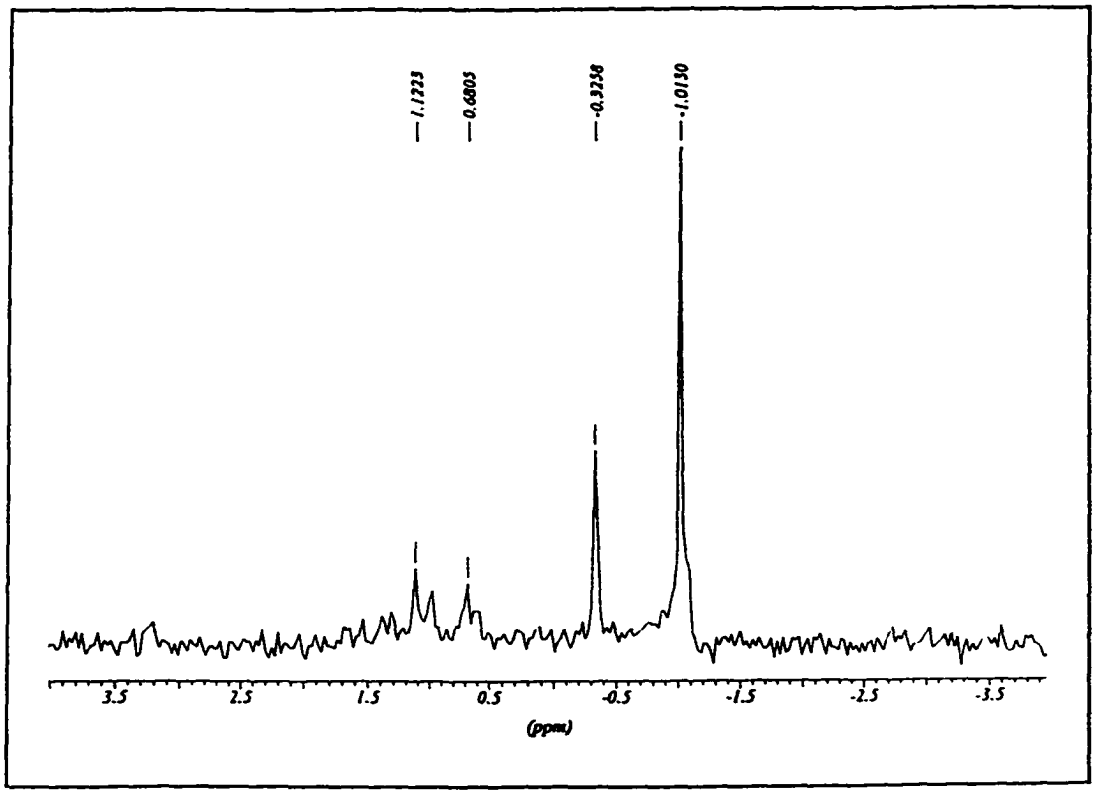
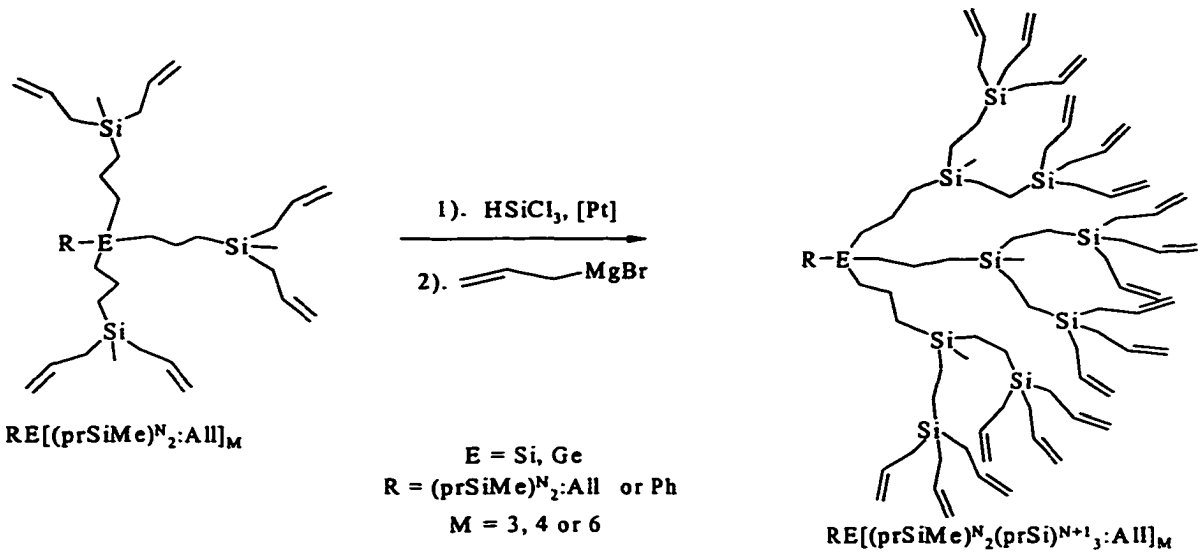


Figure 5.3 ^{29}Si-{^{1}H} NMR spectrum of compound (117) $Si[(prSiMe)^{1}_{2}(prSi)^{2}_{3}:All]_{4}$

Table 5.3 Selected spectral data for compound (117) Si[(prSiMe)$^1_2$(prSi)$^2_3$:All]$_4$

	=CH	CH_2	$Si-CH_3$
δ ppm	5.80	1.6-0.5	0.14-0.00
^1H (Int)	(24±2.4) *24H*	(74±7) *72H*	(=12) *12H*
^{13}C δ ppm	134.4	22.0-15.0	-4.4, -5.0, -5.3
^{29}Si δ ppm	1.12 (Si_{core})	0.68 (Si-Me)	-1.10 ($SiAll_3$)
IR cm^{-1}	3060, 2920, 1625, 1250		
Elemental Analysis	% Calculated		% Found
	C 70.29		C 69.37
	H 10.67		H 10.25

When the step-wise hybrid experiment was repeated with other hypercore molecules (Scheme 5.6) similar multinuclear NMR spectra were observed. The Si-methyl groups are in distinct environments from each other in all spectra (^1H, ^{13}C and ^{29}Si) for the product, which is attributed to steric crowding by the addition of the bulkier peripheral groups thus increasing chain entanglements. All intensities of the silicon methyl signals (^1H, ^{13}C and ^{29}Si) are greatly diminished from those in their respective precursors. Spectroscopic data are summarized in Tables 5.4 and 5.5.



Scheme 5.6 General reaction sequence for stepwise hybrid formation

Table 5.4 Selected spectroscopic data for stepwise hybrid systems

Hybrid	=CH	$=CH_2$	CH_2	$SiCH_3$
^1H integration				
(119) $Si[(prSiMe)^2{}_2(prSi)^3{}_3:All]_4$	(48±5)*48H*	(100±10)*96H*	(98±10)*96H*	(=36)*36H*
(121) $PhSi[(prSiMe)^1{}_2(prSi)^2{}_3:All]_3$	(18±2)*18H*	(36±4)*36H*	(36±4)*36H*	(=9)*9H*
(123) $PhSi[(prSiMe)^2{}_2(prSi)^3{}_3:All]_3$	(36±4)*36H*	(76±7)*72H*	(76±7)*72H*	(=27)*27H*
(125) $Ge[(prSiMe)^1{}_2(prSi)^2{}_3:All]_4$	(24±2)*24H*	(48±5)*48H*	(48±5)*48H*	(=12)*12H*
(127) $Ge[(etSiMe)^1{}_2(prSi)^2{}_3:All]_4$	(24±2)*24H*	(48±5)*48H*	(48±5)*48H*	(=12)*12H*
(129) $Ge_2[(etSiMe)^1{}_2(prSi)^2{}_3All]_6$	(36±4)*36H*	(74±7)*72H*	(76±8)*72H*	(=18)*18H*

^{13}C δ ppm		=CH	$=CH_2$	$SiCH_3$
(119)	$Si[(prSiMe)^2{}_2(prSi)^3{}_3:All]_4$	134.4	113.5	-5.03, -5.34
(121)	$PhSi[(prSiMe)^1{}_2(prSi)^2{}_3:All]_3$	134.4	113.5	-5.03, -5.35
(123)	$PhSi[(prSiMe)^2{}_2(prSi)^3{}_3:All]_3$	134.4	113.5	-5.05, -5.34
(125)	$Ge[(prSiMe)^1{}_2(prSi)^2{}_3:All]_4$	134.4	113.5	-5.40
(127)	$Ge[(etSiMe)^1{}_2(prSi)^2{}_3:All]_4$	134.4	113.5	-5.65, -5.91
(129)	$Ge_2[(etSiMe)^1{}_2(prSi)^2{}_3All]_6$	134.4	113.5	-5.65, -5.91

Table 5.5 ^{29}Si NMR chemical shifts for stepwise hybrid dendrimer systems

Hybrid		Si_{core}	$SiCH_3$	$SiAll_3$
		δ ppm	δ ppm	δ ppm
(119)	$Si[(prSiMe)^2_2(prSi)^3_3:All]_4$	1.12	1.02, 0.70, 0.62	-1.01
(121)	$PhSi[(prSiMe)^1_2(prSi)^2_3:All]_3$	-4.00	1.02, 0.70, 0.62	-1.01
(123)	$PhSi[(prSiMe)^2_2(prSi)^3_3:All]_3$	-4.00	0.95, 0.70, 0.23	-1.02
(125)	$Ge[(prSiMe)^1_2(prSi)^2_3:All]_4$		2.41, 1.11	-1.02
(127)	$Ge[(etSiMe)^1_2(prSi)^2_3:All]_4$		1.11, 0.70, 0.28	-1.02
(129)	$Ge_2[(etSiMe)^1_2(prSi)^2_3All]_6$		2.49, 2.25, 1.13	-1.02

These products have also been characterized by gel permeation chromatography. The chromatograms obtained for these compounds all showed a slight shoulder at a shorter elution time than the major peak (Table 5.6), attributable to material with a higher molecular mass. Also included are the polydispersity index (PDI) measurements *vs* polystyrene standards as a measure of purity for that compound.

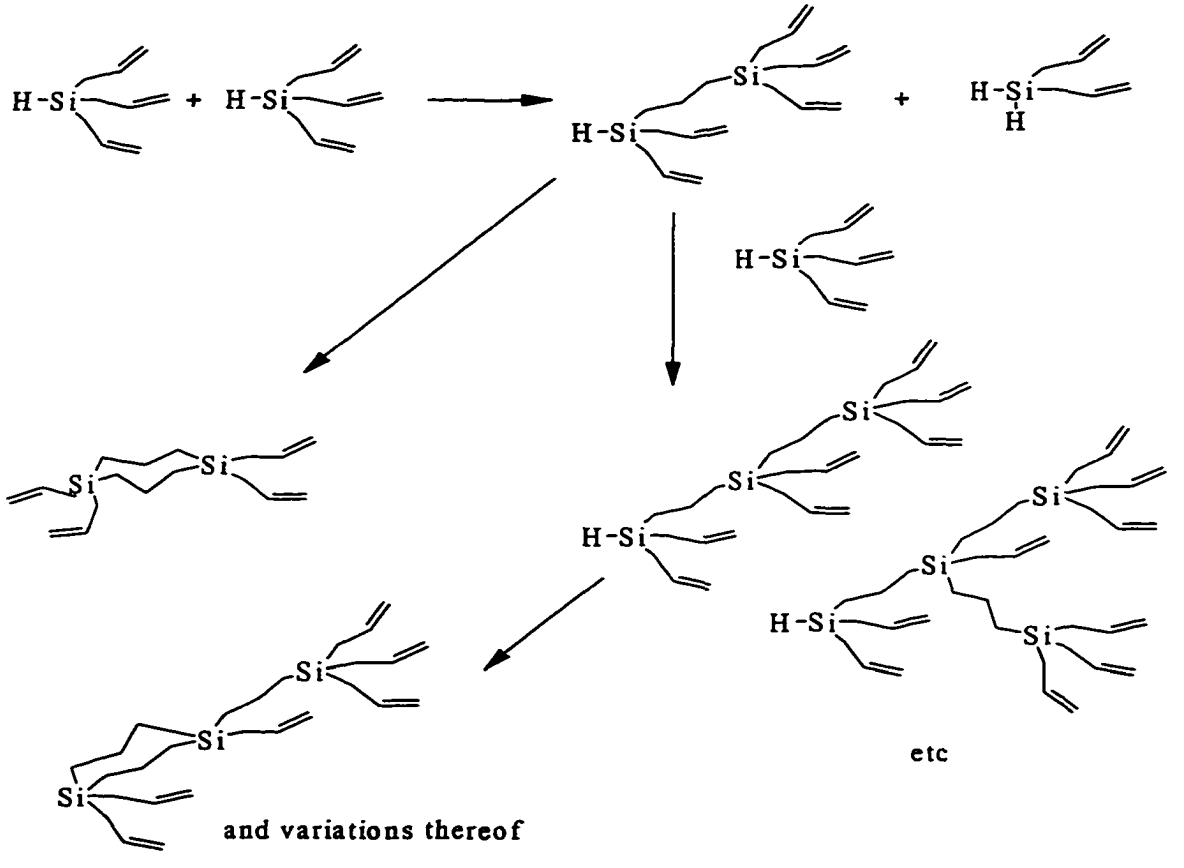
Table 5.6 Selected analytical data for hybrid dendrimer systems

Hybrid		GPC		
		Retention Time (min)	Mass App.* *Calcd.*	PDI
(119)	$Si[(prSiMe)^2_2(prSi)^3_3:All]_4$	16.9	3000 (*4136*)	1.63
(121)	$PhSi[(prSiMe)^1_2(prSi)^2_3:All]_3$	22.5	1450 (*1518*)	1.13
(123)	$PhSi[(prSiMe)^2_2(prSi)^3_3:All]_3$	16.9	3000 (*3186*)	1.47
(125)	$Ge[(prSiMe)^1_2(prSi)^2_3:All]_4$	21.8	1900 (*1957*)	1.20
(127)	$Ge[(etSiMe)^1_2(prSi)^2_3:All]_4$	22.0	1808 (*1901*)	1.28
(129)	$Ge_2[(etSiMe)^1_2(prSi)^2_3All]_6$	21.3	2821 (*2888*)	1.39

*masses are reported as apparent values from GPC software *vs* PS standards

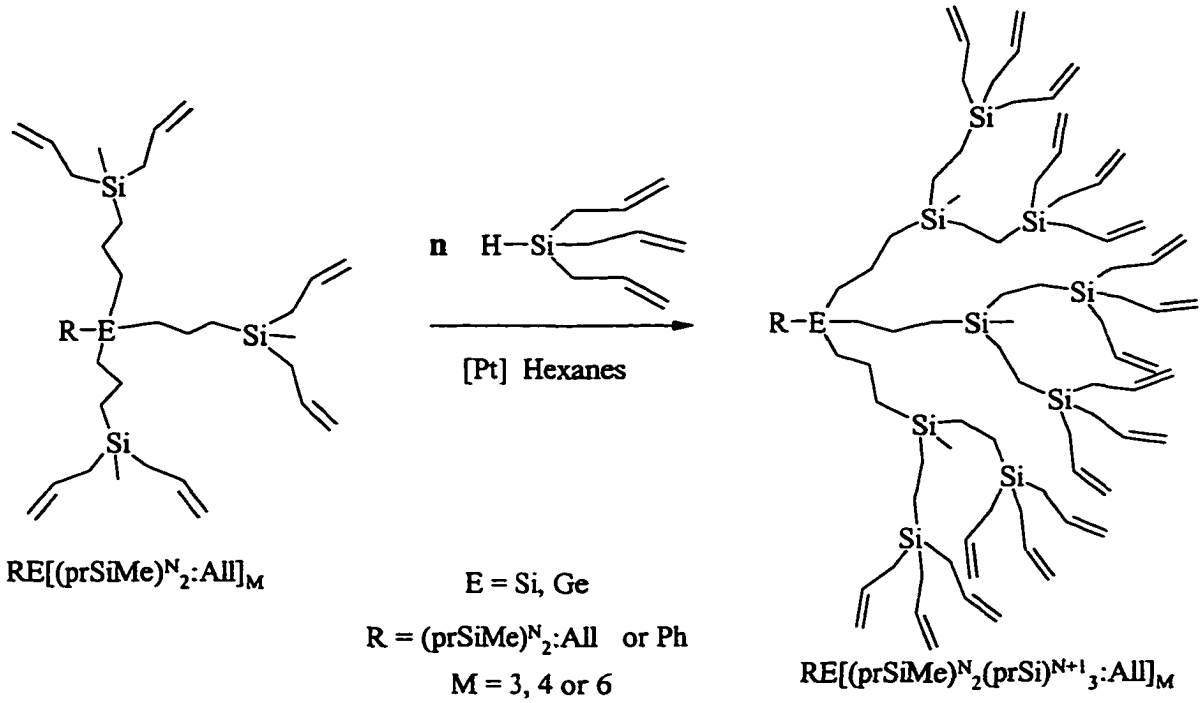
5.3 Rapid Assembly Materials

Two possible methods to synthesize rapid assembly materials have been mentioned earlier, the first method involving placing all of the components necessary into one vessel and allowing them to react. The disadvantage of this 'one-pot' method is the occurrence of two competing reactions, self-condensation of monomer *vs* the wanted condensation onto the core structure. Thus, when all of the repeat unit required for stoichiometric formation of the target product is present, the condensation-polymerization reaction, examples of which are shown below (Scheme 5.7), is strongly favoured statistically.



Scheme 5.7 Polycondensation of triallylsilane

The second strategy (which resembles other high-dilution methods, *e.g.* those used to synthesise macrocycles *vs* polymer analogues),[81] involves slow addition of a very dilute monomer solution into a vessel containing a core structure (with minimum solvent, typically 2 mL) with catalyst present. This attempts to overcome the statistical distribution that favours monomer 'condensation-polymerisation'; by minimising the amount of monomer present over time the reaction conditions are predisposed for reaction of silane with core molecule. Both procedures have been attempted by other workers with varying degrees of success.[19a, 69] The experiments reported in this section have all used slow addition of a very dilute monomer solution to a heated concentrated hypercore solution, as is shown in Scheme 5.8.

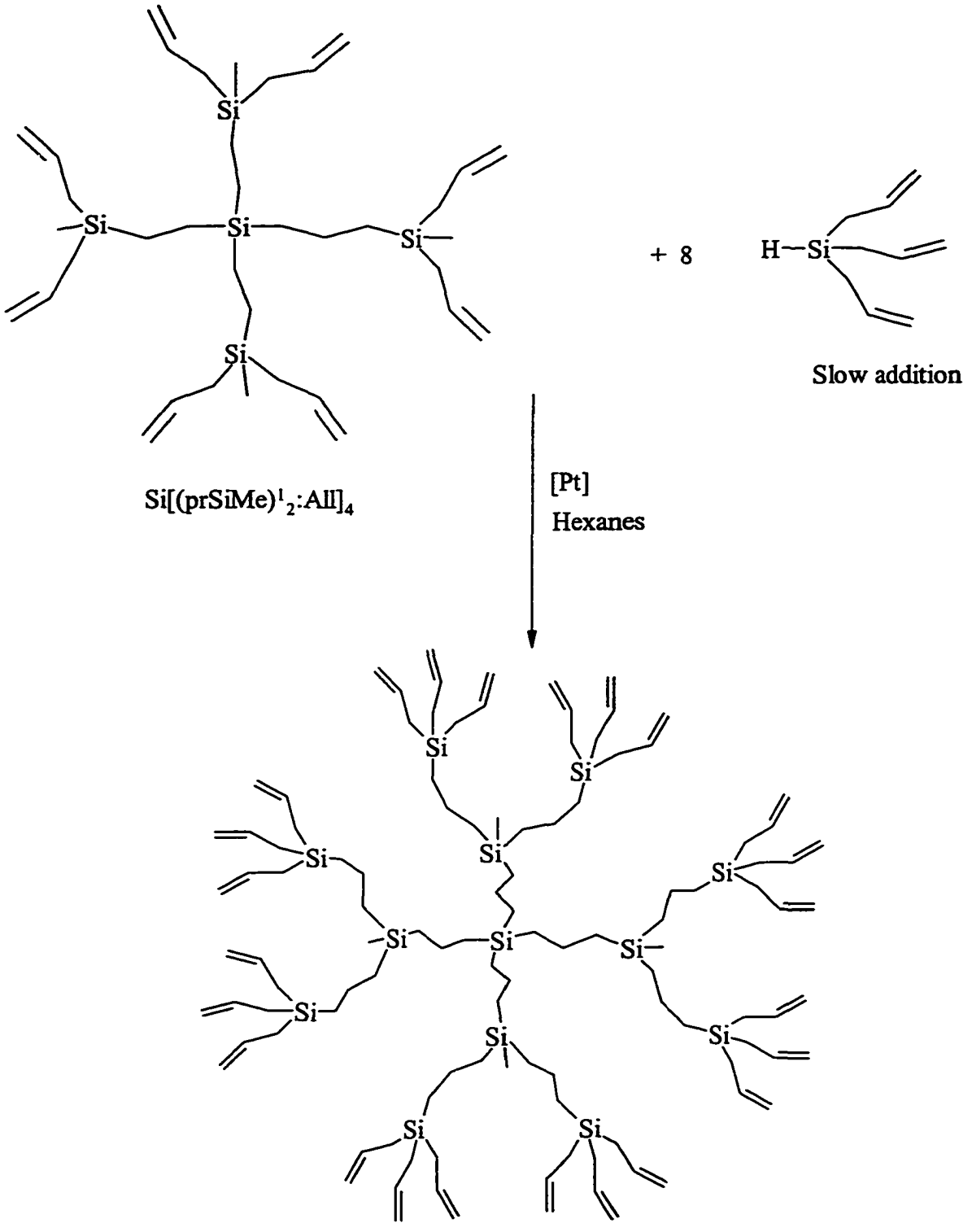


Scheme 5.8 General rapid assembly reaction

5.3.1 Results from Rapid Assembly reactions

The addition of 8 equivalents of triallylsilane to a hypercore molecule of $Si[(prSiMe)^{I}_{2}:All]_{4}$ is one specific example that will be studied in detail, as illustrated in Scheme 5.9 on the following page. The hypercore contains 8 peripheral alkenyl groups and the required stoichiometry of monomer for a one-shell expansion is 8 equivalents of triallylsilane. The latter accounts for 24 reactive alkene groups out of a total of 32 present, so that of the groups present, 8/32 are attached to the core molecule and the remaining 24/32 come from the monomer. On a purely statistical basis, the monomer is therefore three times more likely to self-condense and in order to minimise such behaviour the reaction between hypercore and monomer was accomplished by maintaining a dropwise addition of triallylsilane to a heated core solution. The effect is that the monomer solution is added slowly over time to a concentrated, heated solution of hypercore and thus the addition reaction to the hypercore should also be kinetically favoured.

After removal of all residual volatiles under vacuum, a crude product was isolated and analysed by multinuclear NMR spectroscopy and GPC. Fractions of this crude compound were separated by flash column chromatography, as monitored by thin layer chromatography (TLC), and each fraction was also analysed in a similar manner, see Table 5.7. The crude mass of the material **(130)** recovered from the reaction vessel was 92% of the initial weights added.



Scheme 5.9 Rapid synthesis of spheroidal hybrid dendrimer

Table 5.7 Selected spectroscopic data for column fractions isolated from the reaction between $Si[(prSiMe)^1_2:All]_4$ and 8 equiv. of $HSiAll_3$ product (130)

	Mass (g)	^{1}H integration	GPC		
		=CH : $SiCH_3$	r.t. (min)	Mass	(PDI)
Fraction 1	0.327 (29%)	15±1.5 : =12	23.62	806	(1.08)
Fraction 2	0.356 (31%)	30±3.0 : =12	21.90	1956	(1.53)
Fraction 3	0.461 (40%)	36±3.4 : =12	19.85	6182	(3.09)

^{29}Si data	δ ppm			
	Si_{core}	$SiCH_3$	$SiAll_3$	Si_{other}
Fraction 1	0.95	0.23	-1.06	0.61, -0.26
Fraction 2	0.92	0.23	-1.06	-0.35
Fraction 3	0.95	0.22	-1.07	0.56, -0.41

In the proton NMR spectrum for the crude reaction mixture there appears to only be one very intense Si-methyl peak centred at δ -0.04 ppm, Figure 5.4. The relative integration of this methyl resonance to the terminal allyl groups is consistent with the stoichiometry of the monomer added (12:24). Both the ^{13}C and ^{29}Si NMR spectra (Figures 5.5 and 5.6) also show a single sharp resonance associated with this silicon methyl group with chemical shifts similar to those in the precursor. In the ^{29}Si NMR there is a further peak at δ -1.10 ppm, which can be assigned to a terminal triallylsilyl fragment (chapters two and three).

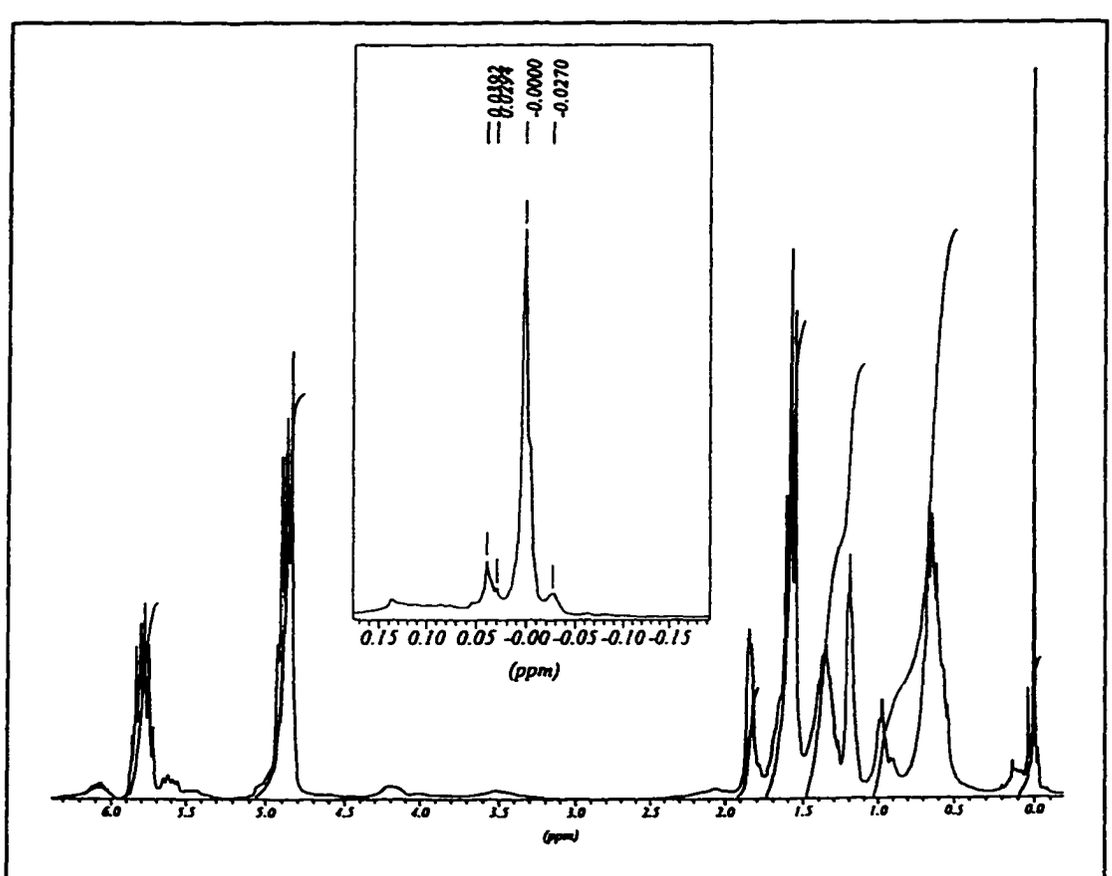


Figure 5.4 ^{1}H NMR of Si[(prSiMe)$^{1}_{2}$:All]$_4$ hypercore reacted with 8 equiv. of triallylsilane crude product mixture (130)

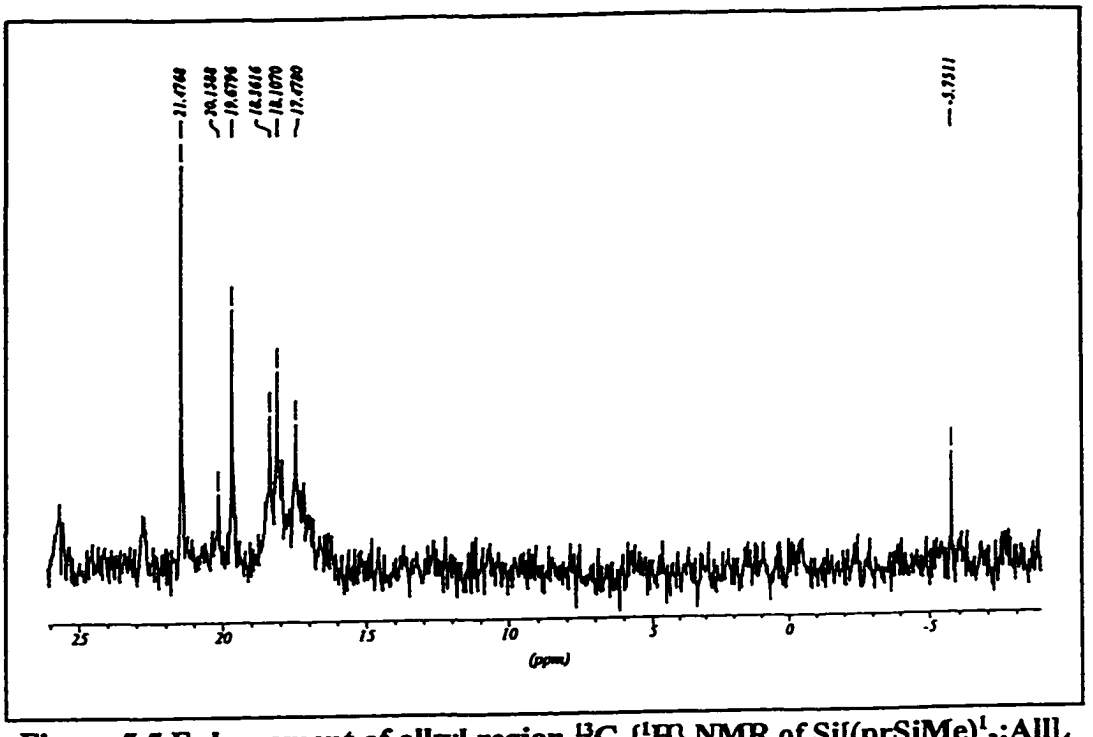


Figure 5.5 Enlargement of alkyl region ^{13}C-{^{1}H} NMR of Si[(prSiMe)$^{1}_{2}$:All]$_4$ with 8 equiv. of HSiAll$_3$ (130)

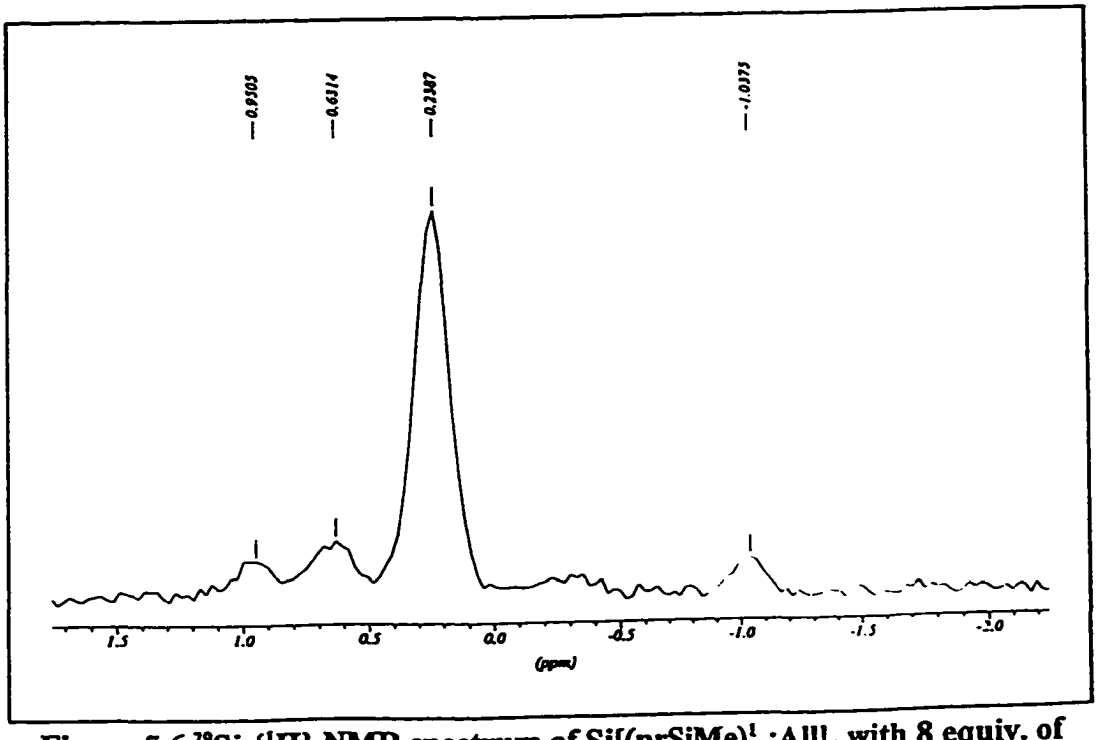


Figure 5.6 ^{29}Si-{^{1}H} NMR spectrum of Si[(prSiMe)$^{1}_{2}$:All]$_4$ with 8 equiv. of HSiAll$_3$ (130)

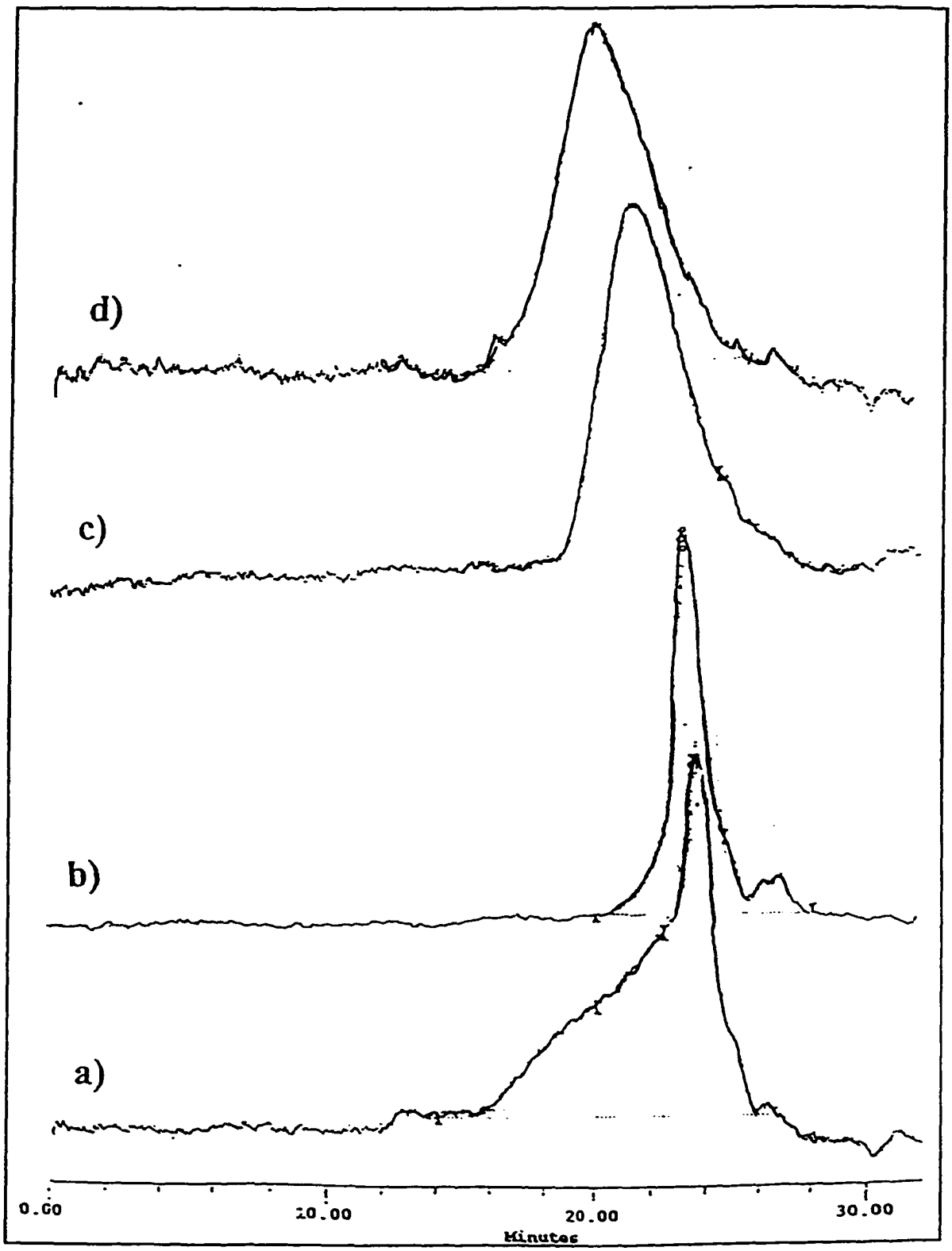


Figure 5.7 GPC traces of the reaction between Si[(prSiMe)$^{1}_{2}$:All]$_4$ and triallylsilane (130): a) crude mixture; b) fraction one; c) fraction two; d) fraction three.

The GPC chromatograms, shown above, for this crude mixture shows one major peak at the apparent mass of the starting material with a very broad tail for masses higher than this (Figure 5.6). There would appear to be no monomer remaining in the mixture and a only very small amounts of low mass oligomers are observed at longer elution times than the core moleule, *i.e.* that would be formed from self-condensation reactions and/or cyclisation. From GPC measurements this major peak is approximately 50% of the material present, with the broad tail accounting for the remainder of the material. These chromatographs were recorded on a Waters Millenium system, calibrated to polystyrene standards, and so a measure of the polydispersity index (PDI) could be calculated as a measure of the area under the main peak relative to the total area under the plot. Although this was not a clean separation, approximately 30% of the core molecule is unreacted after 24 hours, which elutes with what may be oligiomers of triallylsilane. About 30% has an apparent mass and relative integration appropriate for the target material, while the remainder appears to be some highly branched polymer with large mass. The last of these fractions was not investigated further; the GPC of the second (product) fraction gives no information about its structural characteristics but its polydispersity (1.53) is low.

In comparison with the product (**117**), see page 168, obtained by stepwise synthesis there are clear differences in all the multinuclear NMR spectra. The distinguishable methyl resonances that were seen in the stepwise product were attributed to steric constriction of the interior Si-Me groups. The Si-Me resonances in the hyperbranched product shows none of these features, although it has clearly been generated by monomer adduction to the hypercore. This would imply that a new peripheral triallylsilyl group is more reactive than

the remaining diallylmethylsilyl groups on the hypercore, resulting in extension (growth) away from the latter to develop a 3B substructure.

Using a germanium centred hypercore molecule, $Ge[(prSiMe)^1_2:All]_4$, addition of 8 equivalents of triallylsilane resulted in similar observations, Table 5.8. After separation of the crude material into fractions, the first fraction appears to be unreacted core and the remainder has a relative integration and GPC characteristics that suggests growth by addition of triallylsilane.

Table 5.8 Selected spectral data from rapid assembly reaction with $Ge[(prSiMe)^1_2:All]_4$ and 8 equivalents of $HSiAll_3$ product (131)

Core	mass g	^{1}H integration =CH : $SiCH_3$	^{29}Si δ ppm	GPC rt (min)	App Mass
$Ge[(prSiMe)^1_2:All]_4$	8 equivalents of $HSiAll_3$				
Crude	0.342	20±2 : =12	0.35, 0.24, -0.32, -0.96	-	-
Fraction 1	0.117	12±1.2: =12	0.25	23.9	723
Fraction 2	0.030	40±4.0: =12	0.69, 0.24, -0.41, -1.06	22.4	1465

A similar reaction was attempted with a larger hypercore to examine the possibility that more peripheral alkenyl groups would further bias the addition of monomer to the core structure rather than to itself. The hypercore used was $Si[(prSiMe)^2_2{:}All]_4$ with slow addition of 16 equivalents of $HSiAll_3$. Proton NMR integration (Table 5.9) shows that both of the fractions recovered from this reaction are products formed in which the core structure has been extended by addition of monomer; whereas with the previous two examples, a substantial amount of unreacted hypercore was recovered. This is accounted for by the increased number of terminal diallylmethylsilyl groups which are available to react with the monomer, *i.e.* the monomer adds preferentially to the larger hypercore rather than to itself (self-condensation) as in the previous examples. GPC chromatograms were not recorded on any of these products and so this assumption relies upon the proton integration (Figure 5.7). Comparisons to the silicon NMR chemical shifts with known stepwise derivatives are also useful, *i.e.* $pr_3\mathit{Si}Me$ (2B) and $pr\mathit{Si}All_3$ (3B) from Table 5.5 compound **(119)**.

Table 5.9 Selected spectral data for reaction between $Si[(prSiMe)^2_2{:}All]_4$ and 16 equivalents of $HSiAll_3$ product (132)

Core	mass	^{1}H integration	
	g	=CH : $SiCH_3$	^{29}Si δ ppm
$Si[(prSiMe)^2_2{:}All]_4$	16 equivalents of $HSiAll_3$		
Crude	0.830	48±5 : =36	0.99, 0.70, 0.26, -1.06
Fraction 1	0.254	34±3 : =36	0.97, 0.71, 0.28, -1.06
Fraction 2	0.467	47±5 : =36	0.99, 0.70, 0.26, -1.02

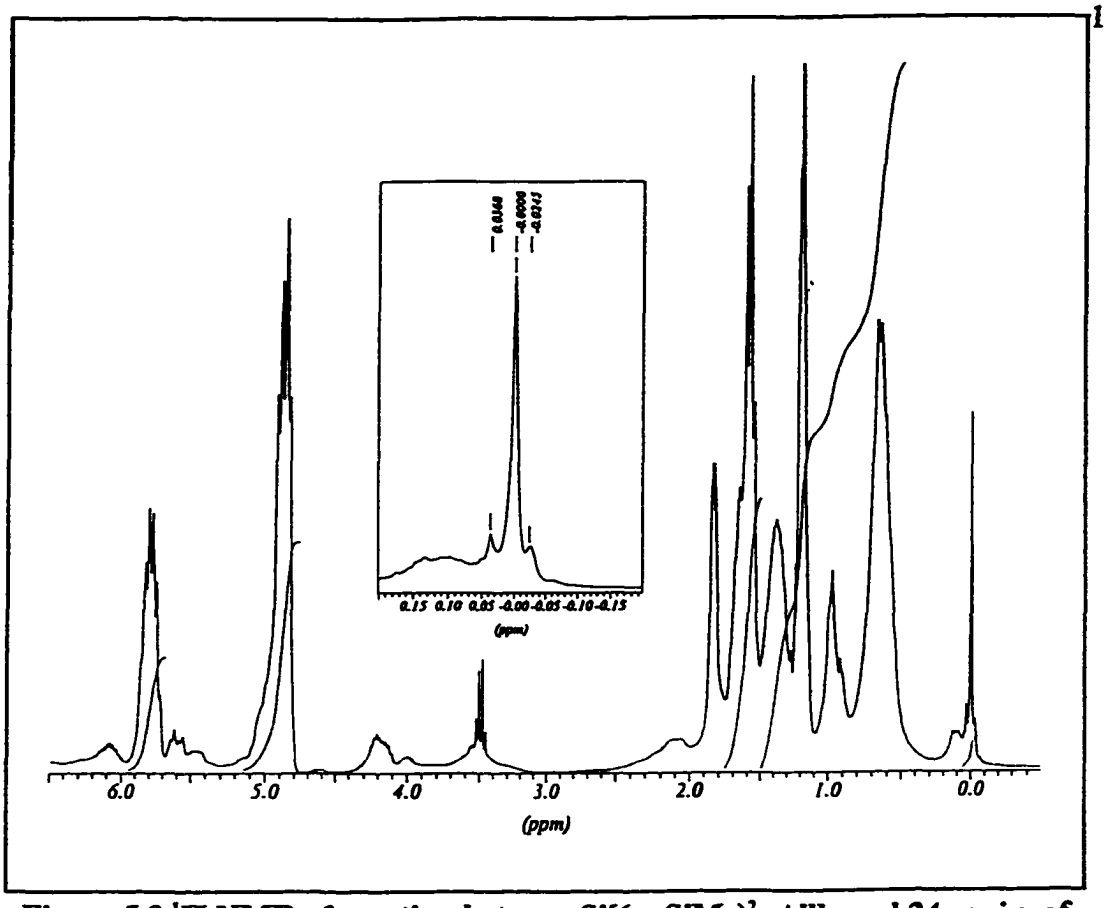
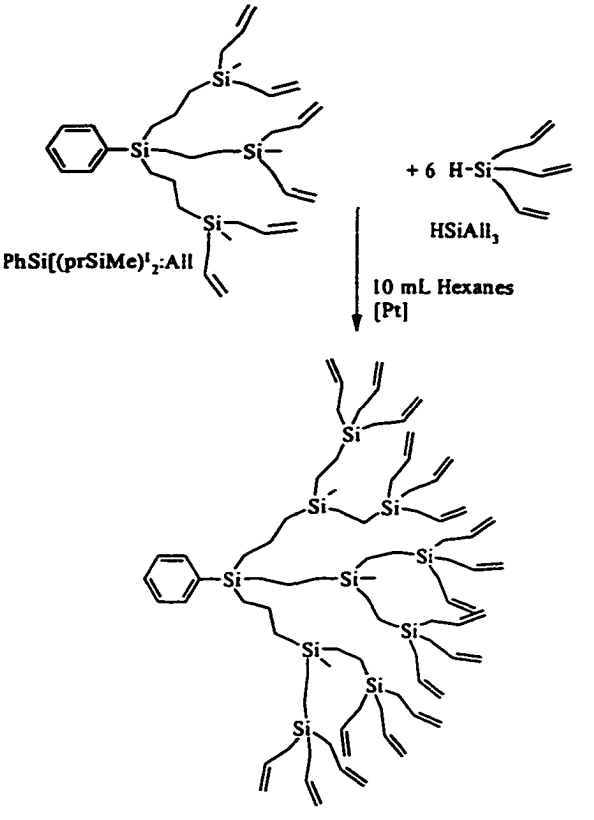


Figure 5.8 ^{1}H NMR of reaction between Si[(prSiMe)$^2_2$:All]$_4$ and 24 equiv. of triallylsilane; crude product (132)

5.4 GPC Experiment using a Rapid Assembly Reaction

In an attempt to further elucidate the results reported above, the addition of 6 equivalents of triallylsilane ($HSiAll_3$) to a Ph[(prSiMe)$^1_2$:All]$_3$ hypercore was monitored by GPC chromatography, Scheme 5.10.



Scheme 5.10 Idealised addition in 'one-pot' reaction

The relative concentrations of the core and monomer must be kept equal to ensure quantitative and consistent chromatographic results, so addition of all the reagents into 'one-pot' in 10 mL of hexanes at time = 0 min was used as the starting point (*i.e.* strategy 1, rather than 2 of section 5.3). Samples of 0.5 mL were removed for analysis at 30 min increments for the first two hours, then hourly intervals until the reaction appeared to be complete, Figure 5.9. These samples were analysed directly as they were removed from the reaction vessel and no attempt was made to remove solvent or catalyst from each sample. After 30 min reaction time a large peak representing the hypercore (Retention Time, RT = 24 min) and a little of the monomer (RT = 28 min) are observed, Figure 5.9. After 90 min no

monomer is visible by GPC, but instead there are peaks that appear to have masses corresponding to dimers and trimers of triallylsilane (RT = 25 and 24 min); these fractions were accompanied by rapid elution of material outside the range of the column assembly (RT = 14 min), *i.e.* high mass fractions. Observation of fractions assigned as dimer and trimer in particular would suggest that monomer self-condensation has occurred in a 'run-away' sense and that little has reacted with the hypercore. After 5 hours, the peaks attributed to smaller mass fractions are no longer seen and there are three major peaks with RT = 13, 23 and 24 min. The last of these is assigned as the hypercore molecule with very little incorporation of triallylsilane, whilst the fraction eluting at RT = 23 min is thought to have some addition of monomer to the hypercore.

Statistically and kinetically this procedure will favour monomer self-condensation, since all reactants are present at the beginning of the reaction. However, the GPC traces also showed that after a period of time no monomer is present and eventually all the low mass materials have been exhausted. Analysis of the final product mixture suggests that its composition resembles that of material obtained by the dropwise addition reactions, compare Table 5.10 with Tables 5.7-5.9. It is evident from the GPC data that these reactions (addition or self-condensation) are fast and that all low mass materials are consumed within the first three hours.

Table 5.10 Selected data points for GPC experiment on a rapid assembly system

Sample Time (min)	Retention Time (min)	Apparent Mass
0	23.98, 27.75	702, 118
30	23.95, 25.60, 27.73	710, 464, 121
90	13.63, 22.73, 24.02, 25.07	excl., 1221, 694, 521
120	12.85, 20.83, 22.75, 24.08, 24.98	excl., 3668, 1210, 679, 531
180	12.85, 20.02, 22.73, 24.08, 25.06	excl., 5694, 1221, 679, 521
300	12.85, 22.93, 23.97	excl., 1101, 706
900	22.93, 23.97	1101, 706

excl. means excluded from the GPC columns

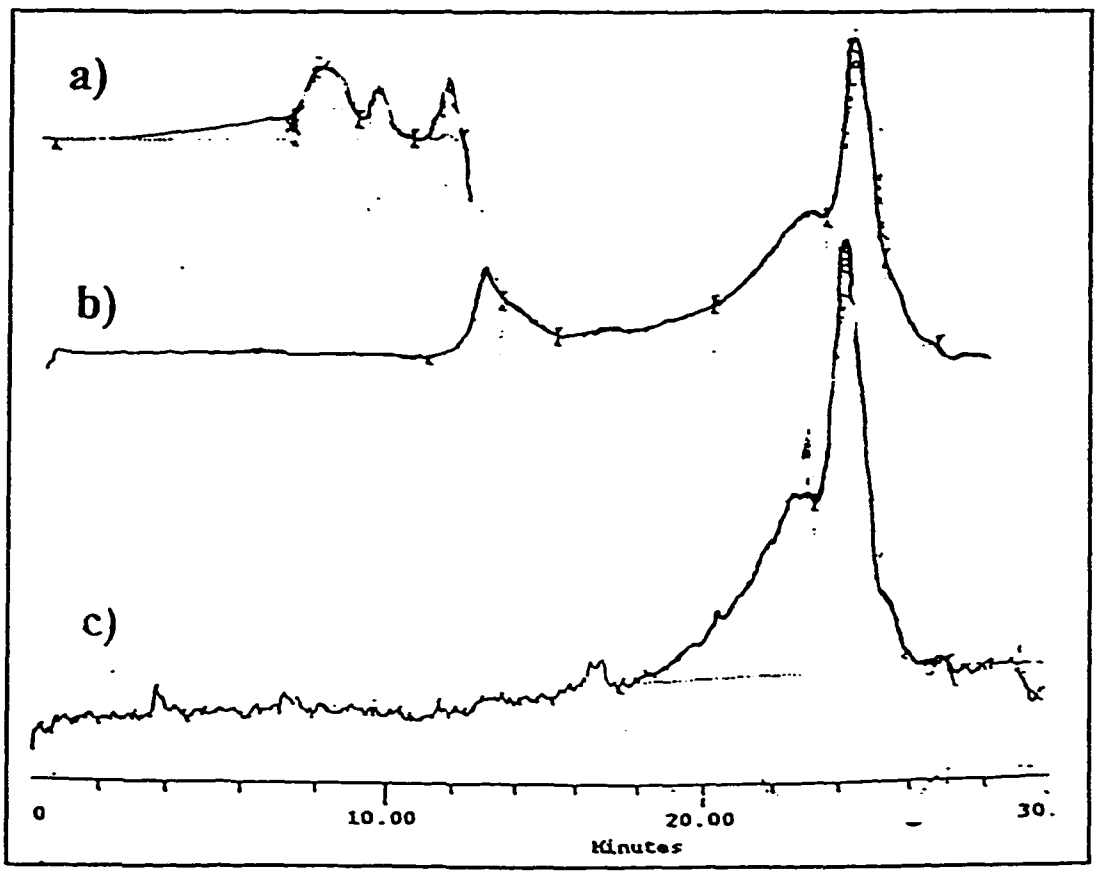


Figure 5.9 GPC traces for the rapid assembly run: a) 30 min; b) 180 min; c) 900 min.

5.5 Self-Condensation Reactions

The GPC experiment, described above, showed that there was some unreacted hypercore molecule remaining at the end of the reaction which has been attributed to monomer self-condensation (and possibly cyclisation reactions) which prevent addition to the presynthesised cores. To try to identify the product(s) of monomer self-condensation, a series of reactions were performed under similar conditions using only triallylsilane or diallylmethylsilane monomers in hexanes with Speier's catalyst, see Scheme 5.7.

It has been shown previously by Curry[43,44] that polymerisation occurs when organosilanes, containing either a vinyl or allyl group attached to a Si-H functionality in the same molecule, are heated in the absence of solvent. By contrast, in the present study when either triallylsilane or diallylmethylsilane were heated in solution in the presence of CPA, the products showed by investigation, using ^{29}Si NMR, a more 'perfect' set of branch sites that exhibited generational behaviour; this is counter to the results reported by Curry[43,44] or Frey,[42] see Table 5.11 and Figures 5.10-5.13. A reaction where triallylsilane was heated in the absence of solvent (a biassed monomer reaction) gave a product which gelled in the reaction vessel. Very little material was soluble in the NMR solvent, but multinuclear NMR spectra of what did dissolve appears to be similar to the product formed in the presence of solvent. This appears to be in agreement with the work by Muzafarov *et al*,[41] where the highly active Pt catalyst produces a gelled product, whereas dilution into solvent suppresses this reaction.

Table 5.11 Selected spectral data for self-condensation reactions in hexanes

		^{1}H δ ppm			^{29}Si δ ppm
		β-allyl		$SiCH_3$	
	Time	5.80	1.6-0.4	0.0--0.1	
$HSiAll_3$	12hrs	=1	4±1	-	0.63, -0.10, -0.41, -1.10, -10.0
$HSiMeAll_2$	12hrs	=1	5±2	1±0.4	1.60, 1.23, 0.80, 0.29

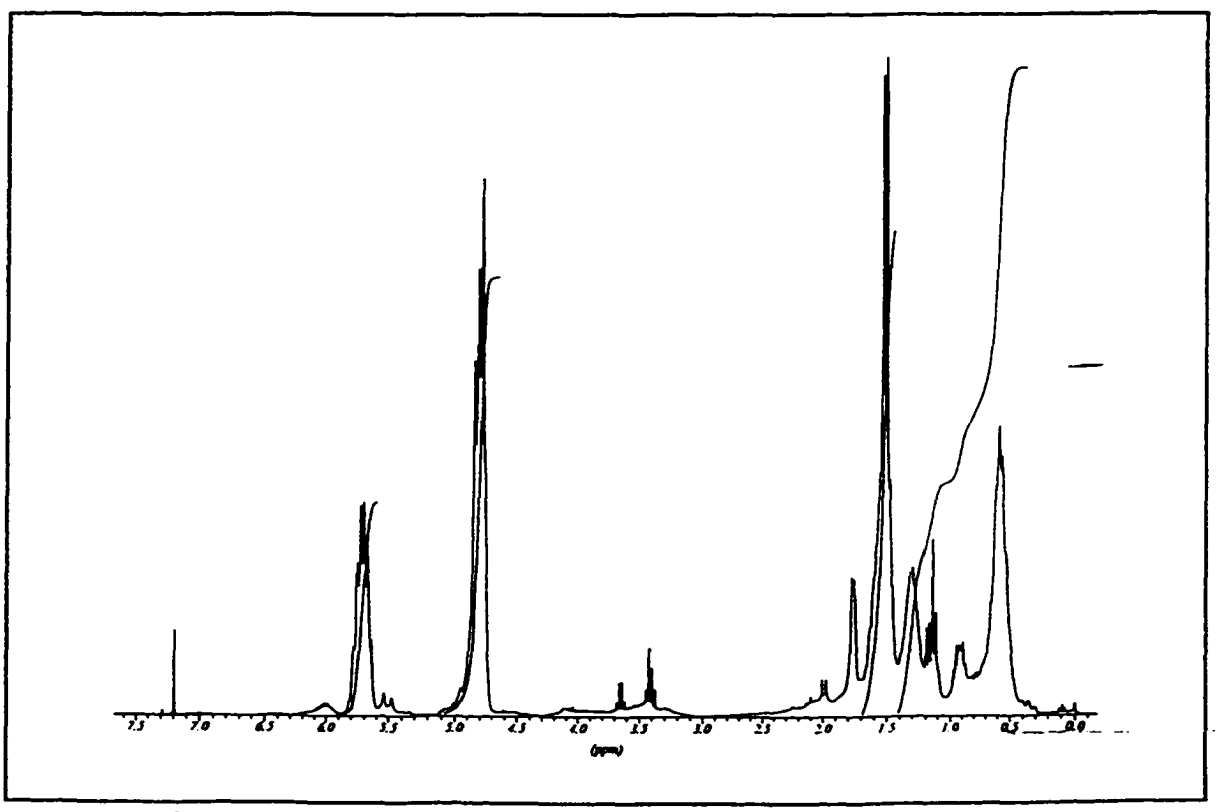


Figure 5.10 ^{1}H NMR spectrum of triallylsilane self-condensation reaction

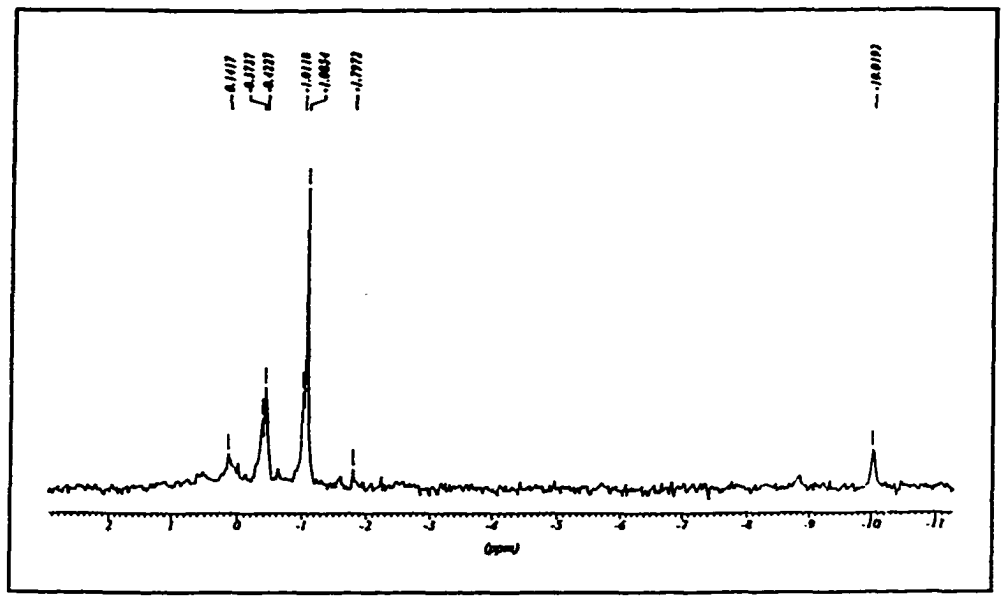


Figure 5.11 ^{29}Si-{^{1}H} NMR spectrum of triallylsilane self-condensation reaction

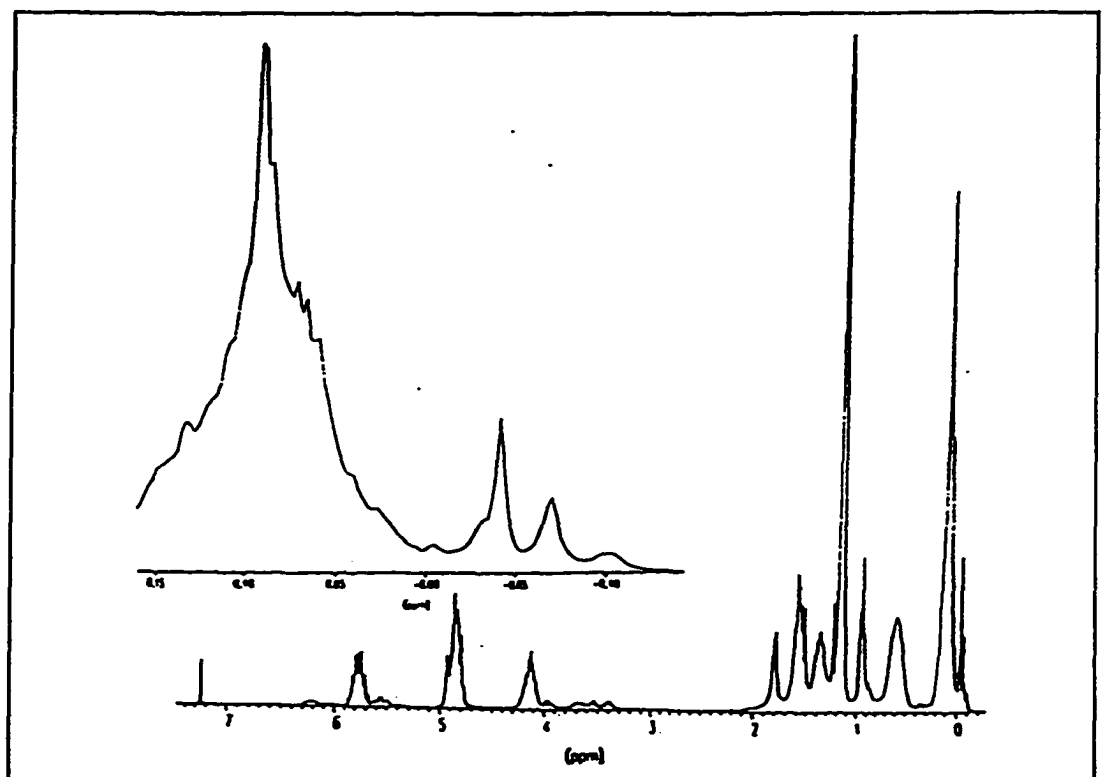


Figure 5.12 ^{1}H NMR spectrum of diallylmethylsilane self-condensation reaction

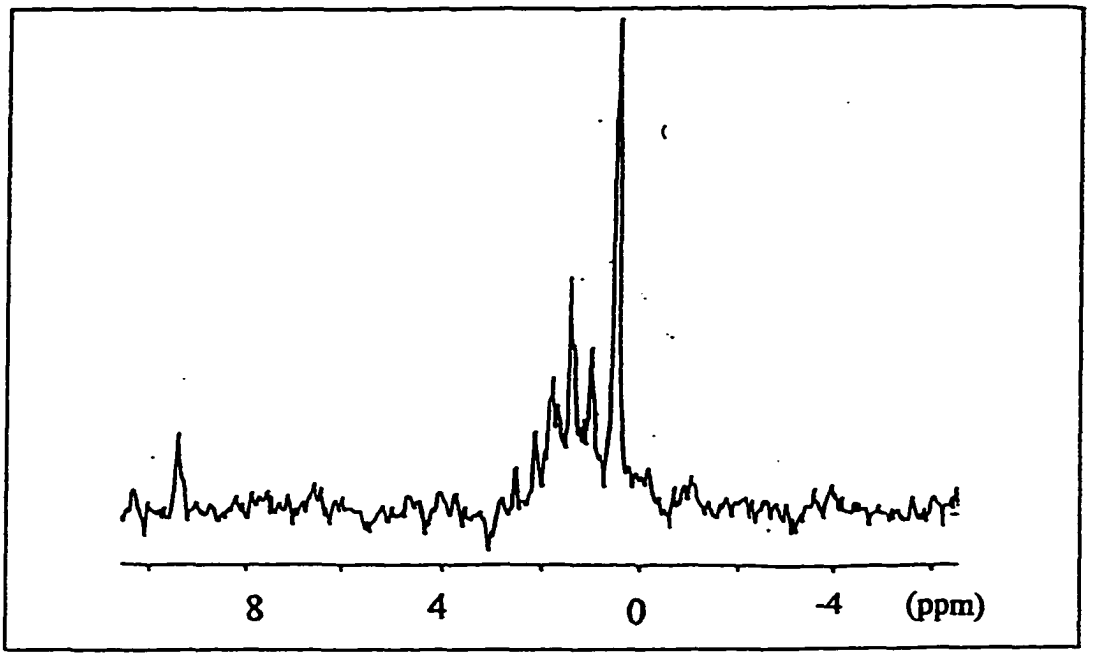


Figure 5.13 ^{29}Si-{^{1}H} NMR spectrum of diallylmethylsilane self-condensation reaction

The ^{1}H NMR spectrum of the diallylmethylsilane self-polymerisation reaction shows some generational behaviour in the upfield area as before, but now there appears to be a considerable amount of polymeric material present (δ 0.1 ppm) which is also confirmed by a wide variety of signals in the ^{29}Si NMR spectrum. For the triallylsilane self-polymerization product the ^{29}Si NMR spectrum (Figure 5.11) shows 'generational shells' at similar chemical shifts to other 3B compounds described previously (chapters two and three). There is also a resonance detected at δ -10 ppm which is thought to be a product which still contains a silicon hydride bond (^{29}Si resonance of triallylsilane appears at δ -13 ppm) and may have one or two of the unsaturated resonances reacted, see chapter 6.1. This is in contrast to work by

Frey *et al,*[42] in which statistical analysis of the possible products was presented and the silicon NMR was claimed to fit this distribution. This could be due to the use of a different catalyst (see Table 5.1), which in turn could affect the products formed in this type of poly-condensation. Another factor could be the simplistic approach employed to develop the predicted statistical distribution; this requires that each of the allyl groups has the same reactivity, which may not be necessarily true after one alkenyl group has reacted. There is also the issue of solvation; in work by both Frey[42] and Curry[43,44] no solvent was used, whereas for the reactions examined here the monomers were diluted in hexanes. In the experiment where no solvent was used only 2% of the initial triallylsilane weight was recovered, with almost all of the substrate being converted to a brittle insoluble polymer. Repeated attempts at self-polymerization reactions in the presence of solvent and without gave identical results to those described above.

The GPC chromatograms, Figure 5.14, of the self-polymerisation products show a broader polydispersity than those counterparts formed around a core focal point: a broad, poorly resolved envelope was observed that showed none of the narrow features referred to in the controlled reactions described earlier, see Section 5.3.

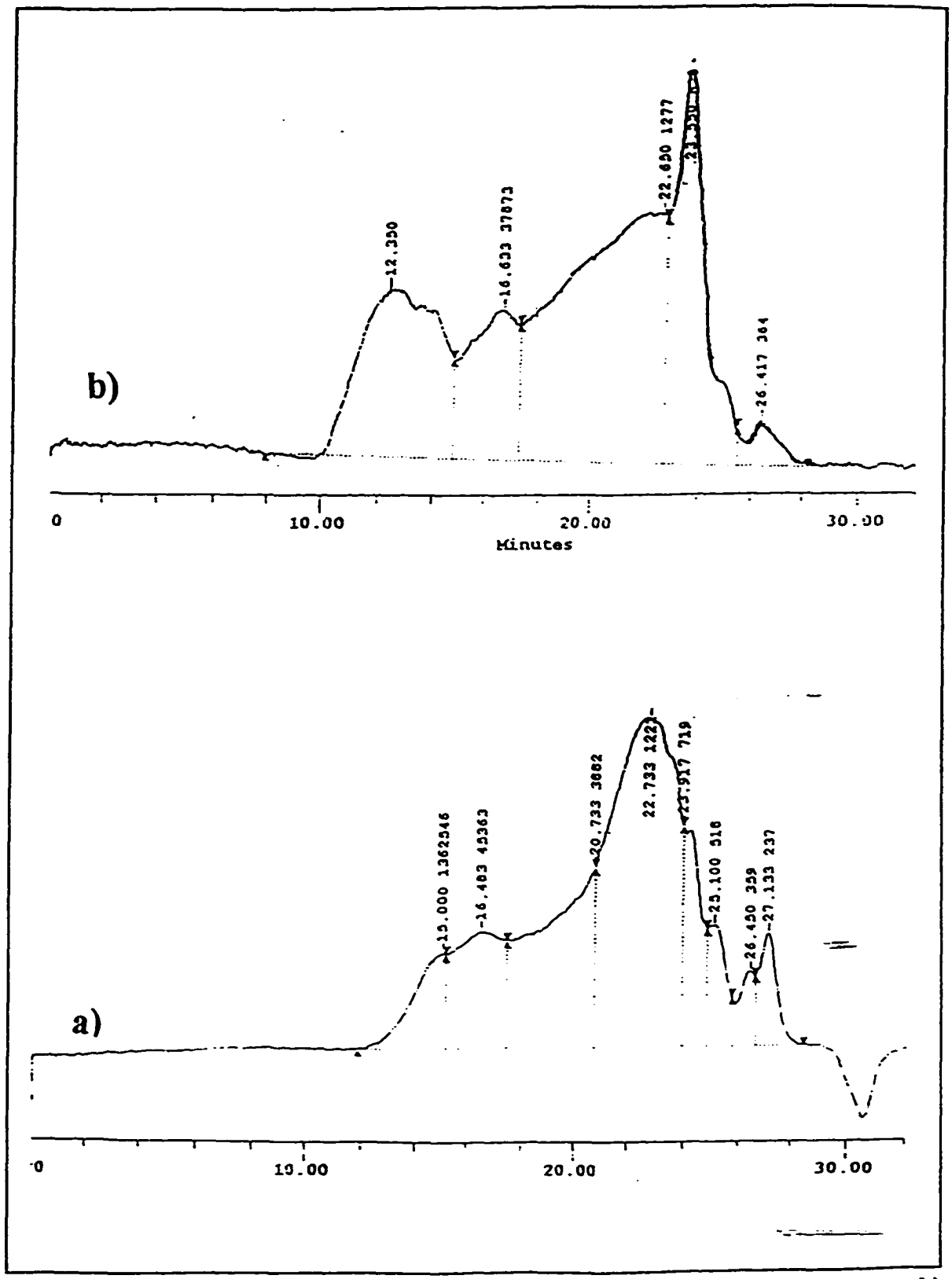


Figure 5.14 GPC chromoatograms for self-condensation reactions: a) triallylsilane; b) diallylmethylsilane.

5.6 Summary

For the products obtained using stepwise methodology for 'one-shell' expansion, NMR features assigned to the interior silylmethyl groups appear as multiple resonances that are of low intensity compared to the 2B dendrimers described in chapters two and three. This may be due to steric crowding imposed by the bulk of the exterior triallylsilyl groups causing restriction of mobility in the interior framework.

Attempts to produce a similar product by a 'one-pot' approach were not very successful. A substantial proportion of the hypercore molecule remained unreacted (determined by NMR and GPC chromatography) but there did appear to be some incorporation of the triallylsilane monomer into the structure since a larger mass fraction was detected at a slightly shorter GPC retention time. The use of a hypercore for the rapid assembly reactions has been shown to control both the polydispersity and possibly the degree of branching. Although not all the core molecules react with the monomer (ca. 50%), those that do appear to begin growth into subsequent 3B layers, *i.e.* away from the 2B structure of the hypercore, rather than saturating available end-groups of the latter. This conclusion is based on the observation that no multiplicity is evident in $SiCH_3$ resonances, in contrast with the anomalous behaviour of the interior silylmethyl groups encountered in products of the parallel stepwise chemistry.

The evidence available from comparison of stepwise *vs* 'one-pot' reactions suggests that self-polymerization of the triallylsilane monomer occurs more rapidly than addition to a hypercore structure, *i.e.* leaves the latter largely unreacted.. With the self-condensation

reactions there appears to be some significance in which catalyst is used, also the extent of unwanted (gelled) products is suppressed when the reaction is conducted in solution. The self-condensation products of both triallylsilane and diallylmethylsilane showed some generational hierarchy in the silicon NMR spectra, as well as in the proton NMR spectrum of the product obtained from the $HSiMeAll_2$.

Thus, if hyperbranched polymers are to become more commercially viable the suggested route would be synthesis *via* slow addition in the presence of a core focal point in the presence of a solvent. However, there is still no conclusive experimental evidence to be able to ascertain the overall topology of these rapidly assembled 'one-shell expansion' products.

CHAPTER SIX

LARGE ASSEMBLIES AND HYBRID TOPOLOGIES

This chapter will focus on the materials produced when core molecules are reacted with silane monomers in a rapid assembly approach. Initially phenyl triallylsilane will be used as a core structure since this molecule has also been studied for the stepwise formation of carbosilane dendrimers (chapter two). The phenyl core has been shown to be useful for population analysis studies of peripheral protons (*i.e.* end-group counting) in three different topologies. The central silicon signal (Ph-*Si*; ^{29}Si NMR) has also been observed at a downfield position (relative to the precursor) once dendrimer formation has begun, so that this can be used as a method to determine if addition to the core molecule has occurred; and that when such extension is accomplished, generational silicon NMR shifts (with statistical populations) can be used for topographical mapping of dendritic structures.

The stepwise synthesis of dendrimers using spheroidal (or hexafunctional) core molecules has been discussed in chapter three. Multinuclear NMR analysis of the products obtained in a rapid assembly procedure may therefore be compared to the data collected in chapter three, in a manner that would not have been possible unless the generational structures had been made individually. It has also been established in chapters two and three that introducing the 2B ($HSiMeCl_2$) building block leads to hierarchical growth patterns for

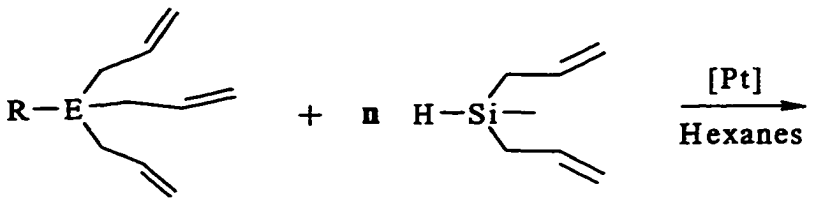
the silicon methyl groups in ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. Therefore, by using a repeat unit of diallylmethylsilane ($HSiMeAll_2$) for rapid growth synthesis, the products can be compared to those produced stepwise.

Hybrid materials having trifurcate, spheroidal or hexafunctional core structures may be extended from presynthesised hypercores, introducing a change in branch topology (2B→3B) that is similar to work in the previous chapter. Relative proton integrations for the Si-Me resonances *vs* peripheral nuclei can be used as a means of 'end-group' counting at large N in generation G(N). Distinct ^{29}Si resonance positions occur for the 2B branch sites as compared to the 3B branch sites; therefore separate peaks will be observed in these 'hybrid' materials and can further aid in topographical mapping by silicon NMR spectroscopy. Such synthesis using slow addition of repeat unit to core molecule in stoichiometric amounts was investigated for a variety of combinations as is shown in Table 6.1.

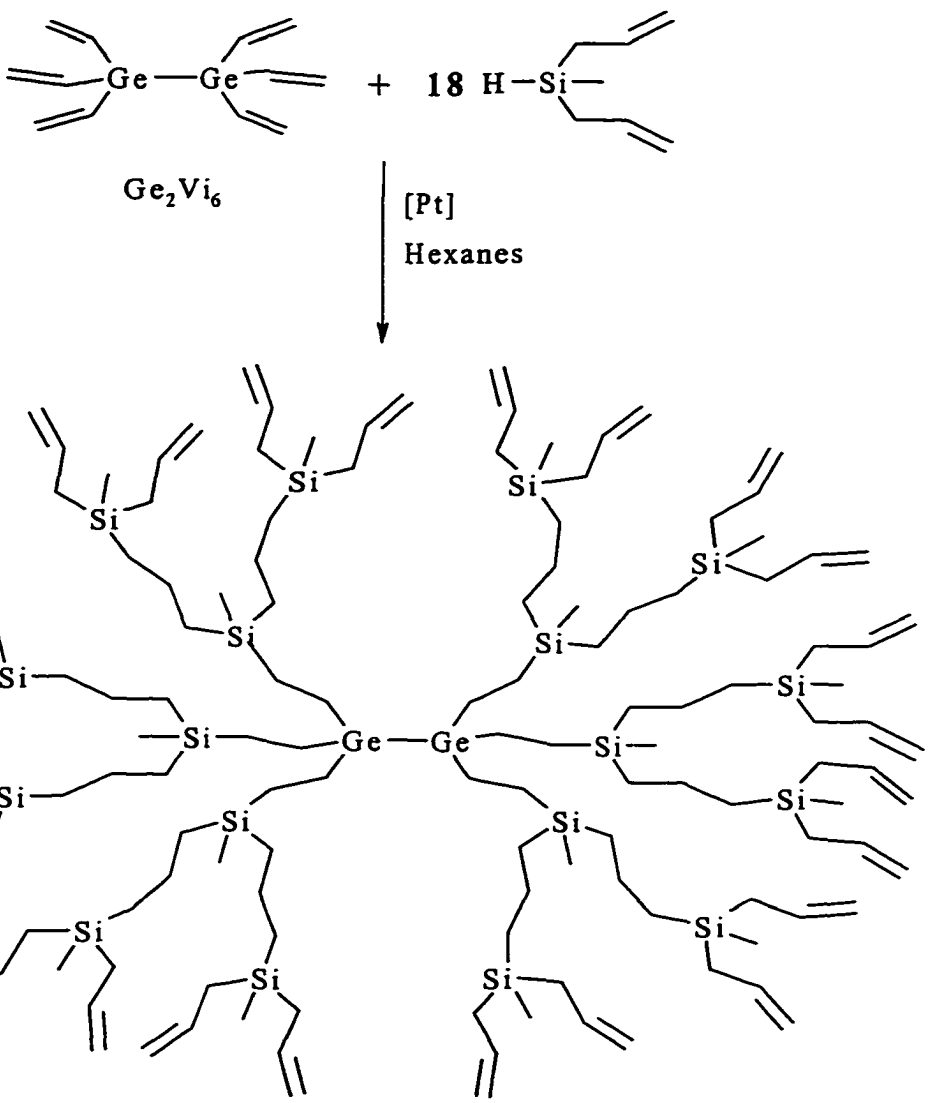
Table 6.1 Polycarbosilane synthesised using hyperbranching methodology

Core Molecule	Monomer	Target Generation Number
$PhSiAll_3$	$HSiMeAll_2$	G(3), G(5)
	$HSiAll_3$	G(3), G(4), G(5)
Ph_2SiAll_2	$HSiMeAll_2$	G(3)
	$HSiAll_3$	G(2), G(3), G(4), G(5), G(5)*
$GeAll_4$	$HSiMeAll_2$	G(2), G(3)
	$HSiAll_3$	G(5)
Ge_2Vi_6	$HSiMeAll_2$	G(2), G(3)
	$HSiAll_3$	G(3), G(5)

* synthesised from a G(1) stepwise derivative



General Reaction Scheme



$Ge_2[(etSiMe)^1{}_2(prSiMe)^2{}_2{:}All]_6$

Scheme 6.1 Schematic of the general hyperbranched growth and for 2B branch growth from a hexavinyldigermane core

6.1 Hyperbranched 2B Compounds

Materials that have been synthesised by adding stoichiometric amounts of diallylmethylsilane repeat unit to the core molecule are discussed in this section. All these products were prepared *via* dropwise slow addition of silane to a heated core molecule in the presence of CPA in hexanes solution. Amounts of the monomer unit to be added for each target generation were calculated according to,

$$RU = \sum_{n=1} C \cdot 2^{n-1}$$

which depends on the initial multiplicity of the core (C), and n is the generation number desired; ie. for a third generation compound with a tetraallylsilane core, RU (number of repeat units needed) is equal to 4 + 8 + 16 = 28 monomer units.

The relative ^{1}H integrations and ^{29}Si chemical shifts observed for crude materials obtained using the above procedure are summarized in Table 6.2, as are the different fractions obtained by flash column chromatography (using an eluent mixture of hexanes/(2%)ethyl acetate). As in chapter two, the phenyl resonance acts as an internal calibration device for end-group counting, and the Si-Me signals can also be used as a means to cross-check the integration values obtained.

Table 6.2 Selected spectral data for rapid assembly reactions: Adding n equivalents of $HSiMeAll_2$ to selected core molecules

Core	Mass (g)	Ph	=CH	$SiCH_3$	^{29}Si δ ppm
$PhSiAll_3$					
(133) calcd.	G(2)	*5*	*12*	*27*	*n = 9 equivalents added*
Crude	2.010	5	8	22	1.02, 0.74, 0.26, -7.92
Fraction 1	0.273	5	5	6	0.99, 0.73, 0.26, -6.48, -7.94
Fraction 2	1.320	5	11	34	1.20, 0.90, 0.70, 0.26, -6.46
(134) calcd.	G(3)	*5*	*24*	*63*	*n = 27 equivalents added*
Crude	4.865	5	25	73	1.02, 0.74, 0.29, -4.00
Fraction 1	1.045	5	20	68	1.02, 0.74, 0.60, 0.29, -4.00
Fraction 2	1.200	5	39	117	1.03, 0.75, 0.29, -4.00
Ph_2SiAll_2					
Calcd.	G(3)	*10*	*16*	*42*	*n = 14 equivalents added*
(135) Crude	3.430	10	18	72	1.02, 0.74, 0.28, -8.40
Fraction 1	0.503	10	38	115	0.77, 0.72, 0.57, 0.26, -8.40
Fraction 2	0.630	10	5	11	1.06, 0.76, 0.29, -8.40, -11.70
Fraction 3	1.522	10	15	54	1.02, 0.74, 0.29, -8.40, -11.70

Observations from the integration values suggest that the synthesis of low generation targets produces only some hyperbranched compound; a large proportion of polymeric material is obtained as the major product. Analysis of the NMR spectra for the two fractions that were isolated from reaction **(133)** show that by proton integration (Figure 6.1) the first

fraction collected (0.273 g) had very little addition of the 2B monomer unit. This interpretation is aided by the ^{29}Si chemical shift data (Figure 6.4), where sharp peaks are observed in the high field region (δ = -7.94 and -6.48 ppm) that are assigned as unreacted core ($PhSiAll_3$) and partially reacted core respectively. The second fraction isolated was found to have integration values close to the calculated ratio for the target compound (Figure 6.2); silicon NMR data showed only a small resonance in the high field region and some resonances that appear generational at the frequency assigned to 2B branch silicons (Figure 6.4), see also chapter two for trifurcate 2B dendrimers (page 54).

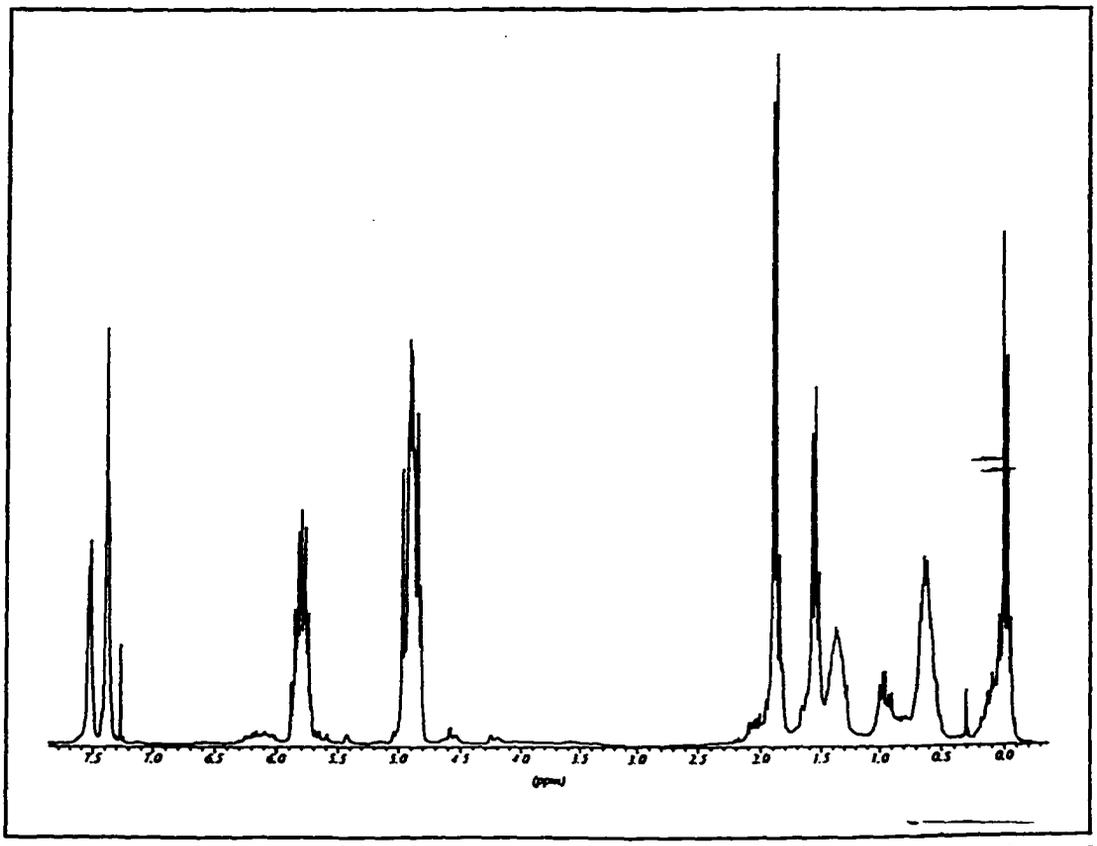


Figure 6.1 ^1H NMR of reaction between $PhSiAll_3$ and 9 equiv. of diallylmethylsilane: (133) fraction 1

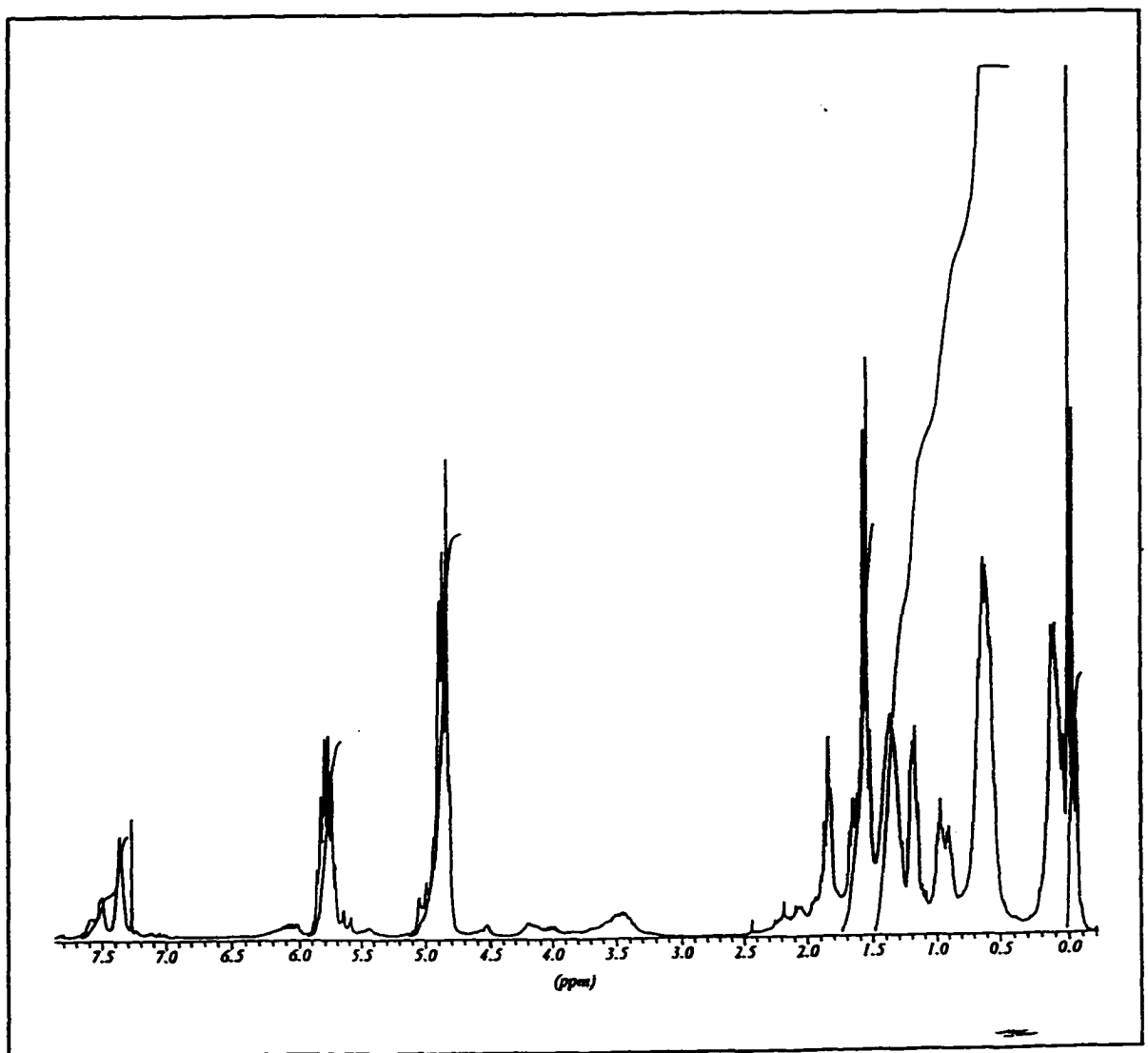


Figure 6.2 ^{1}H NMR of reaction between $PhSiAll_3$ and 9 equiv. of diallylmethylsilane: (133) fraction 2

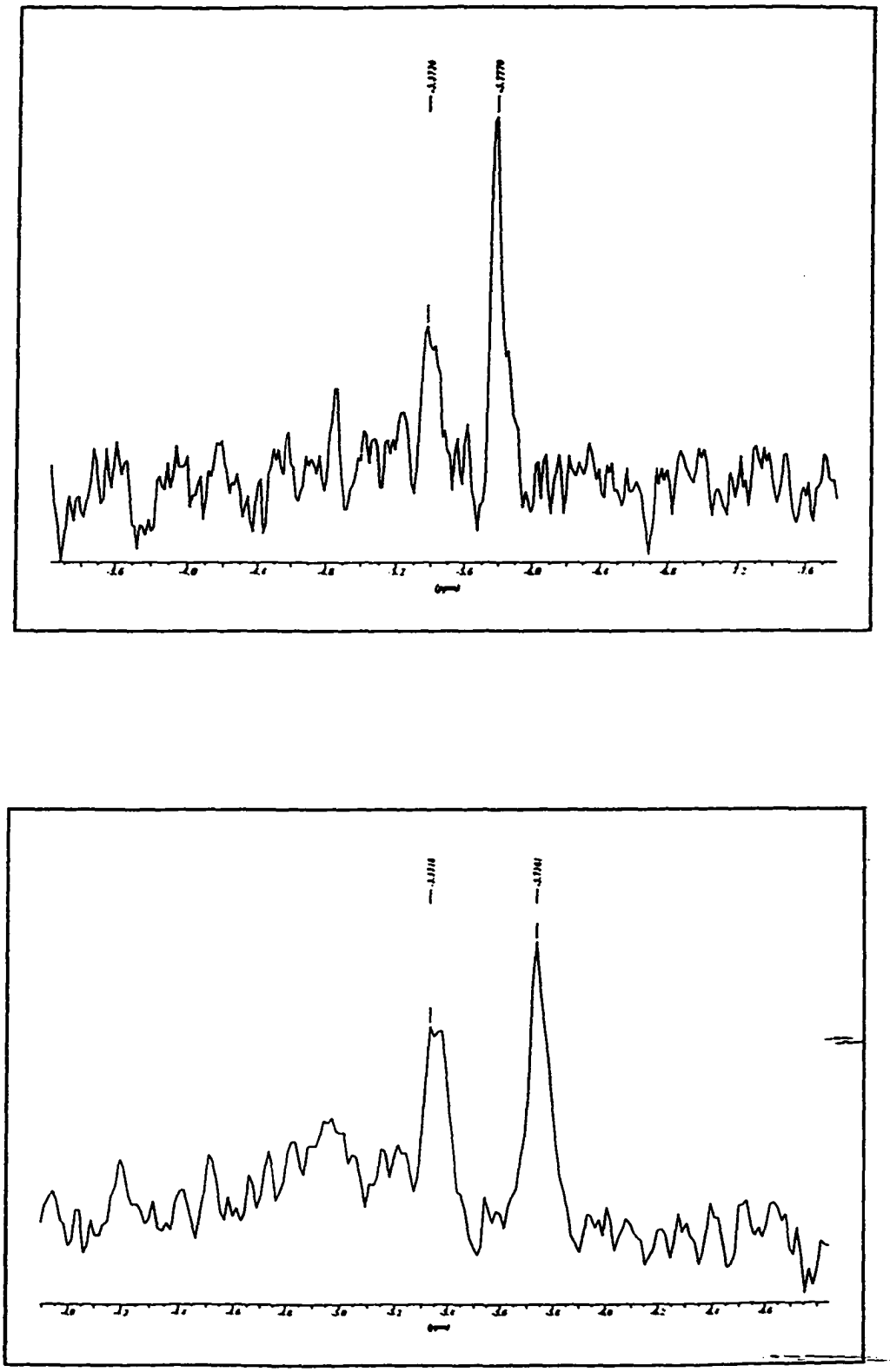


Figure 6.3 Enlargement of ^{13}C NMR spectra of reaction between $PhSiAll_3$ and 9 equiv. of diallylmethylsilane:(133) fraction 1 (top); fraction 2 (bottom)

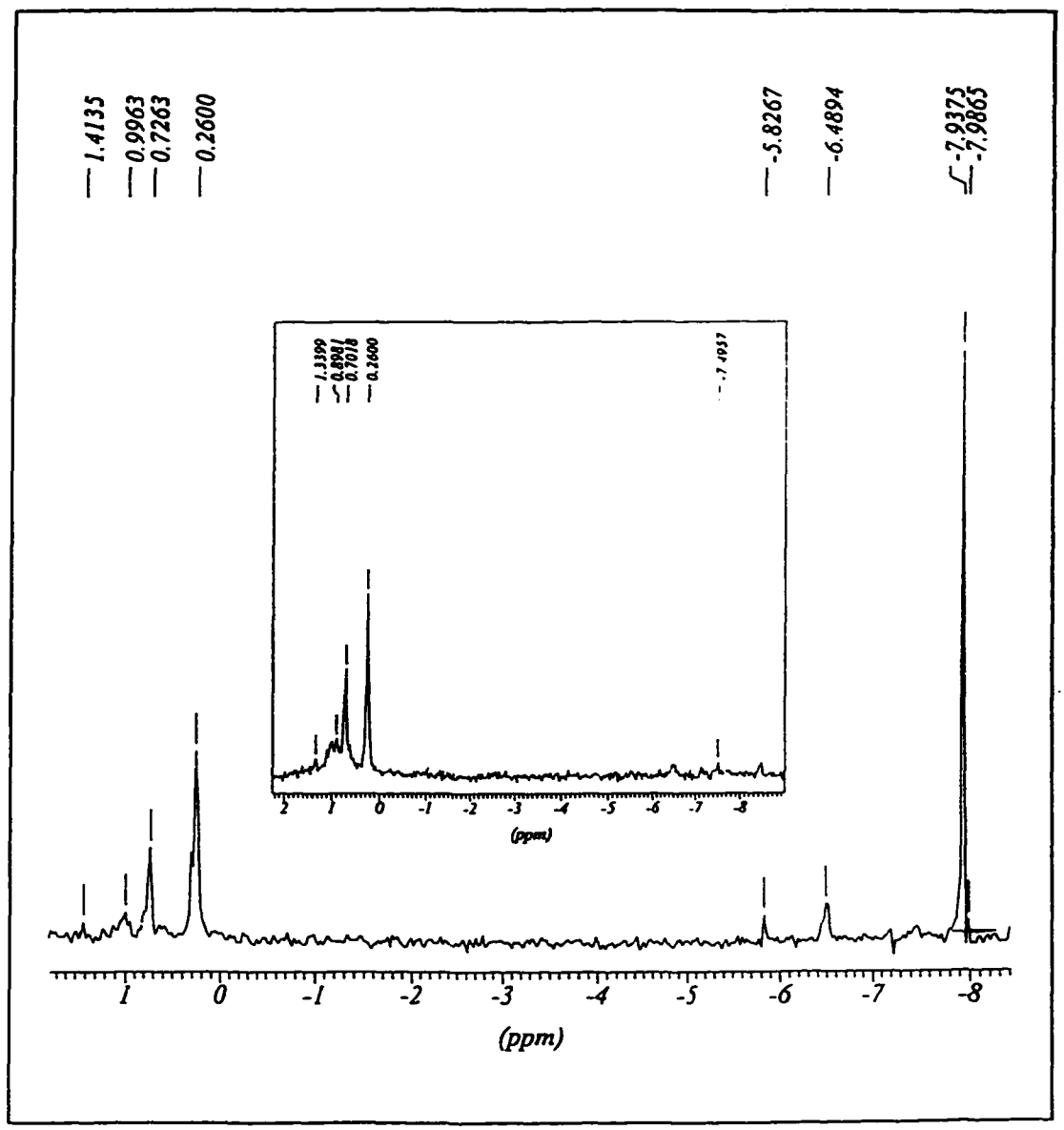


Figure 6.4 ^{29}Si NMR spectra of $PhSiAll_3$ G(2)2B product (133): fraction one (bottom); fraction two (top).

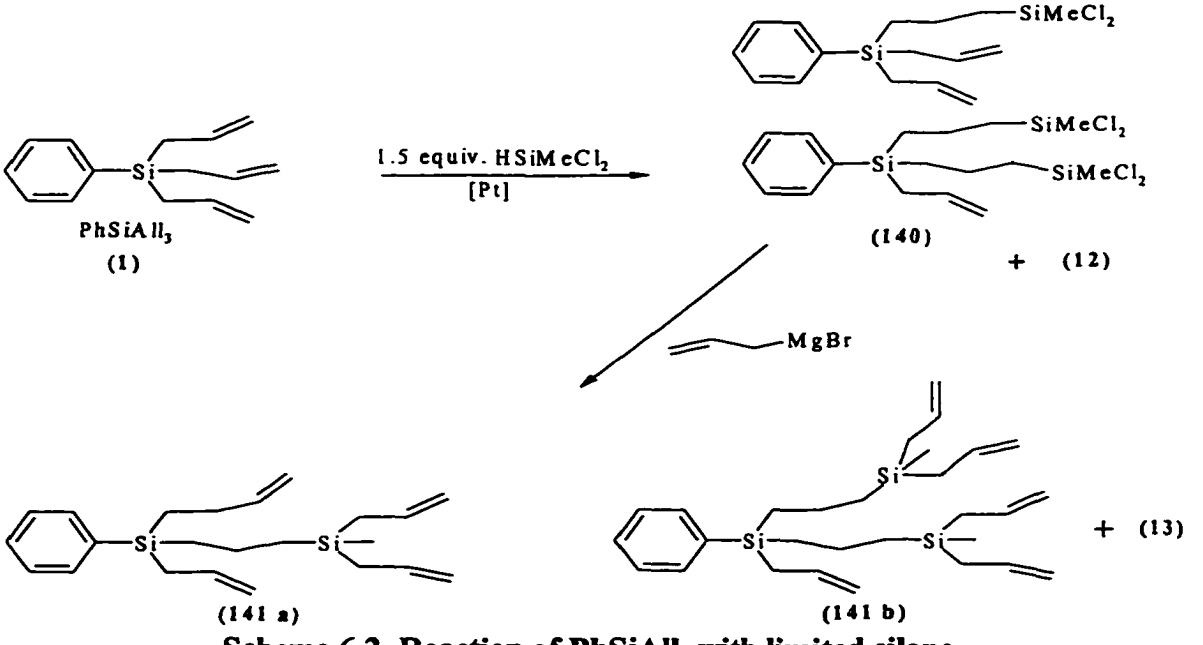
Table 6.3 Selected NMR data for germanium centred hyperbranched polymers

Core	Mass (g)	=CH	$SiCH_3$	^{29}Si δ ppm
$GeAll_4$		^1H integration		
Calcd.	G(2)	*16*	*36*	*n = 12 equiv. added*
(136) Crude	1.396	16	3.7	0.83, 0.73, 0.38, 0.28
Fraction 1	0.173	16	15.8	0.73, 0.28
Fraction 2	0.149	16	26.7	1.03, 0.73, 0.28
Fraction 3	0.320	16	36.8	1.01, 0.73, 0.28
Fraction 4	0.210	16	18.2	1.01, 0.73, 0.28
(137) Calcd	G(3)	*32*	*84*	*n = 28 equiv. added*
Crude	1.814	32	7.4	1.03, 0.77, 0.26
Fraction 1	0.578	32	96	0.76, 0.29
Fraction 2	0.348	32	112	0.75, 0.29
Fraction 3	0.228	32	86	0.75, 0.29
Ge_2Vi_6				
Calcd.	G(2)	*24*	*54*	*n = 18 equiv. added*
(138) Crude	0.527	24	86	1.08, 0.80, 0.71, 0.35, 0.25
Fraction 1	0.230	24	70	1.79, 1.01, 0.73, 0.28
Fraction 2	0.079	24	65	1.95, 0.99, 0.71, 0.25
Calcd.	G(3)	*48*	*126*	*n = 42 equiv. added*
(139) Crude	2.256	48	99	0.73, 0.29
Fraction 1	0.220	48	71	0.70, 0.24
Fraction 2	0.223	48	125	0.98, 0.74, 0.27
Fraction 3	0.143	48	129	0.93, 0.74, 0.28
Fraction 4	0.761	48	144	0.91, 0.73, 0.26

The synthesis of low target generations in a 'one-pot' method produces a large amount of polymeric carbosilane (Tables 6.2 and 6.3); this has also been noted in chapter five, *i.e.* the self-condensation reactions of triallylsilane and methyldiallylsilane. Some hyperbranching occurred but mostly uncontrolled polymer was produced. Hult *et al*[19a] studied the self-condensation reactions of aliphatic polyesters by stepwise addition of monomer units and compared the results obtained with model compounds synthesised from the same building blocks. Similar analysis can also be made for hyperbranched materials by comparing their spectroscopic properties with related results obtained from stepwise dendrimer synthesis (chapters two and three). The NMR active silicon nucleus at each branch point gives another analytical device to interpret the structure of compounds that are formed; hierarchical silicon signals are observed which appear at different chemical shifts depending on the silicon branch site multiplicity, *i.e.* 2B or 3B. The chemical shift of the core silicon, using a phenyl substituted silyl core group, can be used as an important reference point as discussed in chapter two; this signal is observed at δ -8.00 ppm in $PhSiAll_3$ but after hydrosilylation and further alkenylation it is shifted downfield to δ -4.00 ppm. Similar changes occur following substitution of a diphenyldiallylsilane core (δ -11.7 ppm to -7.90 ppm), and also for other silicon based core groups, including the disilanes (chapters two and three).

In the analysis by Hult,[19a] core group and the repeating units are the same so that similar reasoning cannot be used to determine how much core had reacted. In rapid assembly reactions carried out, as detailed in Table 6.2, from the chemical shifts observed in the products it is evident that not all of the core fully reacted with silane monomer (see

also Figures 6.1-6.4); the appearance of extra resonances well separated to high field is attributable to the presence of unreacted and partially reacted core groups, *i.e.* δ -6.40 ppm; Ph*Si*pr$_2$All. Similar signals were also observed for low generation targets synthesised from a diphenyldiallylsilane core, possibly due to the lower number of reactive groups in the latter. In an attempt to mimic this pattern of reactivity, phenyl triallylsilane was treated with a substoichiometric amount of the repeat unit dichloromethylsilane. Following this with a nucleophilic substitution using allylmagnesium bromide, a mixture was produced (Scheme 6.2) which was then analysed by silicon NMR. This led to the observation of several silicon resonances at high field (Figure 6.5), which from their resonance positions suggested formation of a mixture of mono-, di- and tri- substituted components, *i.e.* a similar distribution to that believed to have been formed in the rapid assembly referred to above, compare Tables 6.2 and 6.4.



Scheme 6.2 Reaction of PhSiAll$_3$ with limited silane

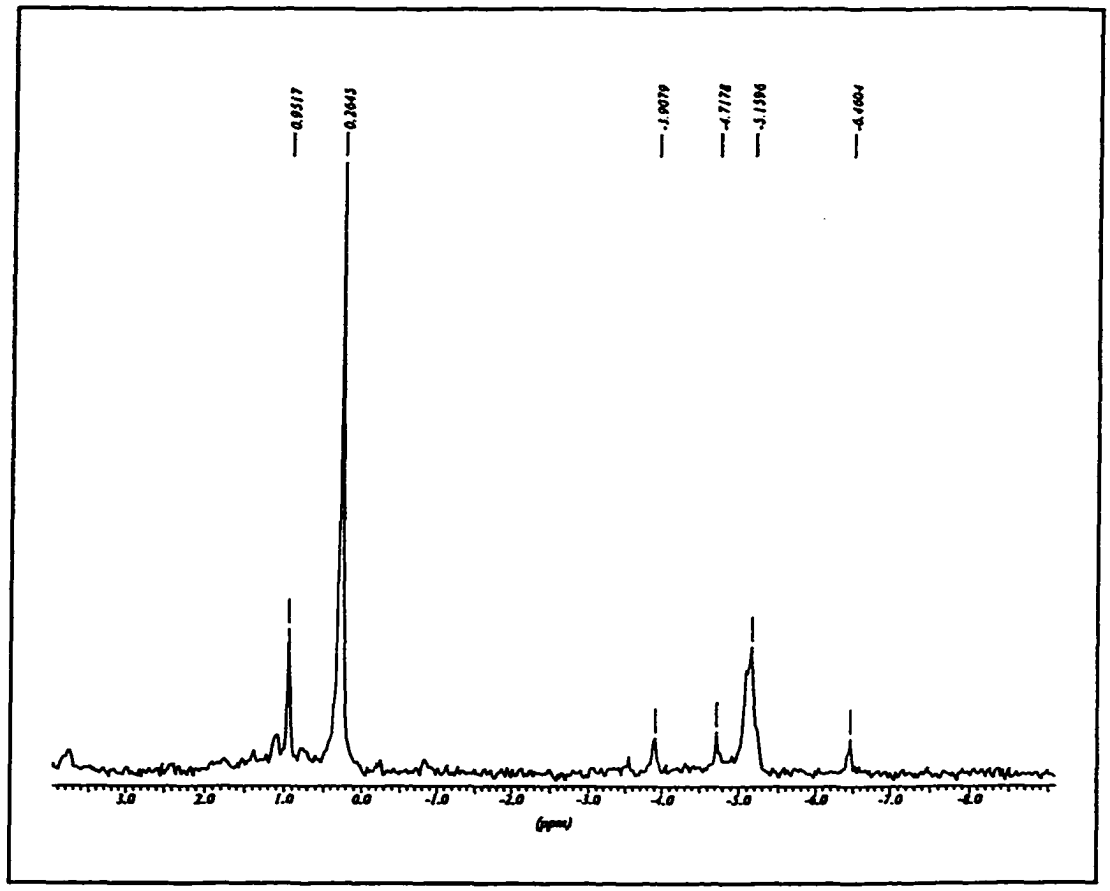


Figure 6.5 ^{29}Si-{^{1}H} NMR spectrum of $PhSiAll_3$ with only 1.5 equiv. of $HSiMeCl_2$ followed by substitution with allylmagnesium bromide compound (141)

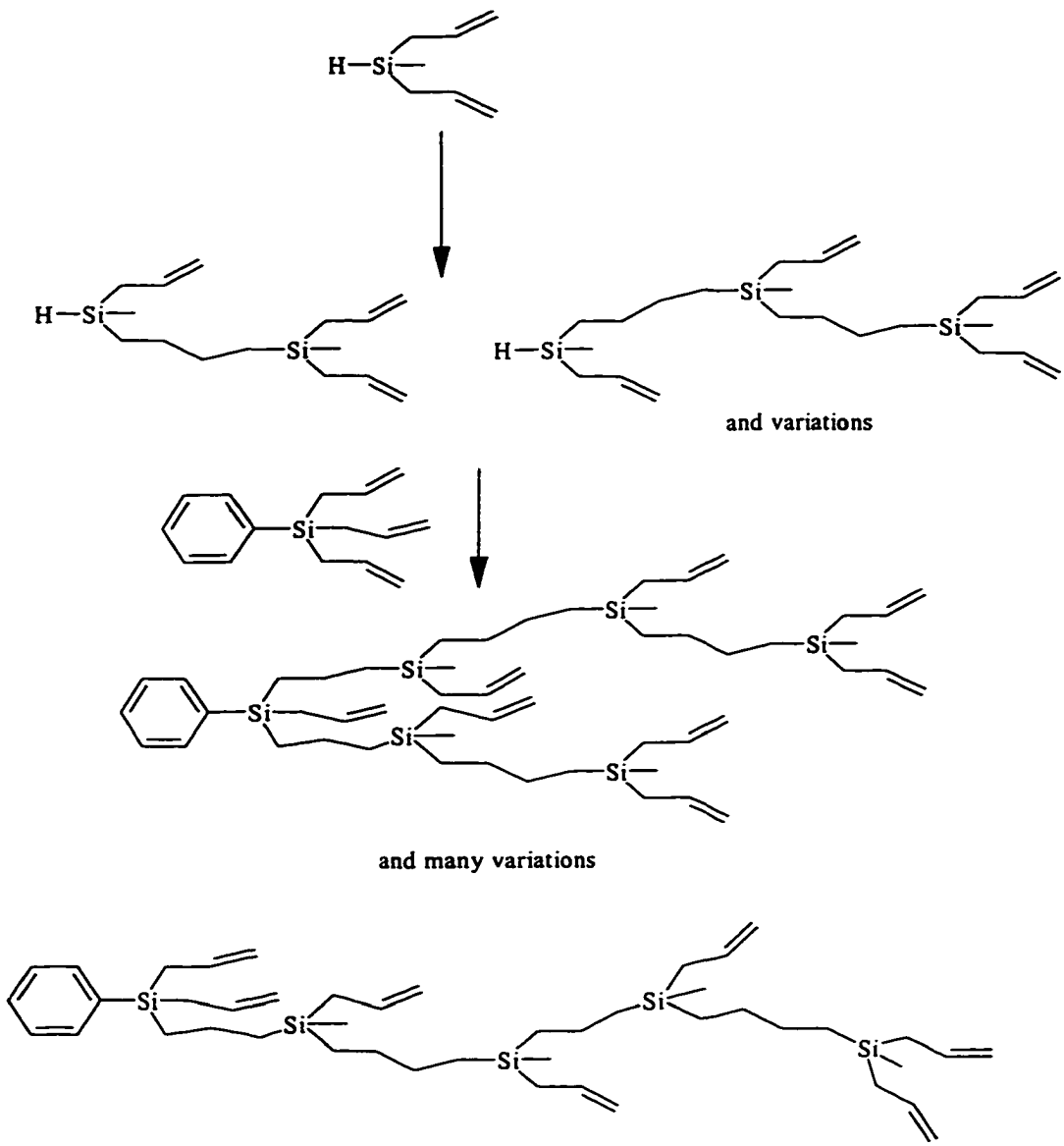
Table 6.4 ^{29}Si chemical shift data for compound (141) addition of 1.5 equiv. of $HSiMeCl_2$ followed by substitution with allylmagnesium bromide, compound (141)

^{29}Si δ ppm		
0.95 ($SiCH_3$) **(141a)**	0.26 ($SiCH_3$) **(141b)**	
-3.9 ($PhSipr_3$) **(13)**	-5.2 ($PhSipr_2All_1$) **(141b)**	-6.5 ($PhSipr_1All_2$) **(141a)**

where pr_n = the number of propyl groups attached to the core silicon

Attempted synthesis of lower generation targets produces a larger amount of cyclic (and polymeric) material than those intended to produce higher mass targets, see Tables 6.1-6.3. This could be explained by a dependance of the degree of reaction on the number of alkenyl groups available at the core.

This may indicate that the reaction proceeds *via* monomer condensation initially to give larger aggregates which then react with the focal core group, compare chapter five section 5.3. If the latter addition is slow, it will be less favoured if fewer core anchoring sites are accessible, as in the diphenyldiallylsilane reactions. For some of the proton NMR integrations the number of peripheral groups far exceeds the calculated value, suggesting that the monomer may have self-condensed initially, possibly in a hierarchical structure similar to the results seen in chapter five, *i.e.* condensation into a hyperbranched fragment but this time in a 2B substructure. Such a fragment can subsequently react with the core, most probably to form a mixture of random hyperbranched arms radiating from a central group; this situation may develop as is suggested in Scheme 6.4. This shows the dimethylallylsilane substrate self-condensing before reaction with the core molecule. This seems most likely since the first fraction isolated, Table 6.2 entry for compound **(133)** above, shows unreacted core molecule at δ -8.0 ppm together with peaks associated with poly-dimethylallylsilane not attached to a core.



Scheme 6.4 Possible reaction pathway for rapid assembly synthesis

6.2 Hyperbranched 3B compounds

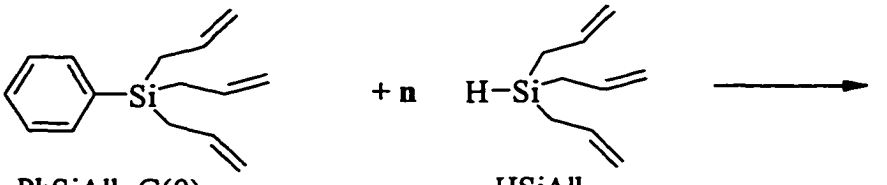
Hyperbranch synthesis with three new branching points per silicon atom (3B) is outlined in Scheme 6.5. As previously mentioned, distinction between successive generations with such topology for the symmetrical cores is very hard to make because the linkages are similar between each generation, resulting in almost identical ^{1}H NMR spectra. The observation of hierarchical ^{29}Si NMR spectra for stepwise dendrimers synthesised individually can be assigned to generational (shell) branch point populations, but parallel conclusions can not be reached for rapidly assembled hyperbranched polymers. This can be seen by considering a mixture of two stepwise compounds, G(2) and G(4), that are analysed by ^{29}Si NMR spectroscopy: the individual spectra will overlap exactly with each other because the internal silicons resonate further downfield after increasing the generation number, but the peripheral sites maintain a consistent chemical shift (δ -1.1 ppm), see chapters two and three. Thus, there will be no chemical shift distinction between the two and the relative proportions cannot even be determined. It follows that in materials made in a rapid assembly approach, approximation to dendritic structure may be concluded from the observation of hierarchical ^{29}Si NMR signals but no attempt can be made to rationalise any specific architecture for any such system.

Similar to the 2B rapid assembly reactions reported in Section 6.1, the number of repeating units that need to be added can be calculated for each target from

$$RU = \sum_{n=1} C \cdot 3^{n-1}$$

where C is the initial core multiplicity and n is the generation target. For example with a hexavinyldigermane core molecule (C = 6) building to a fifth generation target (n = 5) the number of repeat units needed is equal to 6 + 18 + 54 + 162 + 486 = 726 equivalents of triallylsilane.

A summary of ^{1}H NMR integrations and ^{29}Si NMR chemical shift data for compounds isolated from the slow addition of triallylsilane to a core molecule in solution in the presence of catalyst is presented in Tables 6.5 and 6.6.



$PhSiAll_3$ G(0) $HSiAll_3$

Scheme 6.5 3B synthesis of hyperbranched polymers

Table 6.5 Selected NMR data for hyperbranched polymers using n $HSiAll_3$ and $PhSiAll_3$

Core	Mass (g)	Ph	=CH	^{29}Si δ ppm
$PhSiAll_3$				
Calcd.	G(3)	*5*	*81*	*n = 39 equiv.*
(142) Crude	5.885	5	38	0.04, -0.40, -1.08, -4.00
Fraction 1	0.491	5	10	-0.40, -1.08, -4.00
Fraction 2	2.780	5	86	0.04, -0.40, -1.08, -4.00
Calcd.	G(4)	*5*	*243*	*n = 120 equiv.*
(143) Crude	4.380	5	78	0.53, 0.04, -0.40, -1.10, -4.00
Fraction 1	0.153	5	327	0.53, 0.04, -0.40, -1.10, -4.00
Fraction 2	0.357	5	90	0.18, -0.40, -1.10
Fraction 3	0.090	5	72	0.04, -0.40, -1.10, -4.00
Fraction 4	0.680	5	109	0.53, 0.04, -0.40, -1.10, -4.00
Calcd.	G(5)	*5*	*729*	*n = 363 equiv.*
(144) Crude	6.596	5	98	0.60, 0.14, -0.40, -1.10
Fraction 1	0.580	5	45	0.60, 0.14, -0.40, -1.10
Fraction 2	0.715	5	98	0.60, 0.14, -0.40, -1.10
Fraction 3	0.210	5	186	0.60, 0.14, -0.40, -1.10
Calcd.	G(6)	*5*	*2187*	*n = 1092 equiv.*
(145) Crude	4.136	5	1262	0.48, 0.12, -0.42, -1.10
Fraction 1	1.089	5	1199	0.42, 0.14, -0.42, -1.10
Fraction 2	2.368	5	1969	0.95, 0.50, 0.12, -0.44, -1.10

Table 6.6 Selected NMR data for 3B hyperbranched polymers isolated using n $HSiAll_3$ and a core molecule

Core	Mass (g)	Ph	=CH	^{29}Si δ ppm
Ph_2SiAll_2		^{1}H integration		
Calcd.	G(2)	*10*	*18*	*n = 8 equiv. added*
(146) Crude	0.832	10	10	-0.42, -1.10, -8.80, -11.70
Fraction 1	0.228	10	13	-0.42, -1.10, -8.80, -11.70
Calcd.	G(5)	*10*	*486*	*n = 120 equiv. added*
(147) Crude	8.200	10	204	0.45, 0.02, -0.44, -1.10, -8.80
Fraction 1	3.987	10	425	0.45, 0.02, -0.44, -1.10, -8.80
Fraction 2	2.673	10	360	0.45, 0.02, -0.44, -1.10, -8.80

$GeAll_4$	Mass (g)	=CH	CH_2 (int)	^{29}Si δ ppm
Calcd.	G(5)	*1*	*2.98*	*n = 340 equiv. added*
(148) Crude	12.47	1	5.3	0.77, 0.16, -0.37, -1.10
Fraction 1	0.529	1	6.7	0.49, 0.12, -0.44, -1.10
Fraction 2	0.117	1	6.7	0.49, 0.12, -0.44, -1.10
Fraction 3	0.071	1	4.9	0.84, 0.54, 0.15, -0.40, -1.05
Fraction 4	2.611	1	6.5	0.84, 0.54, 0.15, -0.40, -1.05

continued over..

Table 6.6 cont.

Ge_2Vi_6		Mass (g)	=CH	CH_2 (int)	^{29}Si δ ppm
Calcd.	G(3)	*1*	*1.33*		*n = 78 equiv. added*
(149) Crude	1.456	1	3		0.16, -0.40, -1.06
Fraction 1	0.920	1	1.5		0.16, -0.40, -1.06
Fraction 2	0.320	1	1.2		0.52, 0.13, -0.40, -1.06
Calcd.	G(5)	*1*	*2.98*		*n = 726 equiv. added*
(150) Crude	7.260	1	6.1		0.63, 0.14, -0.40, -1.05
Fraction 1	0.496	1	7.4		0.63, 0.13, -0.40, -1.06
Fraction 2	1.285	1	7.2		0.52, 0.13, -0.40, -1.06
Fraction 3	3.362	1	6.8		0.52, 0.13, -0.40, -1.06
Fraction 4	0.298	1	7.0		0.52, 0.13, -0.40, -1.06

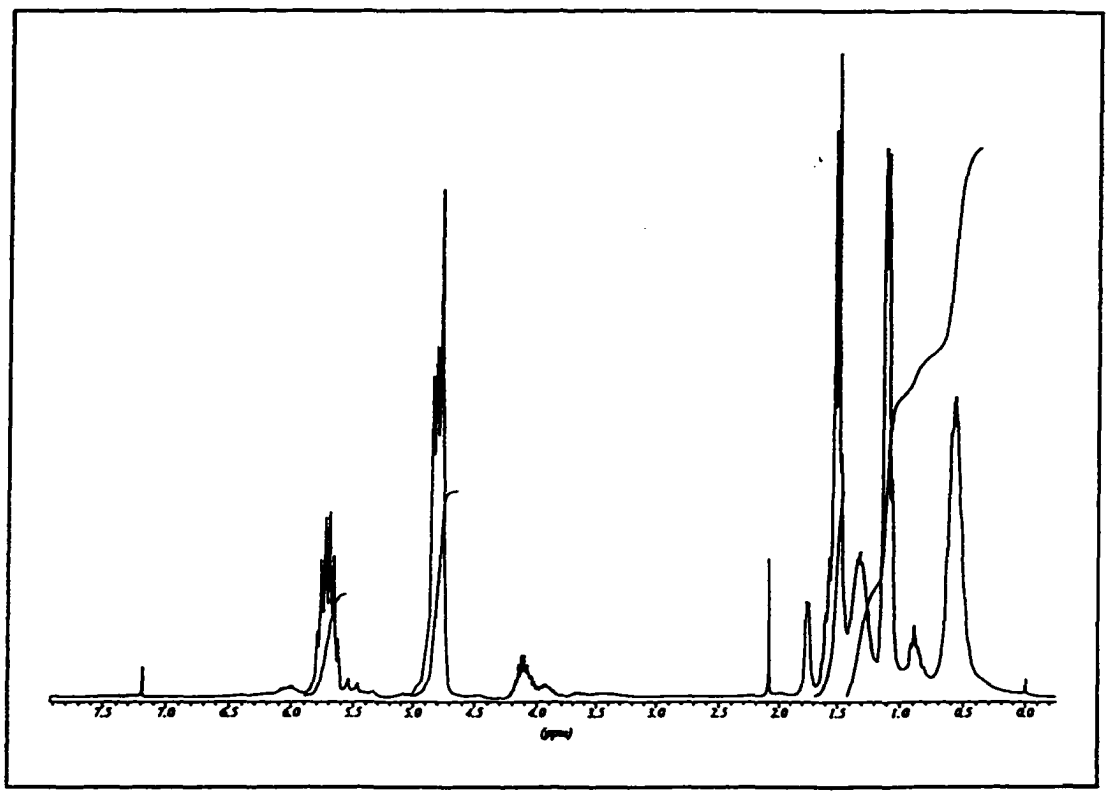


Figure 6.6 ^{1}H NMR of $PhSiAll_3$ G(4)3B (143) from rapid synthesis: fraction one

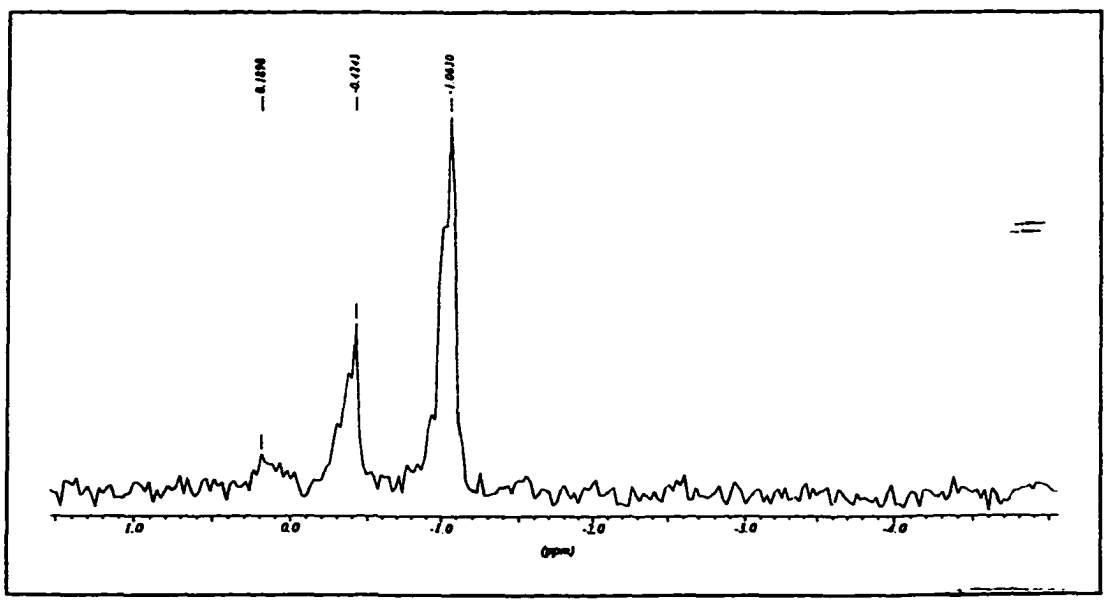


Figure 6.7 ^{29}Si-{^{1}H} NMR of rapid assembly of $PhSiAll_3$ and 120 equivalents of triallylsilane fraction two of compound (143)

The silicon NMR chemical shifts that are observed from the rapid assembly of 3B materials with a phenyl triallylsilane core are distinctive; they exhibit a strong resemblance to the data observed in chapter two, as they appear to show relative 'generational' intensities, *i.e.* are hierarchial as 3^N. For example, **(142)** see Table 6.5, proton NMR integrations for the crude mixture as well as the separate fractions indicate some hyperbranch extension: the first fraction shows a core to periphery integration ratio of 5:10 which implies little incorporation; this ratio for the second fraction (5:86) is close to that of the expected target (5:81). These observations, together with the generational silicon signals observed for the latter fraction, indicate that there is the possibility of monomer self-condensation (*i.e.* aggregates) occurring before reaction (addition) with core alkenyl groups. Similarly, entry **(143)** in Table 6.5 shows the first fraction to have proton integration above the calculated ratio (Figure 6.6), and five separate silicon resonances were observed. The second fraction shows a lesser amount of monomer incorporation, if any, by proton NMR and three distinct resonances are observed in the silicon spectrum (Figure 6.7) but no Ph-*Si* signal was detected.

Not all of these reaction mixtures show integration values appropriate for the desired targets; this could be because the rate of addition of the monomer was too fast,[19a] or because impure monomer was present which affected the rate of hydrosilylation.[70] In either situation this could possibly lead to a large amount of polymeric material similar to the rubbery, insoluble fractions derived from triallylsilane self-condensation, see chapter five. Similar behaviour has also been observed in other hyperbranched reaction mixtures, where part of the material was insoluble; this material may be highly cross-linked or a high molecular mass product formed in a 'run-away' self-condensation.

In products where both the proton NMR integration and the silicon NMR chemical shifts are closely approximate to those observed from the stepwise derivatives, there is still no way of determining the overall topography. For the diphenyldiallylsilane core, the low generation attempt (**146**) showed that not all of the core molecule had reacted (Ph_2Si at δ -11.70 ppm). This may be attributed to the low number of core alkenyl groups as in the 2B hyperbranched case, which would possibly result in self-condensation reactions before addition to the core, *i.e.* see Section 6.1.

While mixtures of different products cannot be distinguished by multinuclear NMR analysis (^1H or ^{29}Si), the observation of characteristics similar to dendritic structures (*i.e.* generational ^{29}Si spectra) may be attributed to discrete 'shell' growth of a 3B substructure. However, in all the product mixtures analysed there is still a large proportion that is hyperbranched polycarbosilane, possibly with no core molecule present, arising from self-condensation which may be suppressed but can not be eliminated when the conditions are biassed for addition to core structures.

6.3 Hybrid Hyperbranched Molecules

The simplest example of a hybrid carbosilane dendrimer is $Si[(prSiMe)^1_2:(prSi)^2_3:All]_4$, where there is a change of the branch point multiplicity at silicon (discussed in chapter five) and a G(1) core is extended to G(2) structure. This one-shell expansion uses the interior Si-CH_3 protons as the internal integration reference and has been studied for both the stepwise and rapid assembly methods. The GPC chromatograms of products isolated from rapid synthesis methodology using small core molecules (Sections 6.1 and 6.2) showed a wide polydispersity, and this has been attributed to the production of a large proportion of self-condensed monomer, *i.e.* to formation of polycarbosilane oligomers. It has also been established that larger hypercores (*i.e.* more peripheral alkenyls) further bias the addition of the monomer onto the core groups, *i.e.* less self-condensation products are observed. The use of a larger hypercore molecule (2B layer structure) that contains many more reactive peripheral groups, *i.e.* higher generation G(N)2B hypercore will now be considered. This should even further favour the statistics for monomer to react with the core rather than self-condensing, *e.g.* using $PhSi[(prSiMe)^4_2:All]_3$, which contains 48 end-groups *vs* the $PhSiAll_3$ substrate with only 3 end-groups. The large hypercores have been synthesised by stepwise methodology and were characterized in chapters two and three. The interior silicon methyl groups will be used as a reference for ^{1}H NMR integration so that larger assemblies may be studied. The hypercores used in these hybrid hyperbranched syntheses are: $PhSi[(prSiMe)^4_2:All]_3$ **(19)**, $Ge[(prSiMe)^3_2:All]_4$ **(51)** and $Ge_2[(etSiMe)^1_2:(prSiMe)^3_2:All]_6$ **(57)**

Table 6.7 Selected NMR data for hybrid hyperbranched materials adding n equivalents of triallylsilane

Hypercore	Mass (g)	=CH	$SiCH_3$	^{29}Si δ ppm
$PhSiAll_3$ G(4)2B		48	135	
G(5)3B Calcd.		*144H*	*135H*	*n = 48 equiv.*
(151) Crude	0.220	220	135	1.14, 0.71, 0.61, 0.45, -0.13, -0.43, -1.10
Fraction 1	0.098	200	135	0.91, 0.71, 0.24, -0.44, -1.10
Fraction 2	0.106	244	135	0.91, 0.71, 0.24, -0.44, -1.10
G(6)3B Calcd.		*432H*	*135H*	*n = 192 equiv.*
(152) Crude	0.508	704	135	0.91, 0.60, 0.24, -0.13, -0.44, -1.10
Fraction 1	0.125	663	135	0.25, -0.44, -1.10
Fraction 2	0.229	1344	135	0.91, 0.60, 0.24, -0.13, -0.44, -1.10
G(7)3B Calcd.		*1296H*	*135H*	*n = 624 equiv.*
(153) Crude	1.526	2589	135	0.67, 0.47, 0.12, -0.41, -1.10
Fraction 1	0.040	539	135	0.63, 0.29, -1.10
Fraction 2	0.328	2702	135	0.67, 0.47, 0.12, -0.41, -1.10
Fraction 3	0.278	2350	135	0.67, 0.47, 0.12, -0.41, -1.10
Fraction 4	0.501	5066	135	0.67, 0.47, 0.12, -0.41, -1.10
Fraction 5	0.079	4423	135	0.67, 0.47, 0.12, -0.41, -1.10
G(8)3B Calcd.		*3888H*	*135H*	*n = 1920 equiv.*
(154) Crude	4.323	5912	135	0.90, 0.72, 0.44, 0.08, -0.42, -1.10
Fraction 1	1.207	1916	135	0.91, 0.71, 0.24, -0.44, -1.10
Fraction 2	0.998	10985	135	0.44, 0.24, -0.44, -1.10
Fraction 3	0.765	3000	135	0.44, 0.24, -0.44, -1.10
Fraction 4	0.800	5640	135	0.44, 0.24, 0.13, -0.44, -1.10

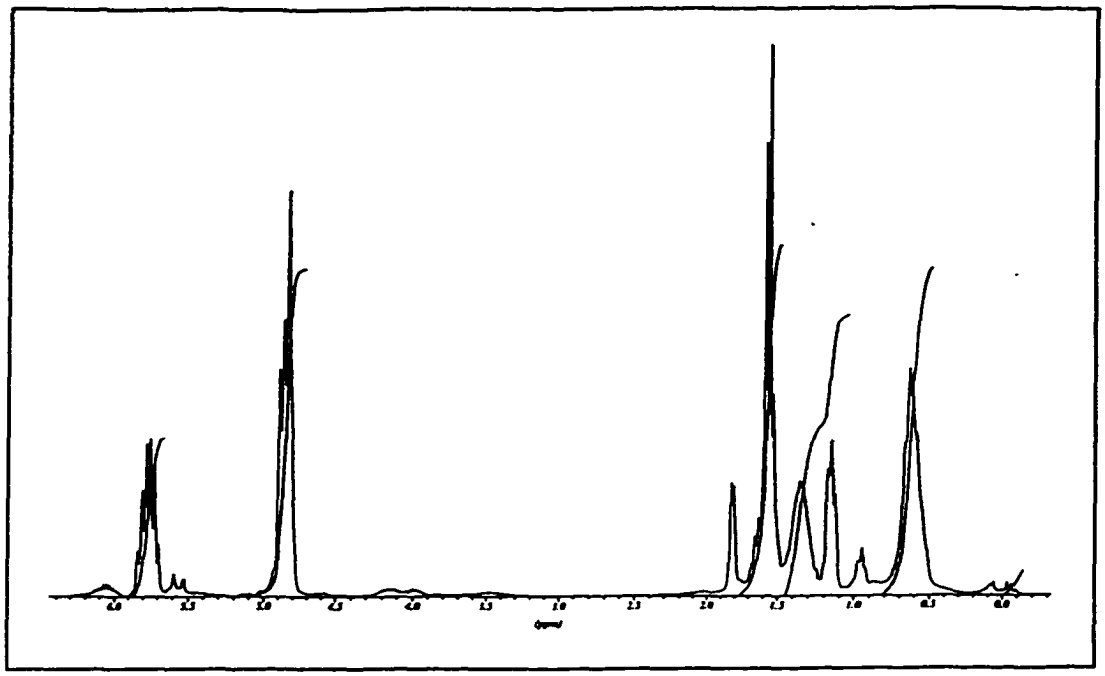


Figure 6.8 ^{1}H NMR spectrum of $PhSiAll_3$ G(4)2B/G(7)3B product (153) fraction 3

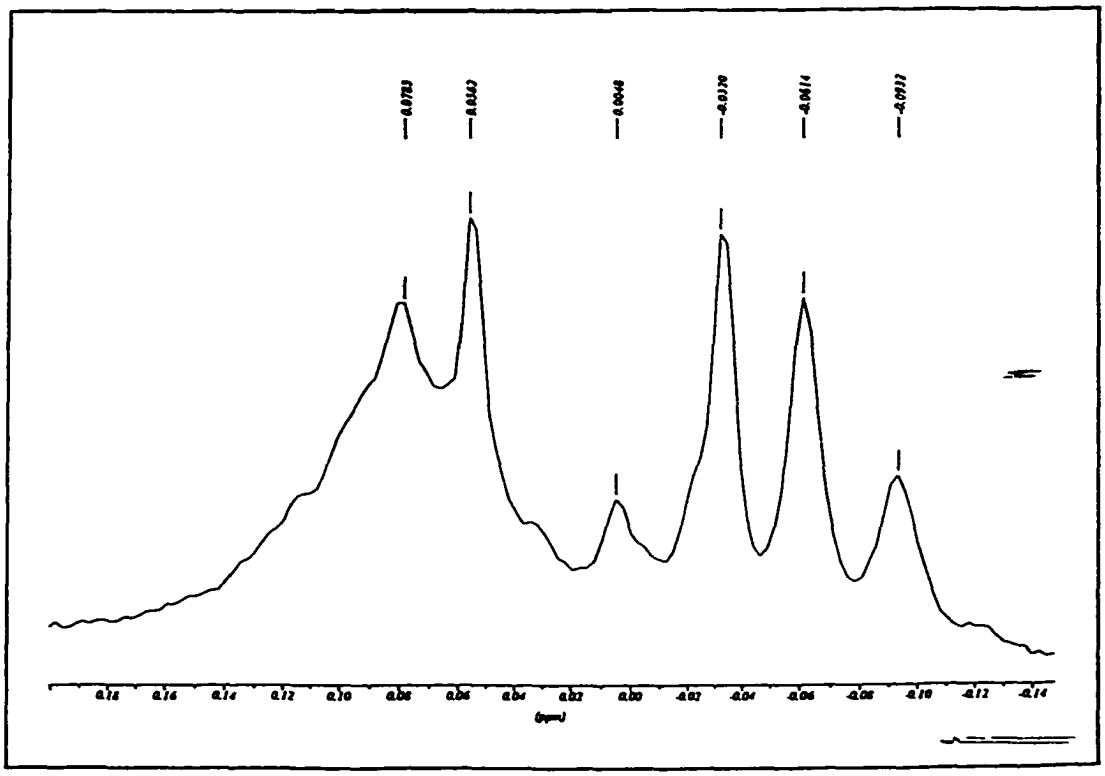


Figure 6.9 Enlargement of methyl region of hybrid hyperbranched product (153) fraction 3

Table 6.8 Selected NMR data for addition of n equivalents of triallylsilane to presynthesised hypercores

Hypercore	Mass (g)	=CH	$SiCH_3$	^{29}Si δ ppm
$GeAll_4$ G(3)2B		32	84	
G(4)3B calcd.		*96*	*84*	*n = 32 equiv.*
(155) Crude	0.228	84	84	1.01, 0.72, 0.26, -0.35, -0.99
Fraction 1	0.060	99	84	1.01, 0.72, 0.26, -0.35, -0.99
Fraction 2	0.045	152	84	1.01, 0.72, 0.26, -0.35, -0.99
Fraction 3	0.043	79	84	1.01, 0.72, 0.26, -0.35, -0.99
G(5)3B calcd.		*288*	*84*	*n = 128 equiv.*
(156) Crude	0.569	323	84	1.00, 0.73, 0.27, -0.42, -1.06
Fraction 1	0.125	505	84	1.00, 0.73, 0.27, -0.42, -1.06
Fraction 2	0.178	405	84	1.00, 0.73, 0.27, -0.42, -1.06
Fraction 3	0.078	223	84	1.00, 0.73, 0.27, -0.42, -1.06
G(7)3B calcd.		*2592*	*84*	*n = 416 equiv.*
(157) Crude	0.359	3698	84	0.63, 0.16, -0.42, -1.06
Fraction 1	0.230	3361	84	0.63, 0.16, -0.42, -1.06
Fraction 2	0.089	4031	84	0.63, 0.16, -0.42, -1.06

Hypercore	Mass (g)	=CH	$SiCH_3$	^{29}Si δ ppm
$GeAll_4$ G(3)2B		32	84	
G(>8)3B calcd.			*84*	*n = 2473 equiv.*
(158) Crude	4.620	7644	84	0.73, 0.54, 0.16, -0.40, -1.06
Fraction 1	0.230	1306	84	0.73, 0.54, 0.16, -0.40, -1.06
Fraction 2	1.784	8919	84	0.73, 0.54, 0.16, -0.40, -1.06
Fraction 3	0.987	5715	84	0.73, 0.54, 0.16, -0.40, -1.06
Fraction 4	0.152	3407	84	0.73, 0.54, 0.16, -0.40, -1.06
G(<4)3B calcd.			*84*	*n = 20 equiv.*
(159) Crude	0.150	72	84	1.02, 0.74, 0.29, -0.37, -1.06
Fraction 1	0.046	53	84	1.02, 0.74, 0.29, -0.37, -1.06*
Fraction 2	0.039	89	84	1.02, 0.74, 0.29, -0.37, -1.06*
Fraction 3	0.027	77	84	1.02, 0.74, 0.29, -0.37, -1.06
Fraction 4	0.016	83	84	1.02, 0.74, 0.29, -0.37, -1.06

* very weak signal

Table 6.9 Selected NMR data for addition of n equivalents of triallylsilane to a presynthesised hypercore

Hypercore	Mass (g)	=CH	$SiCH_3$	^{29}Si δ ppm
Ge_2Vi_6 G(3)2B		48	126	
G(5)3B calcd.		*432*	*126*	*n = 192 equiv.*
(160) Crude	1.396	525	126	0.73, 0.26, -0.41, -1.06
Fraction 1	0.345	185	126	0.73, 0.26, -0.41, -1.06
Fraction 2	0.897	434	126	0.73, 0.26, -0.41, -1.06

The relative proton NMR integrations for all of the hypercores used (Si-C*H*$_3$ interior *vs* β-allyl) are close to the values of the intended target structures; this implies that the larger number of reactive peripheral groups facilitates addition of monomer preferentially to the hypercore, and thus limits polycarbosilane formation *via* self-condensation. For instance, Figures 6.10 and 6.11 show the crude product **(151)** NMR spectra obtained when a hypercore reacts with only one shell stoichiometry for the next layer and the product formed is not easy to interpret by ^{29}Si NMR. This spectrum shows a small peripheral resonance attributed to an *Si*-All$_3$ shell, yet the proton integration indicates that there is a large proportion of β-allyl resonances present (entry **(151)**, Table 6.7). The proton NMR spectrum (Figure 6.10) also shows a large amount of polymeric material present, from the signals observed at δ 0.1 and 1.25 ppm, which are assigned to formation of polycarbosilane, hence the large β-allyl integration. However, the product isolated from entry **(154)** primarily shows 3B branching

silicon signals in the ^{29}Si NMR spectrum (Figure 6.13), the relative proton integrations for the last three fractions may all be interpreted as having a larger amount of monomer addition to the hypercore. The number of end groups available in a hypercore ($PhSi[(prSiMe)^4_2:All]_3$) *vs* a small core ($PhSiAll_3$), where both are reacted with triallylsilane to produce a similar target generation G(5), will be used to demonstrate that addition to the larger structure should be favoured statistically.

$PhSiAll_3$ G(5)3B requires 363 equivalents of triallylsilane; this contains 363 x 3 double bonds = 1089 double bonds. The total number of double bonds present is therefore 1092; of these 3/1092 (0.30%) are from the core molecule and 1089/1092 (99.7%) are from the monomer. Even though the addition of monomer unit is dropwise, these relative percentages do not favour addition to the core. For a hybrid reaction the initial hypercore has 48 allyl groups already present and requires 48 equivalents of triallylsilane containing 144 double bonds to produce the target G(5)3B. The total number of double bonds (192) includes a larger percentage of alkenyl groups at the hypercore (25%) which statistically should allow for preferential addition at these sites.

As larger generation structures become the target, the distribution will again favour the self-condensation reaction because a larger number of monomer units will again be required; for example with the same hypercore (48 allyl groups) a 7th generation target would require the addition of 624 triallylsilane monomers (1872 alkenyl groups). This shows that 2.5% of the reactive alkenyls are available at the hypercore while 97.5% are carried by the monomer; even though this distribution is a factor of 10 less favoured it is still better than the first example discussed above, with only a simple low multiplicity core. For such analysis the

reactivity of all double bonds is taken to be similar, but this may not be true; the one-shell reactions from chapter five suggested that the 'new' periphery of triallylsilyl groups could possibly be more reactive than the existing hypercore alkenyls, leading to 3B substructure growth at sites not associated with the hypercore.

Germanium centred hybrids were reacted with an excess and a substoichiometric amount of triallylsilane in two different experiments, Table 6.8. The reaction where excess monomer was used shows a large incorporation of triallylsilyl groups by proton NMR integration; this could imply that a 7th generation or greater was produced, see Figures 6.14 and 6.15. In a further experiment where only 20 equivalents of triallylsilane were added (deficit: one-shell expansion would require 32), only a very weak signal in the silicon NMR for a peripheral triallylsilyl group (δ -1.06 ppm) was observed for the initial two fractions collected. This suggests that both the latter may be predominantly the initial hypercore with only a small amount of triallylsilane incorporated. The remaining two fractions obtained show proton integrations that are similar to a completed hybrid shell (*i.e.* with 96 terminal groups); corresponding silicon NMR spectra also showed strong signals attributable to peripheral groups and it may be inferred that most of the triallylsilane substrate was incorporated into these products. This would appear to suggest that only some hypercores reacted to increase the molecular mass by attachment of aggregate fragments formed by competing monomer self-condensation. This is consistent with the evidence from Section 6.3 and also the observations discussed in chapter five, where the dominant reaction is monomer self-condensation which may be followed by attachment of the aggregate so formed to the core molecule. However, with a larger hypercore as discussed above, the second reaction

(aggregate attachment) becomes more favourable because of the increased number of peripheral groups present.

6.4 Summary

Although no structures can be proposed for any of the hyperbranched materials prepared, the sum of the evidence from multinuclear NMR data suggests that addition to the hypercore is occurring; the products are highly branched molecules which appear to have similar NMR characteristics to dendritic carbosilane materials (chapters two and three). Addition of substrate in deficit stoichiometry yields sample fractions showing little or no addition, together with others that show a large incorporation of monomer unit.

Formation of these hybrid composites appears to be more successful as a route to highly branched high molecular mass materials than the simpler approach of addition to a small focal point core, see Sections 6.2 and 6.3 compared with chapter five. This is attributed to the way in which the increased number of reactive peripheral groups alters the statistics of addition, away from monomer self-condensation and towards monomer or monomer-aggregate attachment to the hypercore. The following spectra shown in Figures 6.10-6.15 are representative of a typical experiment; no difference in the peripheral group chemical shift values (^{1}H or ^{29}Si NMR) is observed when using different hypercore structures.

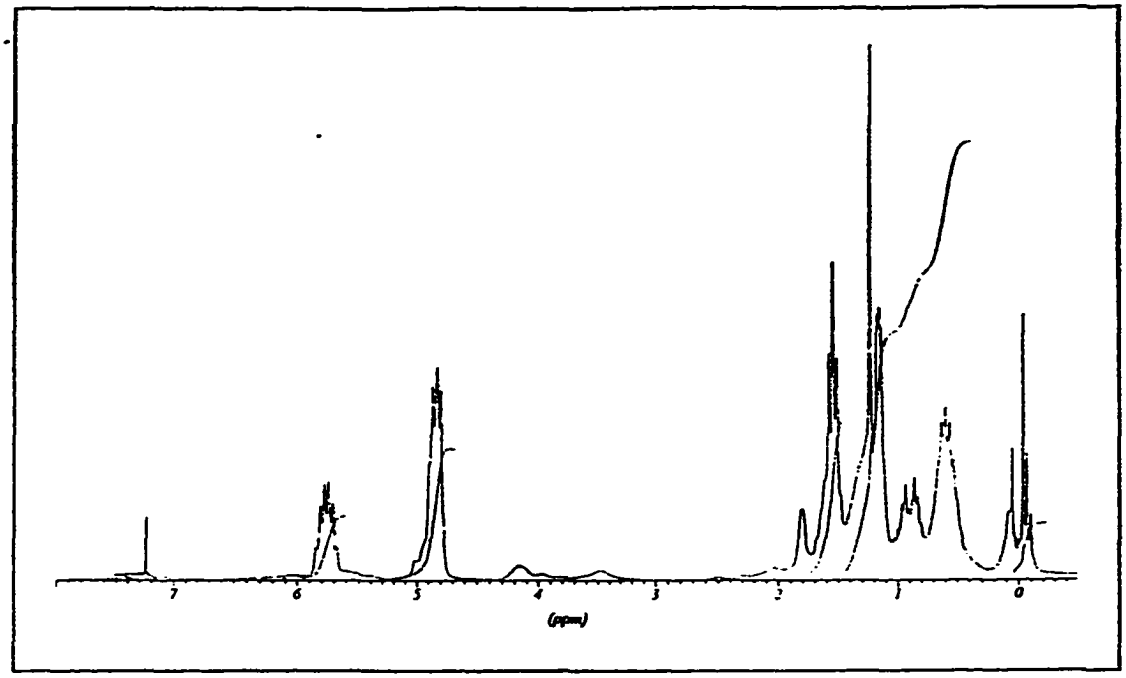


Figure 6.10 ^{1}H NMR spectrum of product (151)

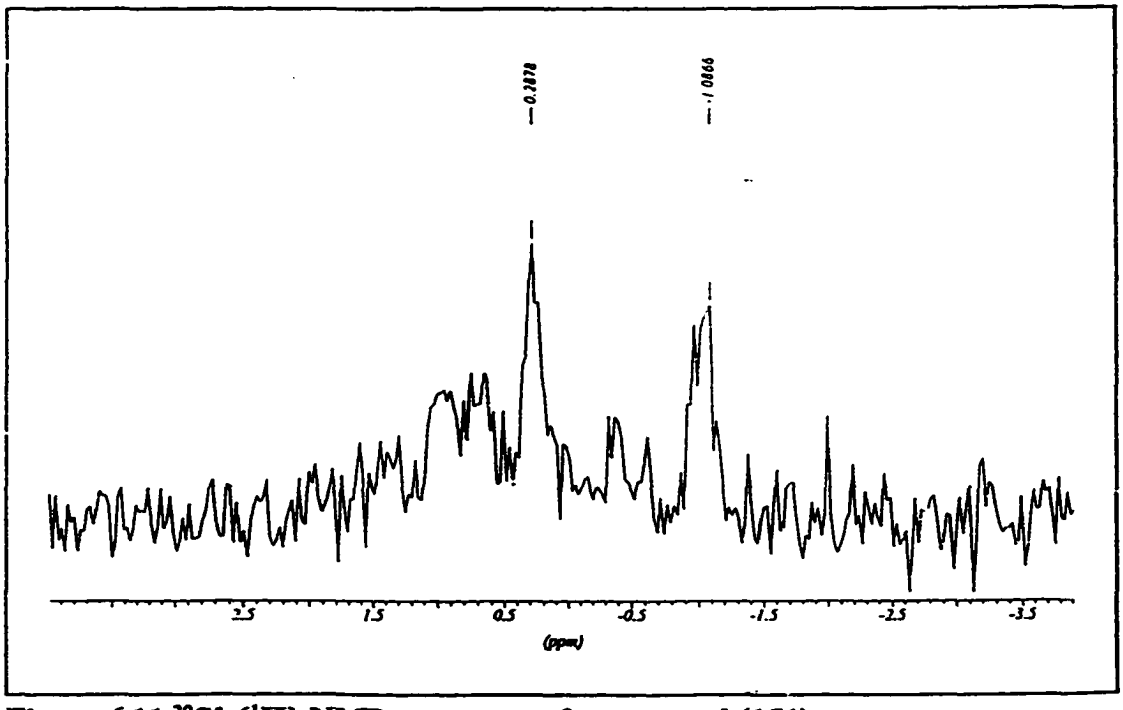


Figure 6.11 ^{29}Si-{^{1}H} NMR spectrum of compound (151)

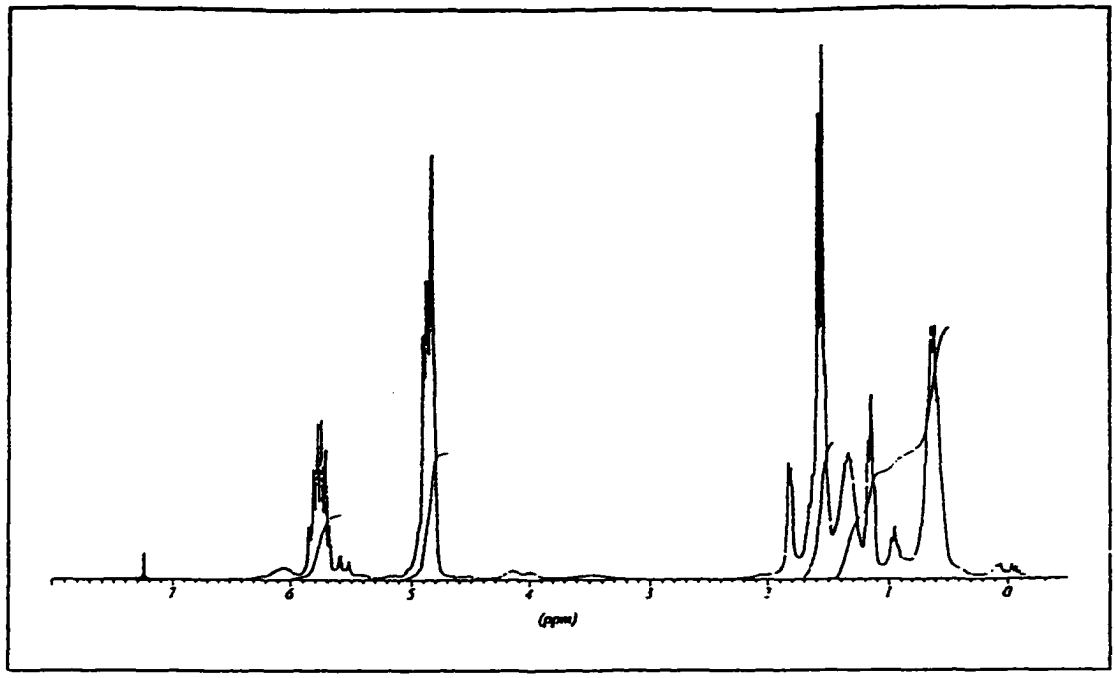


Figure 6.12 ^{1}H NMR spectrum of product (154)

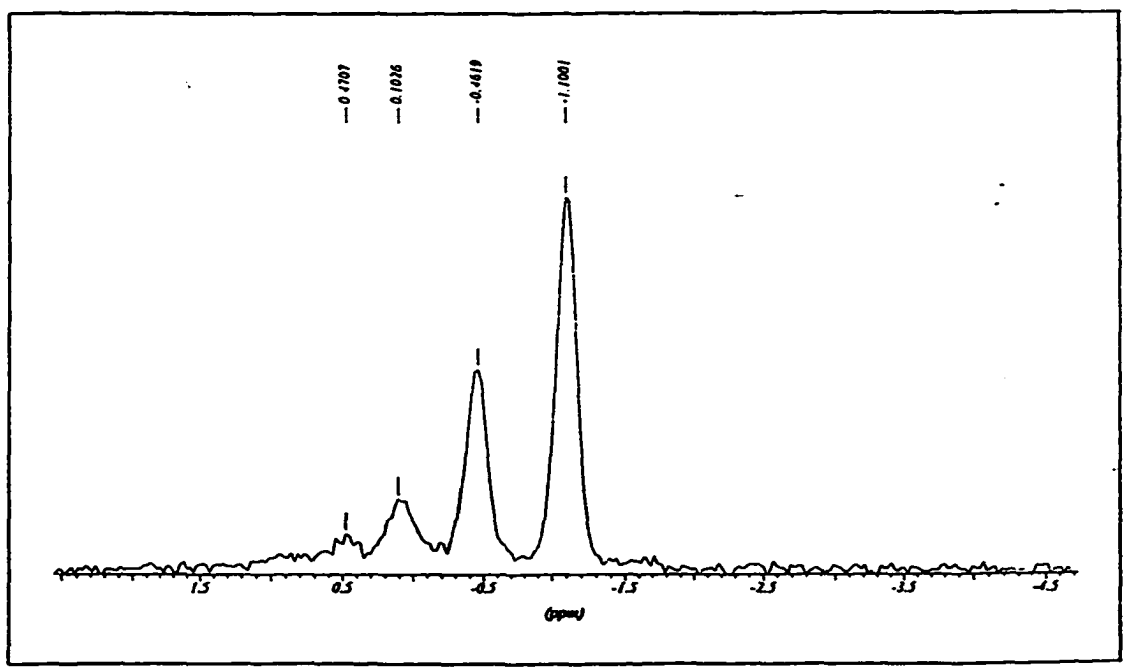


Figure 6.13 ^{29}Si-{^{1}H} NMR spectrum of product (154)

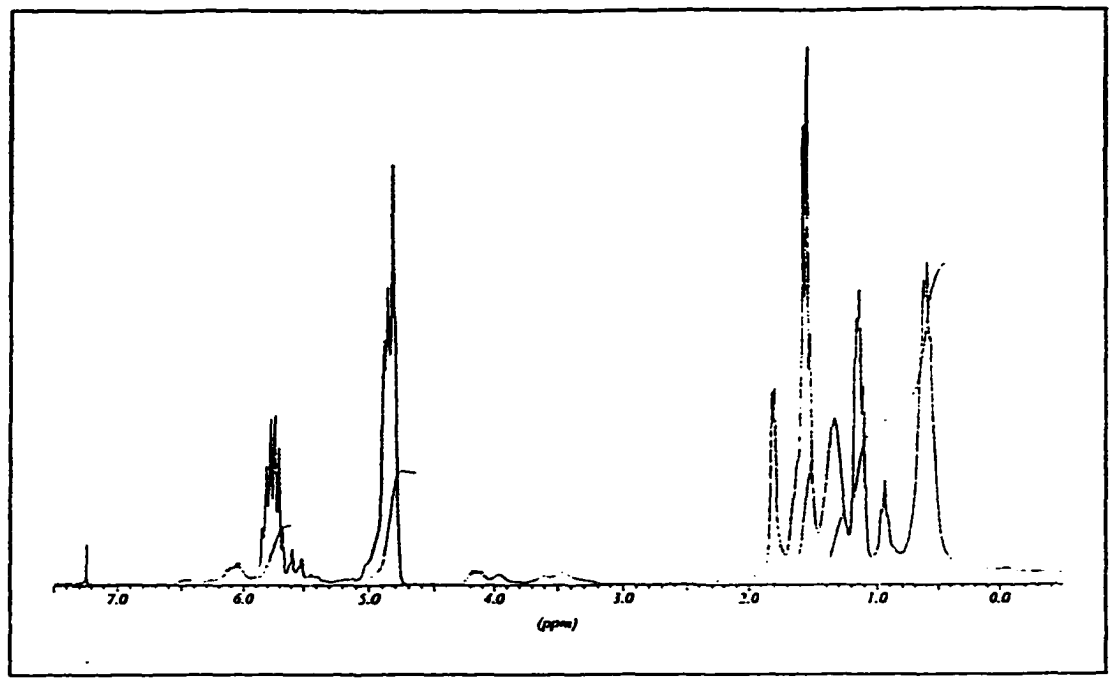


Figure 6.14 ^{1}H NMR spectrum of product (158)

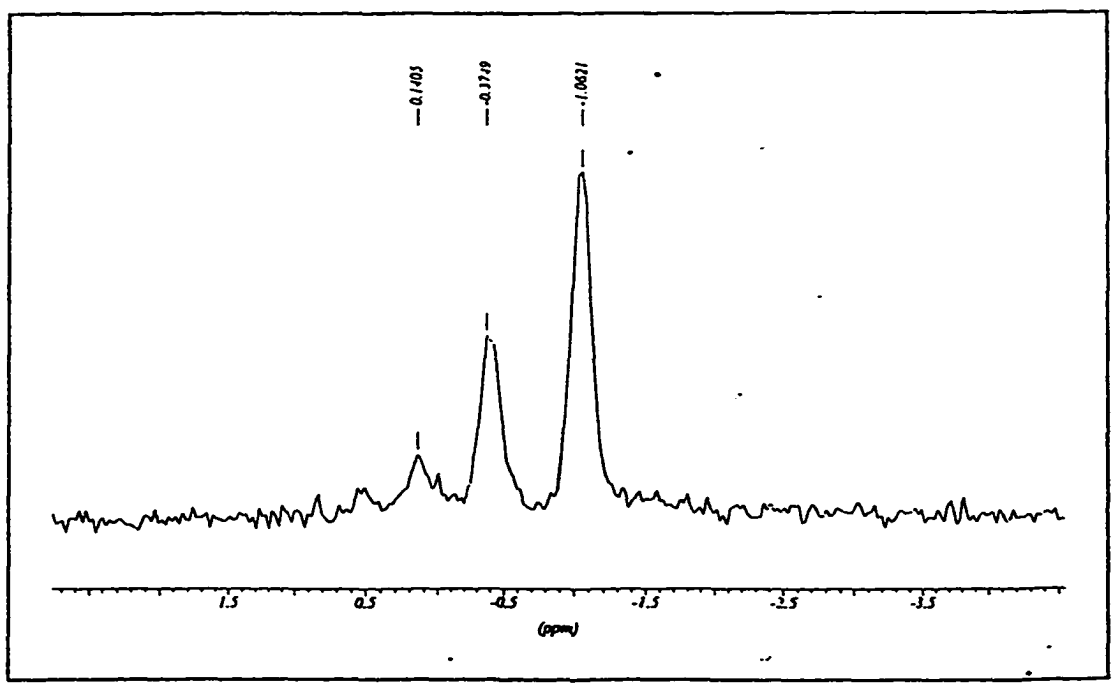


Figure 6.15 ^{29}Si-{^{1}H} NMR spectrum of product (158)

CONCLUSIONS

This thesis has shown that multinuclear NMR spectroscopy can be used as an excellent analytical tool for characterization of carbosilane based dendrimers. Growth from a trifurcate core with a range of dendritic topographies, constructed by iterative methodology, led to materials that could be identified using NMR, mass spectroscopy and gel permeation chromatography. Hierarchical properties were observed in low generation dendrimers for all branch topographies, 1B, 2B and 3B silicon centres. The spectroscopic data collected for the trifurcate series of compounds allows for 'end-group' counting *vs* the central phenyl ring protons. This information aided in the characterization of dendrimers which did not contain an internal integration reference. Analogous multinuclear NMR spectra were observed, and by isolation of each successive generation, compounds were identified as having similar shell completion at each stage.

Substitution of silicon halogen bonds by nucleophilic substrates is a versatile method for changing peripheral functionality. Advantageously for the trifurcate dendrimers, the central phenyl-silicon bond can also be substituted *via* triflic acid scission. This led to an electrophilic silicon triflate salt which readily underwent displacement by a range of alcohol substrates. Similarly, cleavage of the digermane bond by oxidative addition of iodine can be used as a starting point for bifunctional chemistry. Either route led to core substitution with an anthracenyl group; prior exterior modification for the trifurcate dendrimers was necessary due to the more labile allyl silicon bond. Capping with methylnaphthalene groups

could induce an energy gradient within the structure, and with the aid of fluorescence spectroscopy the concept of 'light harvesting' dendrimers may be observable.

Alteration of the silicon branch topography facilitates characterization of dendrimers with a higher core symmetry. Spheroidal 'hypercores' were synthesised to include internal methyl groups; these were then used as an internal reference for proton NMR integration on hybrid systems (branch point change from 2B to 3B). Comparisons between step-wise iterative procedures of hydrosilylation/alkenylation and a 'one-pot' approach have been made. Attempts to form discrete one 'shell' expansion products mainly failed, primarily starting material and hyperbranched polymer (arising from self-condensation of monomer) were recovered. It was concluded that larger hypercores, containing many peripheral groups, were needed to favour the statistics for addition to preformed core rather than self-condensation.

EXPERIMENTAL SECTION

General Techniques

All synthetic manipulations were carried out under an atmosphere of dry dinitrogen gas using standard vacuum line Schlenk techniques. All solvents were degassed and purified prior to use according to standard literature methods: diethyl ether, benzene and tetrahydrofuran were distilled from sodium/benzophenone ketal, hexanes was distilled from sodium. NMR grade deuterochloroform was stored over 4Å molecular sieves.

Instrumentation

NMR spectra were recorded using samples dissolved in $CDCl_3$, unless otherwise stated, on the following instrumentation.

^{1}H NMR

Bruker WM250 (250.1 MHz)

Bruker AC300 (300.1 MHz)

Bruker AMX360 (360.1 MHz)

^{13}C NMR

Bruker AC300 (75.5 MHz)

Bruker AMX360 (90.6 MHz)

^{29}Si NMR

Bruker WM250 (49.7 MHz)

Bruker AMX360 (71.54 MHz)

^{19}F NMR Bruker AMX360 (338.86 MHz)

All NMR chemical shifts are reported in parts per million (δ ppm), downfield shifts are reported as positive values from tetramethylsilane (TMS) as standard at 0.00 ppm. The ^{1}H and ^{13}C chemical shifts are reported relative to the NMR solvent as an internal standard, and the ^{29}Si chemical shifts are reported relative to external TMS standard.

Infra-red (IR) spectra were recorded as neat oils between KBr plates on a Perkin-Elmer 1330 spectrometer.

Mass spectroscopic measurements were recorded on either a Finnigan 3300, chemical ionisation (CI)/Methane, electron impact (EI); or a Kratos Concept H, Low resolution EI.

Microanalytical data were supplied by Canadian Microanalytical Services Ltd. of Vancouver, B. C. or by Atlantic Microanalytical of Atlanta, Georgia and are reported as percentages.

Gel permeation chromatography (GPC) polydispersity measurements were recorded on a Varian Vista 5500 liquid chromatograph using Jordi DVB 100 or 1000Å columns. HPLC grade $CHCl_3$ was used as eluent at 1 mL/min and fractions were detected by UV absorption at 254 nm. Also a Waters Millenium Chromatography System was used with 3 μ Styragel columns (100-, 500- and 1000Å nominal pore size) at 35°C; THF was used as eluent at 1mL/min. Detection was by differential refractometer and UV absorption at 262 nm.

Intrinsic viscosity measurements were carried out in cyclohexane at 25°C. A Cannon-Ubbelhode viscometer was used and solvent flow times were around 110 secs. Measurements were made on concentrations obtained by dilution in the viscometer.

General Procedures

Preparation of an allylmagnesium bromide solution.

To a two-neck 500 mL round-bottomed flask, charged with a magnetic stirring bar and a constant pressure dropping funnel attached to one of the side arms, an excess of magnesium turnings (typically about 20 g (0.82 moles)) was added. The flask was fitted with a reflux

condenser and placed under a nitrogen atmosphere. One crystal of iodine was added to this flask together with 200 mL of distilled diethyl ether. This solution was stirred at room temperature until the iodine colour had dissipated. The dropping funnel was filled with 50 mL of allyl bromide (69.9 g, 0.58 moles) and 50 mL of diethyl ether. A further 2-3 mL of neat allyl bromide was added directly to the magnesium solution to help initiate the Grignard. Upon initiation the colourless Et_2O solution turned slightly pale grey and bubbles started to rise from the solvent. A slow addition of the allyl bromide solution was started, such that a steady reflux was obtained. Once complete addition had finished the solution was refluxed for a further 2 hours, after which the solution looked dark grey in appearance. After cooling to room temperature the dropping funnel was removed and a stopper put in its place. Another two-neck round bottom flask was fitted with a glass U-tube and a nitrogen inlet. The reflux condenser was removed and the two round-bottomed flasks joined together by the U-tube under an atmosphere of nitrogen. The contents of the Grignard containing solution were transferred to the empty flask by means of decanting, and this solution was immediately fitted with reflux condenser. The remaining magnesium turnings were washed carefully with water, highly exothermic reaction, to remove all traces of any precipitated salts. Once the washings became colourless the turnings were washed with acetone and placed in an oven to dry for 2 hours. The magnesium turnings were then reweighed and the yield of alllylmagnesiumbromide formed was calculated from reacted magnesium. Typical yields were between 65-85%, and typical concentrations of solutions were between 1.2-1.6M.

General procedure for hydrosilylation

The same procedure is followed for all hydrosilylation reactions unless otherwise stated. Times and amounts of solvents used vary for each reaction. The alkenyl compound that is to be reacted is added to a thick-walled resealable glass tube. To this the catalyst is added, chloroplatinic acid hexahydrate (CPA) 0.1 M solution in isopropanol, followed by the solvent (hexanes or THF). Finally excess (at least two-fold) silane is added carefully, an

exothermic reaction takes place immediately upon addition, and the tube is sealed with a screw cap. This reaction mixture is heated in an oil bath at 120°C for the specified time and then cooled to room temperature. The contents are transferred into a pre-weighed flask *via* syringe and all remaining volatiles are removed under vacuum.

General procedure for reacting chlorosilane groups with an allyl Grignard

A solution of excess Grignard is either prepared or purchased and added to a two-neck round-bottom flask fitted with a reflux condenser, magnetic stirring bar, and a pressure equalising dropping funnel. The chlorosilane to be reacted is dissolved in solvent, usually Et_2O, and transferred into the dropping funnel *via* syringe. This is added to the Grignard solution dropwise at room temperature. After complete addition the reaction mixture is heated to reflux for the specified time.

General work-up for alkenyl terminated dendrimers

Once the above reflux is finished the flask is cooled in an ice bath. Usually a 10% by weight solution of NH_4Cl is added to the dropping funnel and slowly dropped into the reaction mixture. Occasionally a 1 M or 2 M HCl solution is added to help clarify the emulsified solutions. This two-phase solution is placed into a separatory funnel and the aqueous layer is extracted three times with organic solvent, usually Et_2O. The combined organic layers are then dried with $MgSO_4$ and excess solvent is removed by rotary evaporation. The remaining oil is then transferred into a pre-weighed flask and all residual volatiles are removed under vacuum.

Preparation of Starting Materials

All starting materials were purchased commercially or synthesised according to the literature preparations listed below. Triallylsilane[64] **(115)** and diallylmethylsilane[64] **(114)** were freshly prepared prior to use.

Phenyl triallylsilane[64] (1)

A 500 mL two-neck round-bottom flask containing allylmagnesium bromide (0.157 moles) in Et_2O (250 mL) was fitted with a reflux condenser and a constant pressure dropping funnel. The funnel was charged with phenyltrichlorosilane 5 mL (6.605 g, 31.2 mmoles) in 30 mL of Et_2O, which was slowly added to the Grignard solution at rt. A white precipitate was formed during this time due to the magnesium salts. After complete addition the reaction mixture was refluxed for a further 3 hours and then allowed to cool to room temperature. The flask was put into an ice bath and excess Grignard was quenched with 10% NH_4Cl solution (100 mL). This mixture was then extracted three times with Et_2O in 60 mL portions and the resulting organic layer was dried over anhydrous $MgSO_4$. The solvent was removed on a rotary evaporator to give a colourless oil which was pure phenyltriallylsilane, yield 6.90 g (30.2 mmoles, 97%). Occasionally a pale yellow oil is obtained which can be purified by vacuum distillation. ^{1}H-NMR ($CDCl_3$, 300 MHz); δ 7.53 (d), 7.34 (d) (5H), 5.8 (s, 3H), 4.9 (m, 6H), 1.9 (d, 6H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz); δ 135.2, 134.2, 133.8, 129.3, 127.7, 114.3, 19.5. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz); δ -8.0. IR (Neat, KBr plates); 3063, 2920, 1630, 1428 cm^{-1}. MS (CI, Methane); 229 (M + 1), 187, 153.

Diallyldiphenylsilane[64] **(30)**

Dichlorodiphenylsilane 2.53 g (10 mmoles) dissolved in 30 mL of Et_2O was added slowly to a solution containing excess allylmagnesium bromide. This was refluxed for 6 hours after

which an aqueous acidic work-up was carried out. A colourless oil was isolated as product, yield 2.27 g (8.6 mmoles, 86%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.58, 7.41 (m, 10H), 5.87 (s, 2H), 4.96 (m, 4H), 2.22 (m, 4H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.0, 134.8, 133.7, 129.4, 127.8, 114.7, 19.9. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -11.70. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (CI, Methane): 265 (M + 1), 223, 187.

Tetraallylgermane[67] **(32)**

In an analogous procedure to that mentioned above, germanium tetrachloride 3 mL (5.64 g, 26 mmoles) in 30 mL of Et_2O was slowly added to a solution of allylmagnesium bromide in Et_2O (0.156 moles, 220 mL). After quenching with NH_4Cl (100 mL) and extraction with Et_2O (3 x 50 mL) the organic layer was dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation to yield a colourless oil which was pure tetraallylgermane 5.48 g (23 mmoles, 89%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 4H), 4.80 (m, 8H), 1.55 (d, 8H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.94, 113.10, 19.00. IR (Neat, KBr plates): 3060, 1630 cm^{-1}. MS (CI, Methane): 237 (M + 1), 196, 155.

Tetravinylgermane[67] **(33)** and Hexavinyldigermane[67] **(34)**

A three-neck 500 mL round-bottom flask was fitted with a reflux condenser and a 100 mL constant pressure dropping funnel. A few magnesium turnings were added to the flask and it was charged with 280 mL of 1.0 M Vinylmagnesiumbromide solution in THF (0.280 moles). The dropping funnel was filled with germanium tetrachloride 5 mL (9.40 g, 44 mmoles) in 40 mL of Et_2O and this solution was slowly added. After complete addition, 1 hour, the mixture was refluxed for a further 4 hours and then allowed to cool to room temperature. Excess Grignard was quenched using 1 M HCl solution, the aqueous layer was extracted 3 times with Et_2O (40 mL) and then consequently dried with anhydrous $MgSO_4$. Removal of the solvent left a brown oil which was transferred to a 50 mL round-bottomed

flask fitted for a short-path distillation. The first fraction to be collected was pure tetravinylgermane 2.54 g (14 mmoles, 32%) bp 52-54°C at 27 mmHg. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.10 (m, 8H), 5.73 (dd, 4H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.40, 132.58. MS (CI, Methane): 181 (M + 1). The experimental set-up was changed so that a trap at -78°C was attached to the distillation flask and full vacuum was used so that pure hexavinyldigermane followed next, 3.68 g (11.9 mmoles, 54%) bp 68-72°C at 0.1 mmHg. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.10 (m, 8H), 5.73 (dd, 4H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.93, 132.30. MS (CI, Methane): 308 (M + 1), 281, 154. The residue left in the flask is a mixture of various polygermane species.

Tetraallylsilane[64] (**45**), analogous procedure for tetravinylsilane using vinylmagnesiumbromide.

Using the same experimental conditions as above silicon tetrachloride 5 mL (7.415 g, 44 mmoles) in 50 mL of Et_2O was added dropwise to a solution of allylmagnesium bromide (0.26 moles) in 250 mL of Et_2O. After aqueous work-up followed by drying and removal of solvent pure tetraallylsilane was obtained, yield 8.02 g (41.8 mmoles, 95%). Occasionally a yellow oil is produced instead which can be distilledunder vacuum to give pure starting material. ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.75 (m, 4H), 4.80 (m, 8H), 1.55 (d, 8H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 133.95, 113.86, 19.10. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -1.52. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (CI, Methane): 192 (M + 1), 151.

Tetravinylsilane b.pt 131°C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.10 (m 8H), 5.85 (dd, 4H). ^{13}C-NMR ($CDCl_3$, 62.89 MHz): δ 135.06, 133.87. ^{29}Si-NMR ($CDCl_3$, 71.54 MHz): δ -27.69. IR (Neat, KBr plates): 3060, 2920, 1630 cm^{-1}.

Hexavinyldisilane[64]

Hexachlorodisilane 5 mL (7.81 g, 29 mmoles) in 40 mL Et_2O was added to an excess of 1 M Vinylmagnesiumbromide in THF (174 mL, 0.174 moles). The solution was refluxed for 3 hours and then allowed to cool. After the aqueous work-up and fractional distillation pure hexavinyldisilane was isolated 1.174 g (5.38 mmoles, 18%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.10 (m, 12H), 5.85 (dd, 6H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.77, 133.39. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -35.02. IR (Neat, KBr plates): 3060, 2920, 1630cm^{-1}. MS (CI, Methane) 218 (M + 1), 177, 109.

Hexaallyldisilane[64]

Hexachlorodisilane 5 mL (7.81 g, 29 mmoles) in 50 mL of Et_2O was slowly added to an excess of allylmagnesium bromide in Et_2O (0.186 moles, 230 mL). This solution was refluxed for 2 hours and then allowed to cool. Following the usual work-up procedure and fractional distillation, pure hexaallyldisilane was recovered 1.931 g (6.39 mmoles, 23%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 6H), 4.80 (m, 12H), 1.57 (d, 12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.54, 113.82, 20.02. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -16.80. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (CI, Methane): 302, 260, 151.

PHENYL TRIALLYLSILANE BASED DENDRIMERS

1B BRANCHING

$PhSi[(prSiMe_2)^N{}_1{:}X]_3$ G(N), X = Cl or All

(2) G(0.5)Cl

Phenyl triallylsilane 1.02 g (4.47 mmoles), $H_2PtCl_6{\cdot}6H_2O$ 50 μL (5 nmoles), hexanes 15 mL and chlorodimethylsilane, $HSiMe_2Cl$, 2 mL (1.704 g, 18 mmoles) were heated in a resealable tube for 5 hours. Once the residual silane and solvent had been removed in vacuo a light brown oil remained, yield 2.08 g (4.07 mmoles, 91%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.46, 7.35 (d, d, 5H), 1.48 (m, 6H), 0.9 (t, 12H), 0.37 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 137.0, 133.9, 128.9, 127.8, 23.4, 17.6, 16.5, 1.8. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 31.2 (Si-Cl), -3.7 (Si-Ph). IR (Neat, KBr plates): 3060, 3040, 2920, 1420, 1405, 1250, 470 cm^{-1}.

(3) G(1)All

The chlorosilyl compound from above, 2.08 g (4.07 mmoles) was dissolved in 10 mL of Et_2O and an excess solution of allylmagnesium bromide was added. This mixture was stirred overnight at room temperature and following an aqueous work-up a colourless oil was isolated, yield 1.231 g (2.33 mmoles, 57%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.46 (d, 3H), 7.33 (d, 2H), 5.74 (m, 3H), 4.80 (m, 6H), 1.54 (d, 6H), 1.38 (m, 6H), 0.84 (t, 6H), 0.59 (t, 6H), -0.06 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 137.9, 135.2, 134.0, 128.6, 127.6, 112.5, 23.6, 19.7, 18.3, 17.3, -3.6. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.73 ($Si-CH_3$), -3.95 (Si-Ph). IR (Neat, KBr plates): 3060, 2910, 1625, 1250 cm^{-1}. MS (CI, Methane): 527 (M - 1), 513, 488. Anal. Calcd for $C_{30}H_{56}Si_4$: C, 68.18; H, 10.61. Found: C, 67.37; H, 10.54.

(4) G(1.5)Cl

G(1)All 0.693 g (1.31 mmoles), $H_2PtCl_6 \cdot 6H_2O$ 50 μL (5 nmoles), $HSiMe_2Cl$ 0.6 mL (5.25 mmoles) and 10 mL of hexanes were heated together in a resealable tube for 8 hours. Removal of all residual volatile material left a brown oil, yield 1.03 g (1.27 mmoles, 97%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.44 (d, 3H), 7.32 (d, 2H), 1.38 (m, 12H), 0.84 (q, 12H), 0.53 (q, 12H), 0.38 (s, 18H), -0.07 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 138.0, 134.0, 128.6, 127.6, 20.2, 19.5, 18.4, 17.6, 17.3, 1.82, -3.24. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 31.2 (Si-Cl), 1.12 (Si-CH_3), -3.95 (Si-Ph). IR (Neat, KBr plates): 3060, 2920, 1250, 470 cm^{-1}.

(5) G(2)All

G(1.5)Cl 1.03 g (1.27 mmoles) was dissolved in 15 mL of Et_2O and to this an excess of allylmagnesium bromide was added, the solution was stirred at rt overnight. After the work-up a colourless oil remained, yield 0.774 g (0.93 mmoles, 73%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.46 (d, 3H), 7.33 (d, 2H), 5.76 (m, 3H), 4.80 (m, 6H), 1.56 (d, 6H), 1.38 (m, 18H), 0.84 (m, 6H), 0.73 (m, 12H), -0.04 (s, 18H), -0.08 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 138.2, 135.3, 134.0, 128.6, 127.6, 112.5, 23.4, 20.1, 19.5, 18.5, 18.4, 18.3, 17.4, -3.2, -3.4. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.98 (Si-CH_3), 0.78 (Si-CH_3), -3.99 (Si-Ph). IR (Neat, KBr plates): 3060, 2920, 1625, 1250 cm^{-1}. Anal. Calcd for $C_{45}H_{92}Si_7$: C, 65.22; H, 11.11. Found: C, 65.17; H, 11.04.

(6) G(2.5)Cl

G(2)All 0.40 g (0.48 mmoles), 50 μL of $H_2PtCl_6 \cdot 6H_2O$ (5 nmoles), chlorodimethylsilane 0.22 mL (1.93 mmoles) and 15 mL of hexanes were heated in an oil bath for 12 hours. Once the remaining volatile material had been removed *in vacou* a brown oil remained, yield 0.53 g(0.48 mmoles, 100%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.44 (d, 3H), 7.33 (d, 2H), 1.35 (m, 24H), 0.85 (m, 12H), 0.55 (m, 18H), 0.38 (s, 18H), -0.06 (s, 18H), -0.09 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 138.2, 134.0, 128.6, 127.6, 23.4, 20.3, 20.1, 20.0, 19.5, 18.5, 17.7, 17.4, 1.8, -3.2, -3.23. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 31.3 (Si-Cl), 1.12, 0.98 (Si-CH_3),

-3.98 (Si-Ph). IR (Neat, KBr plates): 3060, 2910, 1250, 470 cm^{-1}.

(7) G(3)All

G(2.5)Cl 0.53 g (0.48 mmoles) was dissolved in 10 mL of Et_2O and to this a solution containing excess allylmagnesium bromide was added. This mixture was stirred overnight at rt, once work-up was completed a colourless oil remained, yield 0.473 g (0.42 mmoles, 89%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.45 (d, 3H), 7.33 (d, 2H), 5.75 (sep, 3H), 4.80 (m, 6H), 1.5 (d, 6H), 1.30 (m, 18H), 0.84 (m, 6H), 0.73 (m, 30H), -0.04 (s, 18H), -0.08 (s, 18H), -0.10 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 138.2, 135.3, 134.0, 128.6, 127.6, 112.5, 23.4, 20.3, 20.1, 20.0, 19.5, 18.5, 18.4, 18.3, 17.4, -3.2, -3.6. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.977 (Si-CH_3), 0.774 (Si-CH_3), -3.99 (Si-Ph). IR (Neat, KBr plates): 3060, 2910, 1625, 1245 cm^{-1}. MS (CI, Methane): 1130 (M), 1088, 1052, 790. Anal. Calcd for $C_{60}H_{128}Si_{10}$: C, 63.83; H, 11.35. Found: C, 62.85; H, 11.24.

(8) G(3.5)Cl

A solution containing G(3)All 0.34 g (0.30 mmoles), $H_2PtCl_6 \cdot 6H_2O$ 50 μL (5 nmoles), $HSiMe_2Cl$ 0.13 mL (1.2 mmoles) and hexanes 15 mL was heated in an oil bath for 8 hours. Once the excess silane and solvent had been removed by vacuum a brown oil remained, yield 0.382 g (0.27 mmoles, 90%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.35 (m, 5H), 1.35 (m, 18H), 0.87 (m, 30H), 0.55 (m, 24H), 0.39 (s, 18H), -0.04 (s, 18H), -0.08 (s, 18H), -0.10 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 138.2, 134.0, 128.6, 127.6, 23.3, 22.5, 20.2, 20.0, 19.9, 19.4, 18.3, 18.2, 17.5, 17.3, 1.70, -3.29, -3.35. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 31.2 (Si-Cl), 1.12, 0.97 (Si-CH_3), -3.98 (Si-Ph). IR (Neat, KBr plates): 3060, 2920, 1250, 470 cm^{-1}.

(9) G(4)All

An excess solution of allylmagnesium bromide was added to G(3.5)Cl 0.382 g (0.27 mmoles) in 15 mL of Et_2O. After stirring overnight at rt an aqueous work-up followed, yielding a colourless oil as product 0.305 g (0.21 mmoles, 78%). ^{1}H-NMR ($CDCl_3$, 300

MHz): δ 7.45 (d, 3H), 7.33 (d, 2H), 5.75 (sep, 3H), 4.80 (m, 6H), 1.5 (d, 6H), 1.30 (m, 24H), 0.84 (m, 6H), 0.73 (m, 40H), -0.04 (s, 18H), -0.07 (s, 18H), -0.08 (s, 18H), -0.10 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 138.2, 135.3, 134.0, 128.6, 127.6, 112.5, 23.4, 20.3, 20.1, 20.0, 19.5, 18.5, 18.4, 18.3, 17.4, -3.2, -3.6. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.977 (Si-CH_3), 0.774 (Si-CH_3), -3.99 (Si-Ph). IR (Neat, KBr plates): 3060, 2910, 1625, 1245 cm^{-1}. Anal. Calcd for $C_{75}H_{164}Si_{13}$: C, 63.02; H, 11.54. Found: C, 62.94; H, 11.63.

(10) G(4.5)Cl

In a resealable tube G(4)All 0.158 g (0.11 mmoles), $H_2PtCl_6 \cdot 6H_2O$ 50 μL (5 nmoles), chlorodimethylsilane 50 μL (0.44 mmoles) and 15 mL of hexanes were heated for 6 hours. Once all the excess silane and solvent had been removed a dark brown oil was left, yield 0.19 g (0.11 mmoles, 100%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.38 (m, 5H), 1.35 (m, 36H), 0.90 (t, 16H), 0.55 (m, 44H), 0.38 (s, 18H), -0.06, -0.07, -0.08, -0.10 (s, 18H, 18H, 18H, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 138.2, 134.0, 128.6, 127.6, 31.6, 23.4, 20.3, 20.1, 20.0, 9.5, 18.5, 18.4, 17.7, 17.4, 1.82, -3.17, -3.24. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 31.2 (Si-Cl), 1.10, 0.94 (Si-CH_3), -4.0 (Si-Ph). IR (Neat, KBr plates): 3060, 2910, 1250, 470 cm^{-1}.

(11) G(5)All

The above compound was dissolved in 10 mL of Et_2O and a solution containing excess allylmagnesium bromide was added. This was stirred at rt overnight and after the work-up a colourless oil was obtained, yield 0.10 g (57.9 μmoles, 58%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.40 (m, 5H), 5.76 (m, 3H), 4.82 (m, 6H), 1.51 d, 6H), 1.34 (m, 42H), 0.83 (m, 6H), 0.53 (m, 42H), 0.06 (s, 18H), -0.03 (s, 18H), -0.08 (s, 36H), -0.09 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 138.2, 135.3, 134.0, 128.6, 127.6, 112.5, 23.4, 20.3, 20.1, 20.0, 19.5, 18.4, 18.3, 17.4, 1.02, -3.17, -3.62. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.98, 0.76, -3.98. IR (Neat, KBr plates): 3060, 2900, 1630, 1250 cm^{-1}. Anal. Calcd for $C_{90}H_{200}Si_{16}$: C, 62.42; H, 11.63. Found: C, 62.16; H, 11.59.

2B BRANCHING

$PhSi[(prSiMe)^{N}_{2}:X]_3$ G(N), X = Cl or All

(12) G(0.5)Cl

Phenyl triallylsilane (0.4 g, 1.75 mmoles) and $H_2PtCl_6 \cdot 6H_2O$ (0.5 mL, 50 nmoles) were added to a resealable tube in 15 mL of hexanes, to this dichloromethylsilane (1.1 mL, 10.5 mmoles) was carefully added and the tube sealed with a screw cap. The contents were heated at 120°C for 4 hours and then allowed to cool to room temperature. All volatiles were removed under vacuum yielding a slightly brown oil (0.93 g, 1.62 mmoles, 93%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.45, 7.33 (m, 5H), 1.60 (m, 6H), 1.20 (t, 6H), 0.95 (t, 6H), 0.73 (s, 9H). ^{13}C-NMR ($CDCl_3$, 300MHz): δ 136.0, 133.9, 129.2, 127.9, 25.7, 17.2, 15.7, 5.41. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 32.1 (Si-Cl), -3.59 (Ph-Si). IR (Neat, KBr plates): 3060, 2920, 1260, 535 and 470 cm^{-1}.

(13) G(1)All

To the above mentioned compound (0.93 g, 1.62 mmoles) dissolved in 20 mL of Et_2O a prepared solution of allylmagnesium bromide (20 mL, 20 mmoles) was added. This solution was stirred at room temperature overnight and quenched with a 10% solution of NH_4Cl (50 mL). After extracting with Et_2O (3 x 20 mL), drying with $MgSO_4$ and removal of all volatiles under vacuum a colourless oil was obtained, yield 0.713 g (1.18 mmoles, 73%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.45, 7.33 (m, 5H), 5.73 (m, 6H), 4.79 (m, 12H), 1.52 (m, 12H), 1.38 (m, 6H), 0.85 (t, 6H), 0.63 (t, 6H), -0.05 (s, 9H). ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 137.6, 134.7, 133.9, 128.7, 127.6, 113.0, 21.7, 18.2, 17.9, 17.3, -5.8. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.24 ($Si-CH_3$), -3.94 (Si-Ph). IR (Neat, KBr plates): 3060, 2910, 1625, 1250, 590 cm^{-1}. MS (CI, methane): 607 (M + 1), 591 (M - Me), 564 (M- allyl), 529 (M - Ph).

Anal. Calcd for $C_{35}H_{62}Si_4$: C, 71.29; H, 10.23. Found: C, 70.82; H, 9.85.

(14) G(1.5)Cl

G(1)Cl (0.595 g, 0.98 mmoles) and $H_2PtCl_6 \cdot 6H_2O$ (0.5 mL, 50 nmoles) were added to a resealable tube in 15 mL of hexanes. Dichloromethylsilane (1.23 mL, 11.8 mmoles) was carefully added and the tube sealed with a screw cap. This solution was heated at 120°C for 12 hours and then allowed to cool to room temperature. All remaining volatiles were removed under vacuum to give a viscous brown oil, yield 1.14 g (0.88 mmoles, 89%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.45, 7.33 (m, 5H), 1.60 (m, 18H), 1.20 (m, 18H), 0.95 (m, 18H), 0.75 (s, 18H), 0.60 (s, 9H). ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 136.0, 133.9, 129.2, 127.9, 25.7, 22.7, 17.2, 16.9, 15.7, 15.5, 5.44, -5.17. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 32.2 (Si-Cl), 1.51 (Si-CH_3), -3.98 (Si-Ph). IR (Neat, KBr plates): 3060, 2920, 1260, 530, 470 cm^{-1}.

(15) G(2)All

G(1.5)Cl (1.14 g, 0.88 mmoles) was dissolved in Et_2O (20 mL) and stirred at room temperature whilst a prepared solution of allylmagnesium bromide (20 mL, 20 mmoles) was added. This mixture was stirred at rt overnight and then quenched with a 10% solution of NH_4Cl (50 mL). After extracting with Et_2O (3 x 25 mL), drying with $MgSO_4$ and removal of residual volatiles under vacuum, a pale yellow oil was obtained, yield 0.666 g (0.49 mmoles, 50%). This was further purified *via* flash column chromatography, 60Å silica gel as stationary phase and hexanes/ethyl acetate (2%) as the mobile phase, yield 0.405 g (0.30 mmoles, 31%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.45, 7.33 (m, 5H), 5.75 (m, 12H), 4.82 (m, 24H), 1.52 (m, 24H), 1.30 (m, 18H), 0.83 (m, 18H), 0.55 (m, 18H), -0.04 (s, 18H), -0.12 (s, 9H). ^{13}C-NMR ($CDCl_3$, 300MHz): δ 138.1, 133.9, 128.6, 127.6, 134.8, 113.0, 21.4, 18.9, 18.7, 18.5, 18.2, 17.9, 17.5, -5.0, -5.8. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): 1.01, 0.93 (Si-CH_3 interior), 0.26 (Si-CH_3 exterior), -4.06 (Si-PH). IR (Neat, KBr plates): 3060, 2910, 1630,

1250, 590 cm^{-1}. MS (EI): 1321, 1280, 1244, 1203. Anal. Calcd for $C_{78}H_{146}Si_{10}$: C, 68.72; H, 10.72. Found: C, 68.99; H, 10.68.

(16) G(2.5)Cl

G(2)All, 92 mg (67.5 μmoles), together with dichloromethylsilane (0.2 mL, 1.62 mmoles) and $H_2PtCl_6 \cdot 6H_2O$ (50 μL, 5 nmoles) were placed into a resealable tube in 15 mL of hexanes. After 18 hours all the residual volatiles were removed to give a dark brown oil, yield 0.150 g (54.7 μmoles, 81%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.45, 7.33 (m, 5H), 1.60 (m, 72H), 1.20- 0.95 (m, 126H), 0.75 (s, 36H), 0.10--0.21 (s, 27H). ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 134.0, 129.2, 127.9, 25.9, 19.0, 18.8, 18.6, 18.4, 17.7, 17.5, 17.3, 16.5, 5.44, -5.01, -5.13. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 32.2 (Si-Cl), 1.51 (Si-CH_3), -3.98 (Si-Ph). IR (Neat, KBr plates): 3060, 2920, 1260, 530, 470 cm^{-1}.

(17) G(3)All

To a round-bottomed flask containing an excess solution of allylmagnesium bromide in Et_2O, G(2.5)Cl (0.150 g, 54.7 μmoles) in 20 mL of Et_2O was added. This was stirred overnight at rt and followed by the usual work-up producing a pale yellow oil, yield 0.154 g (53.4 μmoles, 98%). This was purified by flash column chromatography which led to a colourless oil being isolated, 96 mg (33.4 μmoles, 61%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.45, 7.33 (m, 5H), 5.75 (m, 24H), 4.82 (m, 48H), 1.52 (m, 48H), 1.30 (m, 45H), 0.83 (m, 14H), 0.55 (m, 70H), -0.04 (s, 36H), -0.10 (s, 18H), -0.12 (s, 9H). ^{13}C-NMR ($CDCl_3$, 300MHz): δ 134.8, 134.0, 128.6, 127.6, 113.0, 21.5, 18.9-17.5, -4.98, -5.33, -5.74. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.99, 0.73, 0.26, -3.98. IR (Neat, KBr plates): 3060, 2910, 1630, 1250, 590 cm^{-1}.

(18) G(3.5)Cl

G(3)All (0.222 g, 77 μmoles) was dissolved into 15 mL of hexanes and to this $HSiMeCl_2$ (0.38 mL, 3.7 mmoles) and $H_2PtCl_6 \cdot 6H_2O$ (50 μL, 5 nmoles) were added. The contents of

the tube were heated at 120°C for 20 hours after which time the residual volatiles were removed, yield 0.41 g (73 μmoles, 95%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.45, 7.33 (m, 5H), 1.60 (m, 144H), 1.20- 0.95 (m, 126H), 0.75 (s, 72H), 0.10--0.21 (s, 63H). ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 134.0, 129.2, 127.9, 25.9, 19.0, 18.8, 18.6, 18.4, 17.7, 17.5, 17.3, 16.5, 5.44, -5.01, -5.13. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 32.2 (Si-Cl), 1.51, 0.98 (Si-CH_3), -3.98 (Si-Ph). IR (Neat, KBr plates): 3060, 2920, 1260, 530, 470 cm^{-1}.

(19) G(4)All

G(3.5)Cl (0.41 g, 77 μmoles) was added to an excess solution of allylmagnesium bromide in Et_2O and stirred at rt overnight. After the aqueous work-up a pale yellow oil was isolated, yield 0.43 g (73 μmoles, 100%). This was purified by flash column chromatography using hexanes/ethyl acetate (2%) to give a colourless oil as the only product, yield 0.29 g (49.2 μmoles, 67%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.45, 7.33 (m, 5H), 5.75 (m, 48H), 4.82 (m, 96H), 1.52 (m, 96H), 1.30 (m, 126H), 0.83 (m, 42H), 0.55 (m, 144H), -0.04 (s, 72H), -0.10 (s, 36H), -0.12 (s, 27H). ^{13}C-NMR ($CDCl_3$, 300MHz): δ 134.8, 134.0, 128.6, 127.6, 113.0, 21.5, 18.9-17.5, -4.98, -5.33, -5.74. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.99, 0.73, 0.26, -3.98. IR (Neat, KBr plates): 3060, 2910, 1630, 1250, 590 cm^{-1}.

3B BRANCHING

$PhSi[(prSi)^{N}_3:X]_3$ G(N), X = Cl, All

(20) G(0.5)Cl

Phenyl triallylsilane 11.4 g (50 mmoles) was dissolved in 30 mL of THF together with $H_2PtCl_6 \cdot 6H_2O$ (500 μL, 50 nmoles) and trichlorosilane, $HSiCl_3$, 30.3 mL (41 g, 0.30 moles). This mixture was heated at 120°C for 5 hours and then all residual volatiles were removed to give 31.07 g (49 mmoles, 98%) of a brown oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.5-7.3

(m, 5H), 1.1-0.4 (m, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 133.8, 129.3, 127.8, 28.2, 23.8, 18.9, 17.5, 17.2, 17.0, 16.0, 15.2. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 11.9, 11.2, -3.50. IR (Neat, KBr plates): 3060, 2090, 1250, 570, 460 cm^{-1}.

(21) G(1)All

The oil from above, G(0.5)Cl (31.07 g, 49 mmoles), was dissolved in 60 mL of Et_2O and slowly dropped into an ether solution containing excess allylmagnesium bromide. The reaction was refluxed overnight and after the aqueous work-up a very pale yellow oil was isolated as pure G(1), yield 26.82 g (39.2 mmoles, 80%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.5-7.3 (m, 5H), 5.74 (m, 9H), 4.84 (m, 18H), 1.53 (d, 18H), 1.4-0.4 (m, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 134.7, 133.8, 129.4, 127.8, 113.0, 20.7, 19.6, 18.6-16.5. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -1.10, -4.00. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (CI, Methane): 684 (M + 1), 647, 607. Anal. Calcd for $C_{42}H_{68}Si_4$: C, 73.68; H, 9.94. Found: C, 74.30; H, 10.00.

(22) G(1.5)

Into a resealable tube G(1)All (1.368 g, 2.0 mmoles), $H_2PtCl_6 \cdot 6H_2O$ (50 μL, 5 nmoles), 20 mL of THF and 3.6 mL (4.87 g, 36 mmoles) $HSiCl_3$ were added. This was heated for 10 hours at 120°C. Removal of solvent and excess $HSiCl_3$ yielded a brown oil 3.618 g (1.90 mmoles, 95%) of G(1.5). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.5-7.3 (m, 5H), 1.1-0.4 (m, 72H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 133.8, 129.3, 127.8, 24.8, 21.8, 18.8-17.6. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 0.98, -4.00. IR (Neat, KBr plates): 3060, 2090, 1250, 570, 460 cm^{-1}.

(23) G(2)All

Using standard procedure for reacting the chlorosilane end groups, G(1.5)Cl (3.618 g, 1.90 mmoles) was dissolved into 60 mL of Et_2O and slowly added to a solution of allylmagnesium bromide (0.26 moles). This solution was refluxed for 48 hours and

following a work-up yielded 3.324 g of G(2) (1.62 mmoles, 85%) which was further purified by flash column chromatography, hexanes/ethyl acetate (2%). Yield 3.04 g (1.48 mmoles, 91%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.5-7.3 (m, 5H), 5.74 (m, 27H), 4.84 (m, 54H), 1.53 (d, 54H), 1.4-0.4 (m, 72H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 134.7, 133.8, 129.4, 127.8, 113.0, 21.4, 20.2, 19.5,19.3-17.4. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -0.37, -1.10, -4.00. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (EI): 1970 (M - 2 Allyl), 1893. Anal. Calcd for $C_{123}H_{212}Si_{13}$: C, 71.93; H, 10.33. Found: C, 72.42; H, 10.30.

(24) G(2.5)Cl

G(2)All (0.410 g, 0.2 mmoles) was added to a resealable tube in 10 mL of hexanes together with 100 μL of $H_2PtCl_6 \cdot 6H_2O$ (10 nmoles) and 1.1 mL of $HSiCl_3$ (1.46 g, 1.8 mmoles). This was heated at 120°C for 48 hours after which time all the excess silane and solvent were removed under vacuum to give 0.914 g (0.16 mmoles, 80%) of a brown oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.5-7.3 (m, 5H), 1.1-0.4 (m, 230H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 133.8, 129.3, 127.8, 24.8, 21.8-17.6. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 0.98, 0.04, -4.00. IR (Neat, KBr plates): 3060, 2090, 1250, 570, 460 cm^{-1}.

(25) G(3)All

The chlorosilane terminated dendrimer G(2.5)Cl (0.914 g, 0.16 mmoles) was dissolved into 40 mL of Et_2O and added to a solution of allylmagnesium bromide (0.16 moles) in Et_2O. After a 48 hour reflux and aqueous work-up procedure a pale yellow oil identified as G(3) was isolated. Yield after flash column chromatography, hexanes/ethyl actetate (2%), 0.748 g (0.12 mmoles, 76%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.5-7.3 (m, 5H), 5.74 (m, 81H), 4.84 (m, 162H), 1.53 (d, 162H), 1.4-0.4 (m, 215H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 134.7, 133.8, 129.4, 127.8, 113.0, 21.4, 20.2, 19.5-17.4. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.14, -0.37, -1.10, -4.00. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. Anal. Calcd for $C_{366}H_{644}Si_{40}$: C, 71.34; H, 10.46. Found: C, 62.80; H, 10.48.

(26) G(3.5)Cl

Trichlorosilane 1.63 mL (2.19 g, 16.0 mmoles) was added to a solution of 0.615 g G(3) (100 μmoles) and $H_2PtCl_6 \cdot 6H_2O$ (100 μL, 10 nmoles) dissolved in 10 mL of hexanes. After being heated for 48 hours at 120°C and other volatile material removed a dark brown oil was formed, yield 1.15 g (67 μmoles, 67%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.5-7.3 (m, 5H), 1.1-0.4 (m, 700H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 133.8, 129.3, 127.8, 24.8, 21.8-17.6. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 0.98, 0.04, -0.40, -4.00. IR (Neat, KBr plates): 3060, 2090, 1250, 570, 460 cm^{-1}.

(27) G(4)All

G(3.5)Cl (1.15 g, 67 μmoles) was dissolved in 50 mL Et_2O and added to a solution containing excess allylmagnesium bromide. This was refluxed for 36 hours and then the aqueous extraction was performed with hexanes (3 x 40 mL). The yield of crude product was found to be 1.24 g (67 μmoles, 100%) which was further purified by flash column chromatography, yield 1.04 g (56 μmoles, 83%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.5-7.3 (m, 5H), 5.74 (m, 243H), 4.84 (m, 480H), 1.53 (d, 480H), 1.4-0.4 (m, 700H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 134.7, 133.8, 129.4, 127.8, 113.0, 21.4, 20.2, 19.5-17.4. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.77, 0.14, -0.40, -1.10, -4.00 (very weak). IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

(28) G(4.5)Cl

G(4)All 0.36 g (19.5 μmoles) was dissolved into 5 mL of hexanes together with 200 μL (20 nmoles) of $H_2PtCl_6 \cdot 6H_2O$ and 0.96 mL (1.28 g, 9.5 mmoles) of $HSiCl_3$. This was heated for 60 hours and a brown oil was isolated as product, yield 0.80 g (15.6 μmoles, 80%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.5-7.3 (m, 5H), 1.1-0.4 (m, ?H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 133.8, 129.3, 127.8, 24.8, 21.8-17.6. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 0.98, 0.04, -0.40. IR (Neat, KBr plates): 3060, 2090, 1250, 570, 460 cm^{-1}.

(29) G(5)All

To an excess of allylmagnesium bromide solution in Et_2O (0.15 moles) a solution of G(4.5)Cl (0.80 g, 15.6 μmoles) in 30 mL of Et_2O was added. This was refluxed for 60 hours and following the extraction procedure a yellow oil was isolated, yield 0.45 g (8.1 μmoles, 52%), no attempt was made to further purify this material. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.5-7.3 (m, 5H), 5.74 (m, 729H), 4.84 (m, 1300H), 1.53 (d, 1300H), 1.4-0.4 (m, ?H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 134.7, 133.8, 129.4, 127.8, 113.0, 21.4, 20.2, 19.5-17.4. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.77, 0.14, -0.37, -0.40, -1.10. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

DIALLYLDIPHENYLSILANE BASED DENDRIMERS

$Ph_2Si[(prSi)^N{}_3{:}X]_2$ G(N), X = Cl, All

(31) G(0.5)Cl

Diallyldiphenylsilane **(30)** 0.663 g (2.5 mmoles) in 15 mL of hexanes was added to a resealable tube together with $H_2PtCl_6{\cdot}6H_2O$ 50 μL (5 nmoles) and trichlorosilane 1.01 mL (10 mmoles). This mixture was heated in an oil bath at 120°C for 8 hours and the residual volatiles were removed. A dark brown oil was isolated as product, yield 1.19 g (2.22 mmoles, 89%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.8-7.4 (m, 10H), 1.9-1.3 (m, 12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.8, 134.3, 129.6, 128.1, 28.2, 17.2, 15.5. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.15 (Si-Cl), -7.81 (Si-Ph). IR (Neat, KBr plates): 3060, 2920, 1250, 570, 460 cm^{-1}.

(32) G(1)All

G(0.5)Cl 1.19 g (2.22 mmoles) was dissolved into 30 mL of Et_2O and slowly added to a solution containing an excess of allylmagnesium bromide. This was stirred at reflux for 12

hours and then followed by an aqueous work-up. A yellow oil was isolated, yield 1.03 g (1.81 mmoles, 72%). This was then further purified by flash column chromatography and a colourless oil was isolated, yield 0.670 g (1.18 mmoles, 47%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.6-7.3 (m, 10H), 5.80 (s, 6H), 4.85 (m, 12H), 1.50 (m, 12H), 1.4-0.4 (m, 12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.0, 134.8, 134.4, 129.3, 127.8, 113.5, 19.6, 18.1, 17.5, 16.4. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 1.09, -7.91. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (CI, Methane): 568 (M + 1), 527, 491, 486.

GERMANIUM BASED DENDRIMERS

TETRAALLYLGERMANE BASED DENDRIMERS

1B BRANCHING

$Ge[(prSiMe_2)^{N}_{1}:X]_4$ G(N), x = Cl, All

(35) G(0.5)Cl

Tetraallylgermane (32) (1.097 g, 4.63 mmoles) and chloroplatinic acid hexahydrate, $H_2PtCl_6 \cdot 6H_2O$, (0.2 mL, 20 nmoles) were added to a resealable tube in 15 mL of hexanes. Chlorodimethylsilane (2.6 mL, 23 mmoles) was added carefully and the tube sealed with a screw cap. This mixture was heated at 120°C for 2 hours and allowed to cool to rt. The solution was transferred into a preweighed round bottom flask by syringe, followed by removal of all residual volatiles under vacuum giving a brown oil, yield 2.33 g (3.8 mmoles, 82%). ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.50, 1.25, 0.85 (m, 24H), 0.38 (s, 24H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 23.4, 19.0, 16.8, 1.8. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 31.2. IR (Neat, KBr plates): 2920, 1250, 465 cm^{-1}.

(36) G(1)Cl

A prepared solution of allylmagnesium bromide (40 mL, 30 mmoles) was added to G(0.5)Cl (2.33 g, 3.8 mmoles) dissolved in 25 mL Et_2O. This mixture was stirred overnight and then quenched with 10% NH_4Cl (50 mL). The aqueous layer was extracted 3 times with Et_2O (25 mL), dried over anhydrous $MgSO_4$ and solvent removed by rotary evaporator to yield 1.943 g (3.05 mmoles, 80%) of a colourless oil. ^{1}H-NMR ($CDCl_3$, 75.47 MHz): δ 5.75 (m, 4H), 4.80 (m, 8H), 1.50 (d, 8H), 1.37 (m, 8H), 0.70 (m, 8H), 0.56 (t, 8H), -0.06 (s, 24H). ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 135.3, 112.6, 23.3, 19.8, 19.6, 17.6, -3.6. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.72. IR (Neat, KBr plates): 3035, 2920, 1630, 1250 cm^{-1}. MS (EI) 637 (M), 581, 497, 397, 357, 297. Anal. Calcd for $C_{32}H_{68}Si_4Ge$: C, 60.26; H, 10.74. Found: C, 58.75; H, 10.52.

(37) G(1.5)Cl

In a preparation analogous to that for G(0.5), G(1)All (1.18 g, 1.85 mmoles), $H_2PtCl_6 \cdot 6H_2O$ (0.2 mL, 20 nmoles) and $HSiMe_2Cl$ (1.03 mL, 9.3 mmoles) were heated at 120°C for 3 hours. After removal of all residual volatiles a brown oil was obtained, yield 1.78 g (1.75 mmoles, 95%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.40 (m, 16H), 0.86 (t, 8H), 0.75 (m, 8H), 0.55 (m, 16H), 0.38 (s, 24H), -0.06 (s, 24H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 23.4, 20.0, 19.9, 19.5, 17.8, 17.7, 1.8, -3.2. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 31.31, 1.10. IR (Neat, KBr plates): 2920, 1250, 470 cm^{-1}.

(38) G(2)All

In an identical preparation to G(1), 1.78 g G(1.5)Cl (1.75 mmoles) was stirred overnight with an excess of allylmagnesium bromide in Et_2O. After work-up the yield was 1.53 g (1.47 mmoles, 84%) of a yellow oil. Flash chromatography (60Å silica gel, hexanes/EtOAc (2%)) of this product yielded 1.34 g (1.29 mmoles, 74%) of a colourless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 4H), 4.80 (m, 8H), 1.48 (d, 8H), 1.32 (m, 16H), 0.74 (t, 8H), 0.55 (m, 24H), -0.04 (s, 24H), -0.07 (s, 24H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 112.5, 23.4, 20.1, 20.0, 19.9, 19.5, 18.3, 17.8, -3.2, -3.6. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.97, 0.76.

IR (Neat, KBr plates): 3065, 2920, 1630, 1250 cm^{-1}. MS (EI): 1022 (M -Me), 997 (M - allyl), 797, 558, 458. Anal. Calcd for $C_{52}H_{116}Si_8Ge$: C, 60.13; H, 11.25. Found: C, 60.24; H, 11.15.

(39) G(2.5)Cl

G(2)All (1.16 g, 1.18 mmoles), $H_2PtCl_6 \cdot 6H_2O$ (0.2 mL, 20 nmoles) and $HSiMe_2Cl$ (0.5 mL, 4.5 mmoles) were added together and the mixture heated for 4 hours. Yield 1.49 g (1.05 mmoles, 89%) of a brown oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.36 (m, 24H), 0.86 (t, 8H), 0.72 (dt, 8H), 0.55 (m, 32H), 0.38 (s 24H), -0.06 (s, 24H), -0.07 (s, 24H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 23.4, 20.2, 20.1, 20.0, 19.9, 19.5, 18.4, 17.7, 1.82, -3.17, -3.22. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 31.2, 1.10, 0.93. IR (Neat, KBr plates): 2910, 1250, 470 cm^{-1}.

(40) G(3)All

G(2.5)Cl (1.49 g, 1.05 mmoles) and excess allylmagnesium bromide were stirred at rt overnight in Et_2O (50 mL). After an aqueous work-up a yellow oil was obtained, yield 1.187 g (0.82 mmoles, 78%). Flash chromatography produced a colourless oil, yield 1.017 g (0.7 mmoles, 67%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.74 (m, 4H), 4.82 (m, 8H), 1.49 (dt, 8H), 1.32 (m, 24H), 0.74 (t, 8H), 0.53 (m, 40H), -0.03 (s, 24H), -0.07 (s, 48H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 112.5, 23.4, 20.2, 20.1, 20.0, 19.9, 19.6, 18.4, 18.3, 17.8, -3.2, -3.6. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): 0.96, 0.75. IR (Neat, KBr plates): 3060, 2900, 1625, 1240 cm^{-1}. MS (EI): 1422 (M - Me), 1398 (M - allyl), 1097, 1055, 997, 898, 798, 757, 657, 517, 417.

(41) G(3.5)Cl

The same procedure as previously mentioned was used. G(3)All (0.692 g, 0.48 mmoles), $H_2PtCl_6 \cdot 6H_2O$ (0.1 mL, 10 nmoles) and $HSiMe_2Cl$ (0.26 mL, 2.4 mmoles) were heated together for 6 hours. After work-up a brown oil was isolated, yield 0.83 g (0.45 mmoles, 95%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.34 (M, 32H), 0.87 (t, 8H), 0.72 (t, 8H), 0.54 (m,

48H), 0.38 (s, 24H), -0.05 (s, 24H), -0.07 (s, 48H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 23.4, 20.1, 19.9, 19.5, 18.4, 17.8, 17.7, 1.83, -3.2, -3.3. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 31.2, 1.10, 0.93. IR (Neat, KBr): 3060, 2900, 1250, 470 cm^{-1}.

(42) G(4)All

G(3.5)Cl (0.83 g, 0.45 mmoles) was stirred with an excess of allylmagnesium bromide in Et_2O for 12 hours. After the aqueous work-up a dark yellow oil was obtained, yield 0.546 g (0.297 mmoles, 66%). Following flash chromatography a colourless oil was isolated, yield 0.54 g (0.294 mmoles, 65%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 4H), 4.80 (m, 8H), 1.50 (dt, 8H), 1.31 (m, 32H), 0.73 (t, 8H), 0.52 (m, 56H), -0.04 (s, 24H), -0.07 (s, 72H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 112.5, 23.4, 20.2, 20.1, 20.1, 19.9, 19.5, 18.4, 18.3, 17.8, -3.17, -3.63. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.97, 0.76. IR (Neat, KBr plates): 3060, 2910, 1630, 1250 cm^{-1}. MS (EI): 958, 858.

(43)G(4.5)Cl

G(4)All (0.234 g, 0.13 mmoles), $H_2PtCl_6{\cdot}6H_2O$ (0.1 mL, 10 nmoles) and $HSiMe_2Cl$ (0.07 mL, 0.6 mmoles) were heated together for 6 hours. After residual volatiles were removed a brown oil was isolated, yield 0.28 g (0.126 mmoles, 97%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.30 (m, 36H), 0.86 (t, 8H), 0.72 (t, 8H), 0.51 (m, 68H), 0.36 (s, 24H), -0.04 (s, 24H), -0.07 (s, 72H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 23.4, 20.1, 20.0, 19.9, 19.5, 18.4, 17.8, 17.7, 1.8, -3.17, -3.23. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 31.2, 1.10, 0.93. IR (Neat, KBr plates): 3060, 2920, 1250, 470 cm^{-1}.

(44) G(5)All

G(4.5)Cl (0.28 g, 0.126 mmoles) was stirred with excess allylmagnesium bromide in Et_2O for 12 hours. After the work-up a dark yellow oil was obtained 0.130 g (0.06 mmoles, 48%). No attempt to further purify this compound was attempted. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.85 (m, 4H), 4.80 (m, 8H), 1.50 (dt, 8H), 1.30 (m, 40H), 0.73 (t, 8H), 0.51 (m, 72H), -0.04 (s, 24H), -0.08 (s, 96H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 112.5, 23.4, 20.1,

20.0, 19.9, 19.5, 18.4, 18.3, 17.8, -3.17, -3.63. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.95, 0.73. IR (Neat, KBr plates): 3060, 2900, 1625, 1240 cm^{-1}. MS (EI): 1698, 1159, 1058, 958, 858, 758.

2B BRANCHING

$Ge[(prSiMe)^N_2{:}X]_4$ G(N), X = Cl, All

(46) G(0.5)Cl

Tetraallylgermane **(32)** 0.477 g (2.01 mmoles), $H_2PtCl_6{\cdot}6H_2O$ (0.1 mL, 10nmoles) and dichloromethylsilane, $HSiMeCl_2$, 1.05 mL (1.16 g, 10 mmoles) were heated at 120°C in 15 mL of hexanes for 6 hours. After removal of all remaining volatiles a brown oil was produced, yield 1.05 g (1.5 mmoles, 75%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.8-1.1 (m, 24H), 0.75 (s, 12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 24.8, 21.8, 17.6, 5.3. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 31.6. IR (Neat, KBr plates): 2920, 1260, 530, 465 cm^{-1}.

(47) G(1)All

G(0.5)Cl 0.522 g (0.75 mmoles) dissolved in 20 mL of Et_2O was stirred overnight with excess allylmagnesium bromide solution (30 mL, 48 mmoles). After the aqueous work-up the crude yield was 0.459 g (0.62 mmoles, 82%). Flash chromatography of this material gave pure G(1) as a colourless oil, 0.158 g (0.21 mmoles, 28%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (s, 8H), 4.80 (m, 16H), 1.50 (m, 16H), 1.47-0.45 (m, 24H), -0.03 (s, 12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.7, 113.0, 21.4, 20.2, 19.5, 17.4, -5.76. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.23. IR (Neat, KBr plates): 3060, 2920, 1625, 1250 cm^{-1}. Anal. Calcd for $C_{40}H_{76}Si_4Ge$: C, 64.78; H, 10.27. Found: C, 62.44; H, 9.25.

(48) G(1.5)Cl

G(1)All 0.123 g (0.17 mmoles), $H_2PtCl_6{\cdot}6H_2O$ (0.05 mL, 5 nmoles), and $HSiMeCl_2$ 0.26 mL

(0.28 g, 2.5 mmoles) dissolved in hexanes, were heated in a resealable tube at 120°C for 12 hours. Removal of residuals left a brown oil, 0.24 g (0.14 mmoles, 87%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.53 (m, 16H), 1.20 (m, 32H), 0.93 (m, 16H), 0.75 (s, 24H), 0.60 (m, 16H), 0.42 (m, 16H), -0.035 (s, 12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 24.8, 22.8, 20.8, 18.8, 17.6, 16.5, 5.46, -5.21. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 32.2, 1.73. IR (Neat, KBr plates): 2920, 1255, 530, 465 cm^{-1}.

(49) G(2)All

G(1.5)Cl 0.24g (0.14 mmoles) in 10 mL of Et_2O was stirred overnight with excess allylmagnesium bromide. Crude yield from reaction was 0.205 g (0.12 mmoles, 81%). Flash chromatography gave pure G(2) in a yield of 91 mg (52 μmoles, 36%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (s, 16H), 4.80 (m, 32H), 1.50 (m, 32H), 1.47-0.45 (m, 72H), -0.03 (s, 24H), -0.06 (s, 12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.7, 113.0, 21.4, 20.6, 20.2, 20.0, 19.5, 18.4, 17.4, -5.34, -5.76. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.72, 0.24. IR (Neat, KBr plates): 3060, 2920, 1625, 1250 cm^{-1}. Anal. Calcd for $C_{96}H_{188}Si_{12}Ge$: C, 65.87; H,10.75. Found: C, ; H, .

(50) G(2.5)Cl

G(2)All 91 mg (52 μmoles) in 10 mL of hexanes was heated at 120°C together with $H_2PtCl_6 \cdot 6H_2O$ 50 μL (5 nmoles), and $HSiMeCl_2$ 0.13 mL (0.14 g, 1.24 mmole). After 16 hours the remaining volatiles were removed and a brown oil was recovered, yield 0.180 g (50 μmoles, 96%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.5-0.8 (m, 136H), 0.75 (s, 48H), 0.6 (m, 32H), -0.03 (s, 36H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 24.5-17.2, 5.50, -5.20. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 32.2, 1.73, 1.54. IR (Neat, KBr plates): 2920, 1250, 530, 465 cm^{-1}.

(51) G(3)All

G(2.5)Cl 0.180 g (50 μmoles) was stirred overnight in 10 mL of Et_2O and excess allylmagnesium bromide (3.2 mmoles, 2 mL). Recovery of crude product gave 0.161 g (43 μmoles, 83%) and column chromatography gave 0.108 g (28 μmoles, 38%). ^{1}H-NMR

($CDCl_3$, 300 MHz): δ 5.75 (s, 32H), 4.80 (m, 64H), 1.50 (m, 64H), 1.47-0.45 (m, 168H), -0.03 (s, 48H), -0.06 (s, 24H), -0.09 (s, 12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 135.3, 113.0, 21.4-17.3, -4.64, -5.34, -5.78. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 1.02, 0.73, 0.28. IR (Neat, KBr plates): 3060, 2920, 1625, 1250 cm^{-1}.

3B BRANCHING

$Ge[(prSi)^N_3:X]_4$ G(N), X = Cl, All

(64) G(0.5)Cl

Tetraallylgermane 1 g (4.2 mmoles) was dissolved in 10 mL of THF together with $H_2PtCl_6 \cdot 6H_2O$ (50 μL, 5 nmoles) and trichlorosilane, $HSiCl_3$, 2.13 mL (2.86 g, 21 mmoles). This mixture was heated at 120°C for 5 hours and then all residual volatiles were removed to give 2.89 g (3.71 mmoles, 88%) of a brown oil. ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 1.8-1.1 (m, 24H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 24.8, 21.8, 17.6. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0. IR (Neat, KBr plates): 2090, 1250, 570, 460 cm^{-1}.

(65) G(1)All

The oil from above, G(0.5)Cl (2.89 g, 3.71 mmoles), was dissolved in 60 mL of Et_2O and slowly dropped into an ether solution of excess allylmagnesium bromide. The reaction was refluxed overnight and after the aqueous work-up a very pale yellow oil was isolated as pure G(1), yield 2.46 g (2.91 mmoles, 78%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.74 (m, 12H), 4.84 (m, 24H), 1.53 (d, 24H), 1.4-0.4 (m, 24H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.7, 113.0, 21.4, 20.2, 19.5, 17.4. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -1.10. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

(66) G(1.5)Cl

Into a resealable tube G(1)All (2 g, 2.37 mmoles), $H_2PtCl_6 \cdot 6H_2O$ (50 μL, 5 nmoles), 20 mL

of THF and 6 mL (8.05 g, 59 mmoles) $HSiCl_3$ were added. This was heated for 10 hours at 120°C. Removal of solvent and excess $HSiCl_3$ yielded a brown oil 4.25 g (1.72 mmoles, 72%) of G(1.5). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 1.8-1.1 (m, 96H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 24.8, 21.8, 17.6, 17.5-15.8. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 1.60. IR (Neat, KBr plates): 2090, 1250, 570, 460 cm^{-1}.

(67) G(2)All

Using standard procedure for reacting the chlorosilane end groups, G(1.5)Cl (4 g, 1.62 mmoles) was dissolved into 60 mL of Et_2O and slowly added to a solution of allylmagnesium bromide (0.146 moles). This solution was refluxed for 48 hours and following a work-up yielded 3.79 g of pure G(2) (1.42 mmoles, 82%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.74 (m, 36H), 4.84 (m, 72H), 1.53 (d, 72H), 1.4-0.4 (m, 96H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.7, 113.0, 21.4, 20.2, 19.5, 19.3, 18.6, 18.2, 17.5. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -0.37, -1.10. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

(68) G(2.5)Cl

G(2)All (0.31 g, 0.12 mmoles) was added to a resealable tube in 10 mL of THF together with 100 μL of $H_2PtCl_6 \cdot 6H_2O$ (10 nmoles) and 2 mL of $HSiCl_3$ (2.68 g, 19.8 mmoles). This was heated at 120°C for 48 hours after which time all the excess silane and solvent were removed under vacuum to give 0.79 g (0.1 mmoles, 83%) of a brown oil. ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 1.8-1.1 (m, 312H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 24.8, 21.8, 19.8-16.3. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 1.60, 0.84. IR (Neat, KBr plates): 2090, 1250, 570, 460 cm^{-1}.

(69) G(3)All

G(2.5)Cl (0.79 g, 0.1 mmoles) was dissolved into 40 mL of Et_2O and added to a solution of allylmagnesium bromide (0.196 moles) in Et_2O. After a 48 hour reflux and aqueous work-up procedure a pale yellow oil identified as pure G(3) was isolated. Yield 0.802 g (0.98

mmoles, 98%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.74 (m, 108H), 4.84 (m, 216H), 1.53 (d, 216H), 1.4-0.4 (m, 312H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.7, 113.0, 21.4, 20.2, 19.5, 19.2-17.5. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -0.37, -0.42, -1.10. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

(70) G(3.5)Cl

Trichlorosilane 2 mL (2.68 g, 19.8 mmoles) was added to a solution of 0.351 g G(3)All (43 μmoles) and $H_2PtCl_6 \cdot 6H_2O$ (100 μL, 10 nmoles) dissolved in 10 mL of hexanes. After being heated for 48 hours at 120°C and other volatile material removed a dark brown oil was formed, yield 0.67 g (29 μmoles, 67%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 1.8-1.1 (m, 960H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 24.8, 21.8, 19.8-16.3. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 1.60, 0.84. IR (Neat, KBr plates): 2090, 1250, 570, 460 cm^{-1}.

(71) G(4)All

G(3.5)Cl (0.67 g, 29 μmoles) was dissolved in 50 mL Et_2O and added to a solution containing excess allylmagnesium bromide. This was refluxed for 36 hours and then the aqueous extraction was performed with hexanes (3 x 40 mL). The yield of crude product was found to be 0.49 g (20 μmoles, 69%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.74 (m, 324H), 4.84 (m, 648H), 1.53 (d, 648H), 1.4-0.4 (m, 960H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.7, 113.0, 21.4, 20.2, 19.5, 19.2-17.5. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.14, -0.37, -0.42, -1.10. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

(72) G(4.5)Cl

G(4)All 0.48 g (19.5 μmoles) was dissolved into 5 mL of hexanes together with 200 μL (20 nmoles) of $H_2PtCl_6 \cdot 6H_2O$ and 4 mL (5.37 g, 39 mmoles) of $HSiCl_3$. This was heated for 60 hours and a brown oil was isolated as product, yield 0.61 g (9.4 μmoles, 48%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 1.8-1.1 (m, 2900H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 24.8, 21.8, 19.8-16.3. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 1.60, 0.78. IR (Neat, KBr plates): 2090,

1250, 570, 460 cm^{-1}.

(73) G(5)All

To an excess of allylmagnesium bromide solution in Et_2O (0.15 moles) a solution of G(4.5)Cl (0.61 g, 9.4 μmoles) in 30 mL of Et_2O was added. This was refluxed for 60 hours and following the extraction procedure a yellow oil was isolated, yield 0.45 g (6.1 μmoles, 65%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.74 (m, 972H), 4.84 (m, 1944H), 1.53 (d, 1944H), 1.4-0.4 (m, 2824H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.7, 113.0, 21.4, 20.2, 19.5, 19.2-17.4. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.77, 0.14, -0.37, -0.42, -1.10. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

HEXAVINYLDIGERMANE BASED DENDRIMERS

2B BRANCHING

$Ge_2[(etSiMe)^N{}_2:(prSiMe)^N{}_2:X]_6$ G(N), X = Cl, All

(52) G(0.5)Cl

Hexavinyldigermane (34) 0.924 g (3 mmoles) in 10 mL of hexanes and 100 μL of $H_2PtCl_6 \cdot 6H_2O$ (10 nmoles) were added to a resealable tube. To this $HSiMeCl_2$ (3.75 mL, 36 mmoles) was carefully added and the contents were heated for 4 hours. Removal of all volitile materials left behind a brown oil, 2.36 g (2.36 mmoles, 79%) as the only product. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.4-1.1 (m, 24H), 0.78 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 25.3, 16.8, 4.4. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 31.90. IR (Neat, KBr plates): 2920, 1250, 530, 465 cm^{-1}.

(53) G(1)All

The G(0.5)Cl was dissolved into 20 mL of Et_2O and added to an excess of allylmagnesium

bromide solution in ether and stirred at rt for 12 hours. After the usual aqueous work up and drying 2.022 g (1.9 mmoles, 80%) of material was recovered. This was further purified by flash column chromatography using hexanes/ethyl acetate (2%) to give 0.694 g (28%) of pure first generation. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 12H), 4.80 (m, 24H), 1.60 (d, 24H), 0.9-0.45 (m, 24H), -0.02 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.7, 113.1, 20.9, 8.26, 5.55, -6.29. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 1.75. IR (Neat, KBr plates): 3060, 2920, 1625, 1250 cm^{-1}. MS (EI): 1023 (M - Allyl), 982, 532.

(54) G(1.5)Cl

G(1)All, 0.512 g (0.48 mmoles) in 15 mL of hexanes and 100 μL of $H_2PtCl_6 \cdot 6H_2O$ (10 nmoles) was added to a thick walled resealable tube. To this 1.2 mL (11.6 mmoles) of $HSiMeCl_2$ was carefully added, the contents were then heated for 12 hours at 120°C. After cooling to rt the remaining volatiles were removed under vacuuo to leave a brown oil, 1.03 g (0.42 mmoles, 88%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.4-1.1 (m, 96H), 0.78 (s, 36H), 0.20 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 23.8, 18.2, 17.5, 8.5, 6.4, 5.6, -2.50. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 32.0, 3.40. IR (Neat, KBr plates): 2920, 1250, 530, 465 cm^{-1}.

(55) G(2)All

The above G(1.5)Cl was dissolved into 30 mL of ether and slowly added to an excess solution of allylmagnesium bromide solution in ether. This was heated to 30°C for 12 hours and then quenched with 50 mL of ammonium chloride solution. After extraction with diethyl ether (3 x 40 mL), drying over $MgSO_4$ and removal of residual volatile materials, 0.988 g of a yellow oil was recovered. This was purified by flash column chromatography using hexanes/ethyl acetate (2%) to give 0.772 g (0.3 mmoles, 71%) of a colourless oil. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 24H), 4.80 (m, 48H), 1.53 (d, 48H), 1.4-0.4 (m, 98H), -0.03 (s, 36H), -0.07 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.8, 113.1, 21.5, 21.1, 18.2, 17.9, 8.5, 5.6, -5.70, -6.29. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.98, 0.23. IR (Neat, KBr plates): 3060, 2920, 1625, 1250 cm^{-1}. Anal. Calcd for $C_{138}H_{150}Si_{18}Ge_2$: C, 64.29; H, 10.48. Found: C, 63.33; H, 10.33.

(56) G(2.5)Cl

G(2)All, 0.510g (0.20 mmoles), $H_2PtCl_6 \cdot 6H_2O$, 100 μL (10 nmoles) were added to a resealable thick walled tube in 10 mL of hexanes. After addition of $HSiMeCl_2$, 0.50 mL (48 mmoles) the tube was sealed and heated at 120°C for 24 hours. After cooling to rt and removing any residual volatile material a dark brown oil remained, 1.38 g (0.17 mmoles, 85%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.4-1.1 (m, 240H), 0.78 (s, 72H), 0.20 (s, 54H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 23.6-17.4, 5.65, -3.7. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 32.0, 3.45, 1.75. IR (Neat, KBr plates): 2920, 1250, 530, 465 cm^{-1}.

(57) G(3)All

G(2.5)Cl was dissolved into 20 mL of ether and added to a flask which contained excess of allylmagnesium bromide solution in ether. This was stirred at 35°C for 24 hours before being quenched with ammonium chloride solution, extracted and dried to give a pale yellow oil, 1.32 g. This was then further purified by flash column chromatography, hexanes/ethyl acetate (2%) to give a colourless oil, 0.87 g (0.1 mmoles, 59%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 48H), 4.80 (m, 96H), 1.53 (d, 96H), 1.4-0.4 (m, 240H), -0.03 (s, 72H), -0.05 (s, 36H), -0.07 (s, 18H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.8, 113.1, 21.5, 21.1, 18.2, 17.9, 8.5, 5.6, -5.56, -5.70, -6.29. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.98, 0.23. IR (Neat, KBr plates): 3060, 2920, 1625, 1250 cm^{-1}.

3B BRANCHING

$Ge_2[(etSi)^N{}_3:(prSi)^N{}_3:X]_6$ G(N), X = Cl, All

(74) G(0.5)Cl

Hexavinyldigermane(**34**) 3.5 g (11.4 mmoles) was dissolved in 15 mL of THF together with 100 μL of $H_2PtCl_6 \cdot 6H_2O$ (10 nmoles) and $HSiCl_3$ 14 mL (18.8 g, 0.138 moles) and heated for 8 hours. Upon removal of the residual volatiles a very viscous dark brown oil was

isolated, yield 9.29 g (8.29 mmoles, 73%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 1.5-1.0 (m, 24H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 19.4, 4.67. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0. IR (Neat, KBr plates): 2920, 1250, 570, 460 cm^{-1}.

(75) G(1)All

A 60 mL solution of G(0.5)Cl (9.29 g, 8.29 mmoles) in Et_2O was added to an excess of Grignard reagent in Et_2O and refluxed for 48 hours. After quenching the remainder of the unreacted Grignard and extraction procedure a colourless oil was isolated as pure G(1), yield 7.89 g (6.47 mmoles, 78%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.75 (m, 18H), 4.80 (m, 36H), 1.55 (d, 36H), 0.85 (m, 12H), 0.65 (m, 12H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.4, 113.5, 19.1, 5.20, 3.51. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.29. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (EI): 1179 (M - Allyl), 1138, 610.

(76) G(1.5)Cl

Into a resealable tube were added G(1)All 3 g (2.46 mmoles), $H_2PtCl_6 \cdot 6H_2O$ 100 μL (10 nmoles), THF 15 mL and trichlorosilane 6 mL (8.05 g, 59.4 mmoles). This mixture was heated at 120°C for 12 hours and following the removal of excess trichlorosilane and THF a brown oil was isolated, yield 7.25 g (1.98 mmoles, 80%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 1.5-1.0 (m, 132H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 22.5, 19.4, 17.4, 4.67, 3.45. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 0.98. IR (Neat, KBr plates): 2090, 1250, 570, 460 cm^{-1}.

(77) G(2)All

From the above reaction, 7.25 g (1.98 mmoles) of G(1.5)Cl was dissolved into 50 mL of Et_2O and added to an excess solution of allylmagnesium bromide. Upon work-up a pale yellow oil was found to be pure G(2), yield 3.95 g (0.99 mmoles, 50%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.75 (m, 54H), 4.80 (m, 108H), 1.55 (d, 108H), 1.3-0.5 (m, 132H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.3, 113.0, 21.9, 19.8, 18.4, 17.5, 5.35, 3.50. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -0.37, -1.10. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

(78) G(2.5)Cl

A solution containing 0.825 g G(2)All (0.21 mmoles), $H_2PtCl_6 \cdot 6H_2O$ 100 μL (10 nmoles), THF 10 mL and $HSiCl_3$ 2 mL (2.68 g, 19.8 mmoles) was heated in a resealable tube for 36 hours. Once the excess silane and solvent had been removed in vacuo, a brown oil was isolated, yield 1.77 g (0.16 mmoles, 75%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 1.5-1.0 (m, 456H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 19.4-17.4. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 1.15, 0.30. IR (Neat, KBr plates): 2090, 1250, 570, 460 cm^{-1}.

(79) G(3)All

G(2.5)Cl, 1.77 g (0.16 mmoles) was dissolved in Et_2O (40 mL) and added to a flask containing 0.19 moles of allylmagnesium bromide in Et_2O. After excess Grignard had been quenched and extractions performed a pale yellow oil remained which was found to be pure G(3), yield 1.67 g (0.14 mmoles, 87%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.75 (m, 162H), 4.80 (m, 324H), 1.55 (d, 324H), 1.3-0.5 (m, 430H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.3, 113.0, 21.9, 19.8, 18.4-17.5. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.06, -0.37, -1.10. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

(80) G(3.5)Cl

A hexanes solution (15 mL) containing G(3)All 0.556 g (45.7 μmoles), $H_2PtCl_6 \cdot 6H_2O$ 100 μL (10 nmoles) and $HSiCl_3$ 2 mL (2.68 g, 19.8 mmoles) was heated for 48 hours in an oil bath. A very viscous brown oil was isolated after removal of all other volatile residuals, yield 1.26 g (36.9 μmoles, 81%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 1.5-1.0 (m, 1428H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 19.4-17.3. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 1.15, 0.30. IR (Neat, KBr plates): 2090, 1250, 570, 460 cm^{-1}.

(81) G(4)All

G(3.5)Cl (36.9 μmoles) was dissolved into 60 mL of Et_2O and slowly added to excess Grignard solution, followed by refluxing for 60 hours. After the work-up a yellow oil remained as was identified as G(4), yield 0.78 g (21.2 μmoles, 57%). ^{1}H-NMR ($CDCl_3$, 360

MHz): δ 5.75 (m, 486H), 4.80 (m, 972H), 1.55 (d, 972H), 1.3-0.5 (m, 1200H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.3, 113.0, 21.9, 19.8, 18.4, 17.5, 5.35, 3.50. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.77, 0.14, -0.37, -1.10. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

(82) G(4.5)Cl

This hydrosilylation step used G(4)All 0.76 g (20.6 μmoles), 200 μL $H_2PtCl_6 \cdot 6H_2O$ (20 nmoles), 15 mL hexanes and 5 mL (6.71 g, 49.5 mmoles) $HSiCl_3$. This reaction mixture was heated for 60 hours after which time all the residual volatiles were removed in vacuo and a dark brown oil was isolated, yield 0.88 g (8.6 μmoles, 42%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 1.5-1.0 (m, 4334H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 19.4-17.2. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 1.15, 0.30, 0.06. IR (Neat, KBr plates): 2090, 1250, 570, 460 cm^{-1}.

(83) G(5)All

A solution containing excess allylmagnesium bromide was prepared (0.150 moles) and to this was added a solution of G(4.5)Cl 8.6 μmoles in 40 mL Et_2O, which was then refluxed for 60 hours. After the extraction procedure a pale yellow oil was isolated, yield 0.45 g (6.1 μmoles, 71%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.75 (m, 1458H), 4.80 (m, 2916H), 1.55 (d, 2916H), 1.3-0.5 (m, 3530H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.3, 113.0, 21.9, 19.8, 18.4-17.5. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.77, 0.14, -0.37, -0.40, -1.10. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

TETRAVINYLGERMANE BASED DENDRIMERS

2B BRANCHING

$Ge[(etSiMe)^N{}_2{:}X]_4$ G(N), X = Cl, All

(62) G(0.5)Cl

Tetravinylgermane **(33)** 0.362 g (2 mmoles), $H_2PtCl_6 \cdot 6H_2O$ 150 μL (15 nmoles), $HSiMeCl_2$ 0.83 mL (8 mmoles) in 15 mL of hexanes were heated in a resealable tube for 6 hours. After removal of the residual volatiles a dark brown oil, 1.14 g (1.78 mmoles, 89%) remained. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.4-1.1 (m, 16H), 0.78 (s, 12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 25.3, 16.6, 4.3. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 32.0. IR (Neat, KBr plates): 2920, 1250, 530, 465 cm^{-1}.

(63) G(1)All

The above G(0.5)Cl was dissolved into 25 mL of ether and slowly added, dropwise to a flask containing excess of allylmagnesium bromide solution in ether. This was refluxed for 6 hours before cooling down to rt, quenching with ammonium chloride solution (50 mL) and extrating with three portions of ether (30 mL) to give a pale yellow oil, 1.041 g. This was quickly passed through a plug of silica gel using hexanes to give pure G(1)2B, 0.95 g (1.38 mmoles, 78%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 8H), 4.80 (m, 16H), 1.60 (d, 16H), 0.80-0.45 (m, 16H), -0.02 (s, 12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.8, 113.1, 20.9, 6.81, 3.13, -6.29. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 1.96. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (CI, Methane): 685 (M + 1), 644, 603. Anal. Calcd for $C_{36}H_{68}Si_4Ge$: C, 63.06; H, 9.93. Found: C, 63.00; H, 10.00.

3B BRANCHING

$Ge[(etSi)^N{}_3{:}X]_4$ G(N), X = Cl, All

(89) G(0.5)Cl

Tetravinylgermane **(33)** 0.5 g (2.76 mmoles) was dissolved in 15 mL of THF along with 50 μL of $H_2PtCl_6 \cdot 6H_2O$ (5 nmoles) and trichlorosilane 2 mL (2.68 g, 19.8 mmoles). The

resealable tube was heated in an oil bath for 24 hours after which all the residual volatile material was removed in vacou leaving a dark brown, viscous oil 1.98 g (2.74 mmoles, 99%).^{1}H-NMR ($CDCl_3$, 360 MHz): δ 1.10-0.50 (m, 16H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 3.54, 2.60. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 11.55. IR (Neat, KBr plates): 2920, 1250, 570, 460 cm^{-1}.

(90) G(1)All

G(0.5)Cl 1.98 g (2.74 mmoles) was reacted with excess allylmagnesium bromide in Et_2O for 24 hours. After the aqueous work-up a yellow oil remained, yield 1.55 g (1.96 mmoles, 71%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.75 (m, 12H), 4.80 (m, 24H), 1.55 (d, 24H), 1.3-0.6 (m, 16H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.8, 113.2, 19.8, 5.27, 3.04. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 1.96. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (CI, Methane): 789 (M + 1), 748, 707.

TETRAALLYLSILANE BASED DENDRIMERS

2B BRANCHING

$Si[(prSiMe)^{N}_{2}:X]_4$ G(N), X = Cl, All

(58) G(0.5)Cl

Tetraallylsilane **(45)** 1.988 g (10 mmoles) was added to a tube with dichloromethylsilane 8.4 mL (80 mmoles) and 50 μL of $H_2PtCl_6 \cdot 6H_2O$ in 15 mL of hexanes. This mixture was heated at 120°C for 24 hours followed by the removal of all residual volatile material by vacuum. Yield 5.11 g (7.77 mmoles, 97%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.4-0.6 (m 24H), 0.70 (s,

12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 24.3, 19.8, 16.6, 5.48. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.6, 0.99. IR (Neat, KBr plates): 2920, 1250, 570, 460 cm^{-1}.

(59) G(1)All

G(0.5)Cl was dissolved into 20 mL of Et_2O and this was added to an excess of allylmagnesium bromide solution. The reaction was refluxed overnight and then the usual acidic work-up was followed. A colourless oil was isolated, yield 4.36 g (6.26 mmoles, 81%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 8H), 4.80 (m, 16H), 1.60 (d, 16H), 1.4-0.5 (m, 24H), -0.02 (s, 12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.8, 113.1, 21.5, 18.2, 18.1, 17.5, -5.73. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.95, 0.24. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (CI, Methane): 696 (M + 1), 655, 614.

(60) G(1.5)Cl

G(1)All 0.694 g (1 mmole) was added to a tube with dichloromethylsilane 1.25 mL (12 mmoles) and 50 μL of $H_2PtCl_6 \cdot 6H_2O$ in 15 mL of hexanes. This mixture was heated at 120°C for 24 hours followed by the removal of all residual volatile material by vacuum. Yield 1.58 g (0.98 mmoles, 98%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.4-0.6 (m 72H), 0.70 (s, 24H), 0.00 (s, 12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 24.3, 19.8, 18.5, 17.7, 16.5,16.6, 5.48, -5.33. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.6, 1.40, 0.99. IR (Neat, KBr plates): 2920, 1250, 570, 460 cm^{-1}.

(61) G(2)All

G(1.5)Cl was dissolved into 20 mL of Et_2O and added to an excess of allylmagnesium bromide solution. The reaction was refluxed overnight and then the usual acidic work-up was followed. A colourless oil was isolated after flash column chromatography, yield 1.313 g (0.77 mmoles, 78%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 16H), 4.80 (m, 32H), 1.60 (d, 32H), 1.4-0.5 (m, 72H), -0.02 (s, 24H), -0.07 (12H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.8, 113.1, 21.5, 18.2-17.5, -5.33, -5.73. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.95, 0.70, 0.24. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (EI): 1663 (M - Allyl), 1622,

1607.

3B BRANCHING

$Si[(prSi)^{N}_{3}:X]_4$ G(N), X = Cl, All

(84) G(0.5)Cl

Tetraallylsilane **(45)** 0.83 g (4.35 mmoles) was added to a tube with trichlorosilane 3 mL (30 mmoles) and 50 μL of $H_2PtCl_6 \cdot 6H_2O$ in 15 mL of hexanes. This mixture was heated at 120°C for 24 hours followed by the removal of all residual volatile material by vacuum. Yield 2.97 g (4.05 mmoles, 93%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.4-0.6 (m, 24H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 24.3, 19.8, 16.6. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.6, 0.99. IR (Neat, KBr plates): 2920, 1250, 570, 460 cm^{-1}.

(85) G(1)All

G(0.5)Cl was dissolved into 20 mL of Et_2O and this was added to an excess of allylmagnesium bromide solution. The reaction was refluxed overnight and then the usual acidic work-up was followed. A colourless oil was isolated, yield 2.24 g (2.8 mmoles, 69%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 12H), 4.80 (m, 24H), 1.55 (d, 24H), 1.4-0.5 (m, 24H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.4, 113.5, 19.9, 18.1, 16.5, 16.3. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.98, -1.10. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (CI, Methane): 800 (M + 1), 759, 718.

TETRAVINYLSILANE BASED DENDRIMERS

$Si[(etSi)^{N}_{3}:X]_4$ G(N), X = Cl, All, Vi

(86) G(0.5)Cl

Tetravinylsilane 1 g (7.35 mmoles) was dissolved in 10 mL of pentane and to this trichlorosilane 3.5 mL (1.64 g, 0.12 moles) and $H_2PtCl_6 \cdot 6H_2O$ 100 μL (10 nmoles) were added. This solution was heated at 120°C for 10 hours and the residual volatiles were removed in vacuo to give a pale yellow oil, yield 4 g (5.9 mmoles, 80%). ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 1.4-1.0 (m, 16H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 17.4, 17.2. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.30, 10.08. IR (Neat, KBr plates): 2920, 1250, 570, 460 cm^{-1}.

(87)G(1)Vi

G(0.5)Cl was dissolved in 20 mL of Et_2O and added to an excess of vinylmagnesiumbromide (0.17 moles) in THF. This solution was refluxed for 24 hours and then followed by the usual work-up. A very pale yellow oil was isolated 1.31 g (1.76 mmoles, 30%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 6.21 (m, 24H), 5.85 (m, 12H), 0.6-0.3 (m, 16H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.64, 134.45, 5.39, 3.89. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 10.07, -18.4. IR (Neat, KBr plates): 3060, 2920, 1625, 1250 cm^{-1}.

(88) G(1)All

G(0.5)Cl was dissolved into 20 mL of Et_2O and added to an excess of allylmagnesium bromide (0.17 moles) in Et_2O. This solution was refluxed for 24 hours and then followed by the usual work-up. A very pale yellow oil was isolated 1.31 g (1.76 mmoles, 30%). ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 5.75 (m, 12H), 4.80 (m, 24H), 1.55 (d, 24H), 0.6-0.3 (m, 16H). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): δ 134.3, 113.5, 19.2, 4.24, 3.49. ^{29}Si-NMR ($CDCl_3$, 49.69

MHz): δ 10.07, 0.92. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

HEXAVINYLDISILANE BASED DENDRIMERS

$Si_2[(etSi)^N{}_3:(prSi)^N{}_1:X]_6$ G(N), X = Cl, All

(91) G(0.5)Cl

Hexavinyldisilane 0.5 g (2.3 mmoles) was added to a resealable tube dissolved in 15 mL of hexanes. To this were added trichlorosilane 3 mL (30 mmoles) and 100 μL of $H_2PtCl_6 \cdot 6H_2O$. The reaction was heated at 120°C for 18 hours after which the residual volatile material was removed by vacuum. Yield 2.16 g (2.1 mmoles, 91%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.4-0.9 (m, 24H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 17.90, 3.20. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, -3.3. IR (Neat, KBr plates): 2920, 1250, 570, 460 cm^{-1}.

(92) G(1)All

G(0.5)Cl 2.16 g (2.1 mmoles) was dissolved into 50 mL of Et_2O and slowly dropped into a flask containing excess allylmagnesium bromide. After refluxing the reaction for 48 hours and followed by the usual work-up a pale yellow oil was isolated, yield 1.21 g (1.1 mmoles, 53%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 18H), 4.80 (m, 36H), 1.56 (d, 36H), 0.6-0.3 (m, 24H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.4, 113.1, 19.8, 4.89, 4.23. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 0.75, -4.80. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (EI): 1130 (M^+), 1089, 1048, 565.

(93) G(1.5)Cl

A resealable tube was charged with G(1)All 1.21 g (1.1 mmoles), $HSiCl_3$ 4 mL (40 mmoles), $H_2PtCl_6 \cdot 6H_2O$ 100 μL (10 nmoles) and hexanes (15 mL). This mixture was heated at 120°C for 24 hours and then all the excess volatile material was removed by vacuum, giving a dark

yellow oil, yield 4.2 g (1.1 mmoles, 100%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.6-0.6 (m, 132H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 24.3, 19.8, 16.7, 5.9, 1.0. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.0, 0.98, -4.98. IR (Neat, KBr plates): 2920, 1250, 570, 460 cm^{-1}.

(94) G(2)All

G(1.5)Cl 4.2 g (1.1 mmoles) was dissolved into 40 mL of Et_2O and dropped into an excess of allylmagnesium bromide solution. This was refluxed for 24 hours and followed by the usual work-up to give a pale yellow oil, yield 0.51 g (0.13 mmoles, 11%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 54H), 4.80 (m, 108H), 1.55 (d, 108H), 1.4-0.5 (m, 132H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.4, 113.5, 19.6, 18.1, 16.7, 16.3, 11.6, 0.98. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -0.40, -1.10, -4.98. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

HEXAALLYLDISILANE BASED DENDRIMERS

$Si_2[(prSi)^{N}_3{:}X]_6$ G(N), X = Cl, All

(95) G(0.5)

Hexaallyldisilane 1 g (3.3 mmoles) was dissolved into 20 mL of hexanes along with trichlorosilane 5 mL (50 mmoles) and 100 μL of $H_2PtCl_6{\cdot}6H_2O$. This reaction was heated at 120°C for 24 hours followed by the removal of all residual volatile material to give a pale yellow oil, yield 2.88 g (2.58 mmoles, 78%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.80-0.80 (m, 36H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 19.6, 18.5, 17.9. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.4, -6.3. IR (Neat, KBr plates): 2920, 1250, 570, 460 cm^{-1}.

(96) G(1)All

G(0.5)Cl was dissolved into 60 mL of Et_2O and slowly added to an excess of allylmagnesium

bromide. This was refluxed for 18 hours and then extracted with ammonium chloride solution in the usual way. A colourless oil was isolated as the only product, yield 20.8 g (1.71 mmoles, 66%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 18H), 4.80 (m, 36H), 1.55 (d, 36H), 1.4-0.5 (m, 36H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.3, 113.1, 19.8, 18.5, 17.8, 17.3. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -1.10, -14.4. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}. MS (EI): 1214 (M^+), 1173, 1132, 607.

(97) G(1.5)Cl

Added to a resealable tube were G(1)All 2.08 g (1.71 mmoles), trichlorosilane 6 mL (60 mmoles), $H_2PtCl_6 \cdot 6H_2O$ 100 μL (10 nmoles) and 15 mL of hexanes. This was heated for 18 hours at 120°C and then all volatile material was removed in vacuo, yield 2.42 g (0.66 moles, 39%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.80-0.80 (m, 144H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 19.6, 18.5, 18.3, 18.1, 17.9, 17.3. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ 12.4, 0.98, -6.3. IR (Neat, KBr plates): 2920, 1250, 570, 460 cm^{-1}.

(98) G(2)All

The chlorinated exterior G(1.5)Cl 2.42 g (0.66 mmoles) was dissolved into 60 mL of Et_2O and dropped into a solution containing excess allylmagnesium bromide. This reaction was refluxed for 48 hours and following on from the work-up a pale yellow oil was isolated, yield 0.741 g (0.188 mmoles, 28%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.75 (m, 54H), 4.80 (m, 108H), 1.55 (d, 108H), 1.4-0.5 (m, 144H). ^{13}C-NMR ($CDCl_3$, 75.47 MHz): δ 134.3, 113.1, 19.8, 18.5-17.8, 17.3. ^{29}Si-NMR ($CDCl_3$, 49.69 MHz): δ -0.40, -1.10, -14.4. IR (Neat, KBr plates): 3060, 2920, 1630, 1250 cm^{-1}.

CORE AND PERIPHERAL GROUP MODIFICATION

(99) $Si[(prSiMe)^1_2:F]_4$

(58) (0.640 g, 0.98 mmoles) was dissoleved into 10 mL of hexanes. This was slowly added to a suspension of 2 g ZnF_2 in hexanes (40 mL) and stirred at rt overnight. The solution was filtered and solvent removed under vacuum. The oil was redissolved into 10 mL of hexanes and passed through a plug of celite, after which the solvent was again removed under vacuum. Yield 0.468 g (0.9 mmoles, 90%). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.45 (t, 6.5 Hz, 8H), 0.85 (m, 8H), 0.59 (m, 8H), 0.30 (t, 6.5 Hz, 12H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 17.9 (t, 14.3 Hz), 16.2, 15.9, -4.14 (t, 16.2 Hz). ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 1.10, 3.40 (t, 300 Hz). ^{19}F ($CDCl_3$): δ -135.4. MS (CI, Methane): 521 (M + 1), 501, 482, 467, 448.

(100) $Si[(prSiMe)^2_2:F]_4$

(60) (0.808 g, 0.50 mmoles) was dissoleved into 10 mL of hexanes. This was slowly added to a suspension of 4 g ZnF_2 in hexanes (40 mL) and stirred with warming overnight. The solution was filtered and solvent removed under vacuum. The oil was redissolved into 25 mL of hexanes and passed through a plug of celite, after which the solvent was again removed under vacuum. Yield 0.378 g (0.28 mmoles, 56%). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.45 (t, 6.5 Hz, 16H), 1.00-0.00 (m, 72H), 0.29 (t, 6.5 Hz, 24H), -0.07 (s, 12H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 17.9 (t, 14.3 Hz), 17.9-16.3, -4.09 (t, 16.2 Hz), -5.34. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 1.95, 1.26, 3.45 (t, 300 Hz). ^{19}F ($CDCl_3$): δ -135.4. MS (EI): 1333 (M - F), 1314, 1295, 1276.

(101) $PhSi[(prSiMe)^2_2:Et]_3$

(13) 1.50 g (1.16 mmoles) was slowly added to a premade solution of ethylmagnesiumbromide in THF. This was heated to 50 °C for three hours and then cooled to room temperature. The excess Grignard solution was quenched with 1M HCl solution and the aqueous layer was extracted twice with 30 mL portions of Et_2O, dried over magnesium sulphate and solvent was removed under vacuum. Yield 1.215 g (0.99 mmoles, 86%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.5-7.3 (m, 5H), 1.50-0.40 (m, 124H), 0.40--0.12 (s, 33H). ^{13}C

NMR ($CDCl_3$, 75.47 MHz): δ 134.0, 128.5, 127.6, 19.4-17.5, 7.46, 5.66, -4.33, -5.01, -6.09. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 4.85, 0.97, -4.08. MS (EI): 1219 (M^+), 1190, 1165, 1150, 1142, 1113.

(102) $PhSi[(prSiMe)^2_2:2\text{-}CH_2(C_{10}H_7)]_3$

(13) 0.50 g (0.38 mmoles) was slowly added to a premade 5 mmole solution of 2-$LiCH_2(C_{10}H_7)$ in hexanes. This was prepared from 2-methylnaphthalene (0.647 g, 5 mmoles), TMEDA (tetramethylethylenediamine, 5 mmoles), n-BuLi (3.1 mL, 1.6M, 5 mmoles) and 15 mL of hexanes, deep red in colour. After 30 mins the deep red colour had changed to orange and after 1 hour the solution was yellow in colour. The reaction was stirred at room temperature overnight and then quenched with water. The aqueous layer was extracted twice with 50 mL portions of Et_2O, dried over magnesium sulphate and solvent was removed under vacuum. Yield 0.93 g (0.36 mmoles, 96%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.8-7.3 (m, 89H), 2.53 (s, 23H), 1.6-0.4 (m, 90H), -0.05, -0.07 (s, 27H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 135.4-124.9, 26.7, 26.2, 21.7-16.1, -4.83, -4.97, -5.07. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 2.67, 2.38, 1.77, 1.14, -3.90. MS (EI): 1643, 1559, 1480, 1450, 1302, 1159, 1017. UV/Vis (Hexanes): nm ( ) 228 (183,400), 275 (45,000).

(103) $TfOSi[(prSiMe)^2_2:Et]_3$

(101) 0.528 g (0.43 mmoles) was dissolved into 20 mL of CH_2Cl_2. To this was added a solution of trifluoromethanesulphonic acid (triflic acid) 65 mg (0.43 mmoles, 1 equiv.) in 3 mL of dichloromethane. Initially the solution turned brown in colour and after one hour was a black solution. The solvent was removed under vacuum, no yield was recorded. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.5-0.4 (m, 119H), -0.06--0.11 (s, 27H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 119.0 (q, 320 Hz), 17.9-16.8, 7.4, 5.1, -3.14, -6.1. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 43.5, 5.02, 1.32. ^{19}F NMR ($CDCl_3$): δ -79.7.

This solution was dissolved into 20 mL of dichloromethane and separated into four 5mL portions for the next reactions.

(104) CH_2=$CHCH_2OSi[(prSiMe)^2_2:Et]_3$

(103) was slowly added to a solution containing allylalcohol (6.23 mg, 0.107 mmoles) in 5 mL of CH_2Cl_2 with 0.107 mmoles of triethylamine. The black colour immediately disappeared and the solution was colourless with white fumes emerging. This was stirred at rt overnight after which time the solvent was removed. The oil was redissolved into 10 mL of hexanes and passed through a plug of celite, and all residual volatile material was removed under vacuum. No yield was recorded. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 5.9 (m, 1H), 5.15 (dd, 2H), 4.10 (d, 2H), 1.6-0.4 (m, 132H), 0.04--0.12 (s, 30H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 137.4, 113.0, 40.1, 19.0-17.8, 7.4, 5.2, -4.2, -4.9, -6.0. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 17.4, 4.88, 1.05. MS

(105) $C_6H_5CH2OSi[(prSiMe)^2_2:Et]_3$

(103) was slowly added to a solution containing benzylylalcohol (11.6 mg, 0.107 mmoles) in 5 mL of CH_2Cl_2 with 0.107 mmoles of triethylamine. The black colour immediately disappeared and the solution was colourless with white fumes emerging. This was stirred at rt overnight after which time the solvent was removed. The oil was redissolved into 10 mL of hexanes and passed through a plug of celite, and all residual volatile material was removed under vacuum. No yield was recorded. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.4-7.3 (m, 5H), 4.80 (s, 2H), 1.5-0.4 (m, 152H), -0.01--0.10 (s, 30H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 128.6-127.0, 31.6, 19.0-18.0, 7.4, 5.2, -6.0. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 17.4, 4.85, 0.97. MS

(106) $MeOC_6H_4CH_2OSi[(prSiMe)^2_2:Et]_3$

(103) was slowly added to a solution containing *p*-methoxybenzylalcohol (14.8 mg, 0.107 mmoles) in 5 mL of CH_2Cl_2 with 0.107 mmoles of triethylamine. The black colour immediately disappeared and the solution was colourless with white fumes emerging. This was stirred at rt overnight after which time the solvent was removed. The oil was redissolved into 10 mL of hexanes and passed through a plug of celite, and all residual

volatile material was removed under vacuum. No yield was recorded. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.36 (d, 2H), 6.95 (d, 2H), 4.60 (s, 2H), 3.85 (s, 3H), 1.5-0.4 (m, 96H), 0.00--0.12 (s, 26H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 159.2, 133.1, 128.7, 114.0, 55.3, 31.6, 19.0-18.0, 7.4, 5.2, -4.9, -6.0. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 17.3, 4.90, 1.00. MS

(107) 9-$C_{14}H_9CH_2OSi[(prSiMe)^2_2:Et]_3$

(103) was slowly added to a solution containing 9-anthracenemethanol (22.36 mg, 0.107 mmoles) in 5 mL of CH_2Cl_2 with 0.107 mmoles of triethylamine. The black colour immediately disappeared and the solution was colourless with white fumes emerging. This was stirred at rt overnight after which time the solvent was removed. The oil was redissolved into 10 mL of hexanes and passed through a plug of celite, and all residual volatile material was removed under vacuum. No yield was recorded. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.5-7.9 (m, 9H), 5.70 (s, 2H), 1.5-0.4 (m, 118H), -0.02--0.10 (s, 26H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 131.5-124.0, 57.2, 19.0-18.0, 7.4, 5.2, -5.1. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 17.4, 4.97, 1.07. UV/Vis (Hexanes): nm ( ) 255 (118,500), 346 (5520), 364 (7880), 384 (7100). MS

(108) $PhSi[(prSiMe)^2_2:All/OTf]_3$

(15) 0.500 g (0.37 mmoles) was dissolved into 20 mL of dichloromethane. To this a solution of triflic acid (55 mg, 0.37 mmoles) in dichloromethane (2 mL) was slowly added. The solution turned dark yellow after 10 mins and then brown in colour. The solvent was removed and the brown oil was analysed. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.5-7.3 (m, 5H), 5.85 (m, 11H), 4.80 (m, 22H), 1.5 (m, 22H), 1.4-0.4 (m, 86H), -0.02--0.07 (s, 25H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 134.8, 134.0, 127.6, 113.0, 22.7, 21.5, 19.0-15.0, -5.76. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 43.4, 1.04, 0.26. -3.95.

(109) $PhSi[(prSiMe)^2_2:All/OCH_2C_6H_4CH_2OMe]_3$

(108) was slowly added to a solution of *p*-methoxybenzylalcohol (51 mg, 0.37 mmoles) in 5 mL of CH_2Cl_2 with 0.37 mmoles of triethylamine. The dark colour immediately

disappeared and the solution was yellow with white fumes emerging. This was stirred at rt overnight after which time the solvent was removed. The oil was redissolved into 10 mL of hexanes and passed through a plug of celite, and all residual volatile material was removed under vacuum. No yield was recorded. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.5-7.3 (m, 5H), 7.3-6.8 (m, 4H) 5.85 (m, 11H), 4.80 (m, 22H), 3.80 (s, 2H), 1.5-0.4 (m, 96H), -0.02--0.07 (s, 27H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 134.8-127.6, 113.6, 113.0, 55.2, 31.6, 21.4-17.0, -5.22, -5.71. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 16.4, 1.07, 0.26, -3.90.

(110) $TfOSi[(prSiMe)^2_2:2\text{-}CH_2(C_{10}H_7)]_3$

(102) 0.43 g (0.17 mmoles) was dissolved into 20 mL of CH_2Cl_2. To this was added a solution of trifluoromethanesulphonic acid (triflic acid) 25 mg (0.17 mmoles, 1 equiv.) in 3 mL of dichloromethane. Initially the solution turned brown in colour and after one hour was a black solution. The solvent was removed under vacuum, no yield was recorded. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.0-7.3 (m, 84H), 2.51 (s, 28H), 1.5-0.4 (m, 226H), 0.05--0.7 (s, 27H). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 135.4-124.9, 26.7, 26.2, 19.0-18.0, -5.09. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 43.5, 42.6, 2.47, 1.32, 1.17. ^{19}F NMR ($CDCl_3$): δ -79.7.

(111) $9\text{-}C_{14}H_9CH_2OSi[(prSiMe)^2_2:2\text{-}CH_2(C_{10}H_7)]_3$

(110) was redissolved into 20 mL of dichloromethane and slowly added to a solution of 9-anthracenemethanol (35 mg, 0.17 mmoles) in 10 mL of dichloromethane and 0.17 mmoles of triethylamine. The black colour immediately dissipated and a yellow solution was stirred overnight. The solvent was removed, redissolved into 10 mL of hexanes and passed through a plug of celite. All residual volatiles were removed under vacuum yielding a yellow oil 0.375 g (0.14 mmoles, 83%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 8.5-7.3 (m, 91H), 5.63 (s, 2H), 2.51 (s, 22H), 1.5-0.4 (m, 182H), 0.05--0.07 (s, 27H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 134.5-124.9, 57.2, 26.7, 26.2, 19.0-18.0, -5.09. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 17.4, 2.47, 1.32, 1.17. UV/Vis (Hexanes): nm 226 (131,000), 256 (87,000), 276 (16,700), 346 (4400), 364 (6000), 384 (5400).

(112) $IGe[(etSiMe)^{1}_{2}:All]_3$

(53) 1.06 g (1 mmole) was dissolved into 50 mL of carbontetrachloride. Iodine (2.54 g, 1 mmole) was dissolved into this solution which was then refluxed overnight. The original purple colour had dissipated and all residual volatiles were removed under vacuum. Yield 1.25 g (1.9 mmoles, 95%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 5.80 (m, 6H), 4.80 (m, 12H), 1.50 (m, 12H), 1.25 (m, 6H), 0.65 (m, 6H), -0.07 (s, 9H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 134.5, 113.0, 19.5, 11.1, 7.7, -6.2. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 1.90. MS (EI): 659, 644, 618, 603, 577, 562, 532.

(113) $9\text{-}CH_2C_{14}H_9Ge[(etSiMe)^{1}_{2}:All]_3$

(112) was slowly added to a solution containing $9\text{-}LiCH_2C_{14}H_9$ in hexanes. This was prepared using 9-methylanthracene (0.364 g, 1.90 mmoles), 1.30 mL of 1.6M n-BuLi and 1.90 mmoles of TMEDA in hexanes (30 mL) which was deep red in colour. After 30 mins the deep red colour had disappeared and a yellow solution was formed. This was stirred at rt overnight. The reaction was quenched with water, and the aqueous layer was extracted twice with 20 mL of diethyl ether. The organic layers were dried over magnesiumsulphate and all remaining volatiles were removed under vacuum. A yellow oil remained as the only product, yield 0.755 g (1.04 mmoles, 55%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 5.80 (m, 6H), 4.80 (m, 12H), 3.58 (m, 2H), 1.50 (m, 12H), 1.20 (m, 6H), 0.75 (m, 6H), -0.07 (s, 9H). ^{13}C NMR ($CDCl_3$, 62.89 MHz): δ 134.5, 113.0, 20.8, 19.5, 10.2, 6.1, -6.2. ^{29}Si NMR ($CDCl_3$, 49.69 MHz): δ 2.30. MS (EI): 682, 641, 626, 585, 407.

ONE-SHELL EXPANSION REACTIONS

HYBRID MATERIALS

A core molecule was prepared as outlined above and this was reacted with an excess of trichlorosilane, removal of all residual volatile materials, redissolving in diethyl ether and addition to an excess of allylmagnesium bromide solution in ether. A general work-up procedure was employed followed immediatcly by flash column chromatography using hexanes/ethyl acetate (2%). The following data tables summarise the weights added, masses obtained together with relevant speactral data.

Compound	Wt (g)	Vol (mL) $HSiCl_3$	Integration =CH	$SiCH_3$
(116) $Si[(prSiMe)^1_2:prSiCl_3]_4$	0.694	2.00		=12
(117) $Si[(prSiMe)^1_2(prSi)^2_3:All]_4$	1.683		24	=12
(118) $Si[(prSiMe)^2_2:prSiCl_3]_4$	0.516	1.00		=36
(119) $Si[(prSiMe)^2_2(prSi)^3_3:All]_4$	1.530		48	=36
(120) $PhSi[(prSiMe)^1_2:prSiCl_3]_3$	0.606	1.21		=9
(121) $PhSi[(prSiMe)^1_2(prSi)^2_3:All]_3$	0.810		18	=9
(122) $PhSi[(prSiMe)^2_2:prSiCl_3]_3$	0.257	0.68		=27
(123) $PhSi[(prSiMe)^2_2(prSi)^3_3:All]_3$	0.481		36	=27
(124) $Ge[(prSiMe)^1_2:prSiCl_3]_4$	0.212	0.50		=12
(125) $Ge[(prSiMe)^1_2(prSi)^2_3:All]_4$	0.349		24	=12
(126) $Ge[(etSiMe)^1_2:prSiCl_3]_4$	0.176	0.41		=12
(127) $Ge[(etSiMe)^1_2:(prSi)^2_3:All]_4$	0.360		24	=12
(128) $Ge_2[(etSiMe)^1_2:prSiCl_3]_6$	0.212	0.50		=18
(129) $Ge_2[(etSiMe)^1_2:(prSi)^2_3:All]_6$	0.151		36	=18

RAPID ASSEMBLY REACTIONS

General Procedure

A two-neck round-bottom flask is fitted with a reflux condenser, magnetic stirring bar and a constant pressure dropping funnel under a nitrogen atmosphere. The flask is charged with the core reagent being used, solvent and catalyst. This is then heated to reflux whilst the dropping funnel is filled. The dropping funnel is charged with the monomer unit to be added in the appropriate amount of solvent. Once the contents of the flask are refluxing the monomer unit is dropped in at a rate of one drop per second, approximately, and a constant reflux is maintained. The reaction is carried out for the specified length of time after which the flask is cooled to room temperature. The contents are then filtered through filter paper to remove any solid particles and the solvent removed on a rotary evaporator. The crude product is then weighed and usually flash column chromatography is utilised to separate dendrimer fractions. Occasionally a different method is used. In this procedure all the reagents to be added are placed into a resealable tube and the tube is then sealed. The tube and its contents are then heated in an oil bath at 120°C for the specified length of time. This method is referred to as the concentrated procedure whilst the former is a dilute procedure.

The following are the experiments reported in Chapter Six

PHENYL TRIALLYLSILANE CORE

(133) G(2)2B

Phenyl triallylsilane 0.576 g (2.53 mmoles) was dissolved into 2 mL of hexanes along with 0.5 mL of $H_2PtCl_6 \cdot 6H_2O$ (50 nmoles) in a 500 mL two-neck round-bottom flask and this was

set to reflux. A dropping funnel was charged with diallylmethylsilane 2.865 g (22.7 mmoles, 9 equiv.) in 80 mL of hexanes, and these contents were added at a rate of one drop per second. The reflux was maintained for 24 hours after which the contents were filtered and the solvent removed to yield a dark brown oil as product, 2.010 g (mmoles, %). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.5-7.3 (m, 5H), 5.8 (m, 8H), 4.9 (m, 16H), 1.4-0.6 (m, 56H), -0.04--0.12 (s, 22H). Purification of this material was carried out using flash column chromatography, hexanes/ethyl acetate (2%) as the eluent. Two fractions were collected.

(134) G(3)2B

Phenyl triallylsilane 0.440 g (1.93 mmoles) was dissolved into 2 mL of hexanes along with 0.5 mL of $H_2PtCl_6 \cdot 6H_2O$ (50 nmoles) in a 500 mL two-neck round-bottom flask and this was set to reflux. A dropping funnel was charged with diallylmethylsilane 5.106 g (40.5 mmoles, 21 equiv.) in 80 mL of hexanes, and these contents were added at a rate of one drop per second. The reflux was maintained for 48 hours after which the contents were filtered and the solvent removed to yield a dark brown oil as product, 4.865 g (1.7 mmoles, 88%). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.5-7.3 (m, 5H), 5.8 (m, 25H), 4.9 (m, 51H), 1.4-0.6 (m, 201H), -0.04--0.12 (s, 73H). Purification of this material was carried out using flash column chromatography, hexanes/ethyl acetate (2%) as the eluent. Two fractions were collected.

(142) G(3)3B

Phenyl triallylsilane 0.379 g (1.66 mmoles) and $H_2PtCl_6 \cdot 6H_2O$ 0.5 mL (50 nmoles) were dissolved in 5 mL of THF in a 500 mL flask. The dropping funnel was filled with triallylsilane 9.85 g (6.48 mmoles, 39 equiv.) in 80 mL of THF, which was dropped in at a rate of 2 drops per second. The contents were then refluxed for 36 hours and stirred at rt for a further 36 hours. The mixture was then filtered through a plug of celite and the solvent removed to give a dark brown oil as crude product, yield 5.885 g. This material was purified by flash column chromatography using hexanes/ethyl acetate as eluent. Two fractions were isolated.

(143) G(4)3B

Phenyl triallylsilane 24 mg (0.11 mmoles) was dissolved in 20 mL of hexanes together with 0.5 mL of $H_2PtCl_6 \cdot 6H_2O$ (50 nmoles) and set to reflux. A dropping funnel was charged with triallylsilane 3.952 g (26 mmoles, 236 equiv.) in 80 mL of hexanes, which was dropped in at a rate of 1 drop every 10 seconds. This reaction was refluxed for a further 60 hours after which the solution was filtered and the solvent removed by rotary evaporation. The crude product obtained was a dark brown oil, yield 4.38 g. Flash column chromatography was used to purify this mixture.

(144) G(5)3B

Phenyl triallylsilane 36 mg (0.16 mmoles) was dissolved into 2 mL of hexanes together with $H_2PtCl_6 \cdot 6H_2O$ 0.6 mL (60 nmoles) and this mixture was set to reflux. A constant pressure dropping funnel was filled with triallylsilane 8.71 g (57.3 mmoles, 363 equiv.) and this was added at a rate of one drop per second. The solution was refluxed for 72 hours after which it was filtered and the solvent removed under reduced pressure. A dark brown oil was obtained as the crude product, yield 6.596 g. This was then purified using flash column chromatography (hexanes/ethyl acetate).

(145) G(6)3B

Phenyl triallylsilane G(3)3B 0.2 g (32.5 μmoles) was dissolved into 5 mL of hexanes together with 1 mL of $H_2PtCl_6 \cdot 6H_2O$ (100 nmoles) which was then refluxed. A dropping funnel was filled with triallylsilane 5.20 g (34 mmoles, 1053 equiv.) and this was then added in at a rate of one drop per second. The reaction was refluxed for 72 hours after which the solution was filtered and the solvent removed by rotary evaporation. A very dark brown oil was isolated as the crude product, yield 4.136 g. This oil was then further purified by flash column chromatography.

DIPHENYLDIALLYLSILANE CORE

(135) G(3)2B

Diphenyldiallylsilane 0.528 g (2 mmoles) was put into a 500 mL round-bottomed flask together with $H_2PtCl_6 \cdot 6H_2O$ 0.6 mL (60 nmoles) and hexanes 3 mL. A dropping funnel was charged with Diallylmethylsilane 3.528 g (28 mmoles, 14 equiv.) dissolved in 80 mL of hexanes, which was then added to the refluxing solution at a rate of one drop per two seconds. The reflux was continued for 60 hours total, after this time the solution was filtered and the solvent removed by rotary evaporation. A dark brown product was isolated as a viscous oil, yield 3.43 g. Further purification of this oil was achieved by flash column chromatography.

(146) G(2)3B

Diphenyldiallylsilane 0.146 g (0.55 mmoles), triallylsilane 0.672 g (4.42 mmoles, 8 equiv.), $H_2PtCl_6 \cdot 6H_2O$ 0.4 mL (40 nmoles) and 15 mL of hexanes were all added to a resealable tube. The contents of this tube were heated in an oil bath for 367 hours at 120 C. Once this had cooled to rt the solution was filtered and the solvent removed under vacuo to give a brown oil as the isolated product. Yield of this oil was 0.832 g (>100%) so flash column chromatography using hexanes/ethyl acetate was undertaken to purify this compound.

(147) G(5)3B

Into a 500 mL round-bottom flask diphenyldiallylsilane 60 mg (0.27 mmoles), $H_2PtCl_6 \cdot 6H_2O$ 0.6 mL (60 nmoles) and hexanes (3 mL) were added and this solution was then set to reflux. A dropping funnel was charged with triallylsilane 8.36 g (55 mmoles, 242 equiv.) in 70 mL of hexanes, which was then added to the refluxing solution at a rate of two drops per second. The mixture was refluxed for a total time for 48 hours after which it was filtered and the solvent removed by rotary evaporation. A dark brown oil was isolated as the crude product,

yield 8.20 g. Further purification of this oil was achieved by flash column chromatography.

TETRAALLYLGERMANE CORE

(136) G(2)2B

Tetraallylgermane 0.240 g (1.01 mmoles) was dissolved in 4 mL of hexanes along with $H_2PtCl_6 \cdot 6H_2O$ 0.4 mL (40 nmoles) and this was set to reflux. A dropping funnel was filled with Diallylmethylsilane 1.531 g (12.15 mmoles, 12 equiv.) in 60 mL of hexanes and this was added to the refluxing mixture at a rate of one drop per five seconds. This reaction was refluxed for a total time of 72 hours, after which it was filtered through a plug of celite and the solvent was removed by rotary evaporator. A dark brown oil was isolated as the crude product, yield 1.396 g. This oil was further purified by flash column chromatography.

(137) G(3)2B

Tetraallylgermane 0.118 g (0.49 mmoles) in 3 mL of hexanes, together with 0.5 mL of $H_2PtCl_6 \cdot 6H_2O$ was set to reflux. A constant pressure dropping funnel was filled with Diallylmethylsilane 1.756 g (13.94 mmoles, 28 equiv.) in 60 mL of hexanes, and this solution was added to the flask at a rate of one drop per second. The mixture was refluxed for a total time of 96 hours. Once completed the solution was filtered and the solvent removed to give a dark brown oil, yield 1.814 g. Further purification of this product was attempted by flash column chromatography.

(148) G(5)3B

Tetraallylgermane 50 mg (0.21 mmoles) was dissolved into 3 mL of hexanes along with 0.9 mL of $H_2PtCl_6 \cdot 6H_2O$ (90 nmoles) and the solution was set to reflux. A dropping funnel was charged with triallylsilane 13.54 g (0.1 moles, 484 equiv.) in 80 mL of hexanes and slowly added to the refluxing solution. After 96 hours of reflux the contents were filtered and the

solvent removed under reduced pressure to give a vary dark brown, viscous oil, yield 12.47 g. By using flash column chromatography 4.40 g of this product was further purified.

HEXAVINYLDIGERMANE CORE

(138) G(2)2B

Hexavinyldigermane 0.154 g (0.5 mmoles) in 4 mL of hexanes was added to 0.5 mL of $H_2PtCl_6 \cdot 6H_2O$ (50 nmoles) and the solution was refluxed. A dropping funnel was filled with Diallylmethylsilane 1.134 g (9 mmoles, 18 equiv.) in 100 mL of hexanes and this was then slowly added to the refluxing solution. The solution was refluxed for a total of 24 hours and then filtered and solvent removed under vacou. A dark brown oil was isolated as the only product, yield 0.527 g. Separation of this compound was achieved by using flash column chromatography.

(139) G(3)2B

Hexavinyldigermane 0.308 g (1 mmole) and 0.5 mL of $H_2PtCl_6 \cdot 6H_2O$ were dissolved into 4 mL of hexanes and the flask was heated so that a reflux was obtained. Diallylmethylsilane 5.292 g (42 mmoles, 42 equiv.) in 100 mL of hexanes was slowly added to this refluxing mixture by a dropping funnel. Reflux was maintained for 48 hours after which time the solution was filtered and the solvent removed by rotary evaporation. A dark brown oil was isolated as product, yield 2.256 g. Flash column chromatography was then used to further purify the compound.

(149) G(3)3B

Hexavinyldigermane 35 mg (0.114 mmoles), $H_2PtCl_6 \cdot 6H_2O$ 0.4 mL (40 nmoles), triallylsilane 1.347 g (8.86 mmoles, 78 equiv.) and 15 mL of hexanes were all added to a resealable tube. This tube was placed in an oil bath for 48 hours at 120 C. Once the reaction was completed

the contents were filtered and the solvent removed under vacuo. A brown oil was isolated as the product, yield 1.456 g (>100%). To remove the excess material present and for purification this compound was run through a flash column using hexanes/ethyl acetate (2%) as the eluent. Only one product was isolated from this step, yield 0.920 g.

(150) G(5)3B

Hexavinyldigermane 27 mg (89.5 μmoles) in 2 mL of hexanes, together with 0.8 mL of the catalyst $H_2PtCl_6 \cdot 6H_2O$ (80 nmoles) were set to a reflux temperature. A dropping funnel was charged with triallylsilane 9.881 g (65 mmoles, 726 equiv.) in 80 mL of hexanes, and this was added at a rate of one drop per second. Reflux was maintained for 96 hours and then the solution was filtered and solvent removed by rotary evaporation. A very viscous, dark brown oil was isolated, yield 7.26 g. Purification of this oil was achieved by flash column chromatography.

HYBRID HYPERBRANCHED REACTIONS

$PhSi[(prSiMe)^4_2:All]_3$ Hypercore

(151) G(5)3B

G(4)2B (0.108 g, 18.3 μmoles) was dissolved into 2 mL of hexanes with 0.4 mL of $H_2PtCl_6 \cdot 6H_2O$ (40 nmoles) in a two-neck round-bottomed flask and set to reflux. A dropping funnel was charged with triallylsilane 0.133 g (0.88 mmoles, 48 equiv.) in 40 mL of hexanes which was slowly added into the refluxing solution. Heating was continued for 36 hours and then the contents were filtered through a plug of celite and the solvent removed under reduced pressure. A dark brown oil was isolated, yield 0.220 g, which was then further purified by flash column chromatography.

(152) G(6)3B

G(4)2B (0.100 g, 16.9 μmoles) in 3 mL of hexanes and 0.5 mL of $H_2PtCl_6 \cdot 6H_2O$ were brought to a reflux. The contents of a dropping funnel filled with triallylsilane 0.495 g (3.25 mmoles, 192 equiv.) in 60 mL of hexanes were added in over a period of eight hours. The mixture was refluxed for 48 hours total after which time an extraction with ammonium chloride (3 x 15 mL) was performed, and the solvent removed by rotary evaporation. A brown oil was isolated, yield 0.508 g. This was purified by flash column chromatography.

(153) G(7)3B

G(4)2B (0.103 g, 17.5 μmoles) in 4 mL of hexanes together with $H_2PtCl_6 \cdot 6H_2O$ 0.6 mL (60 nmoles) was set to reflux. Triallylsilane 1.656 g (10.89 mmoles, 624 equiv.) dissolved in 80 mL of hexanes was slowly added over a period of 14 hours. After a period of 36 hours the reflux was stopped and the solution was extracted 3 times with NH_4Cl (20 mL each). The organic layer was dried with magnesium sulphate and the solvent then removed by rotary

evaporation to give a brown oil, yield 1.526 g. This was then further purified by flash column chromatography.

(154) G(8)3B

G(4)2B (0.100 g, 16.9 μmoles) in 3 mL of hexanes and 0.8 mL of $H_2PtCl_6 \cdot 6H_2O$ (80 nmoles) were placed into a two-neck round-bottomed flask and set to reflux. A dropping funnel was charged with triallylsilane 4.932 g (32.4 mmoles, 1920 equiv.) in 80 mL of hexanes, this solution was slowly added in over a 12 hour period. The reflux was stopped after a period of 60 hours, an extraction was performed using ammonium chloride (3 x 20 mL), the organic layer was subsequently dried and solvent removed under vacou. A dark brown oil was isolated as product, yield 4.323 g. This was then purified by flash column chromatography.

$Ge[(prSiMe)^3_2{:}All]_4$ Hypercore

(155) G(4)3B

G(3)2B (0.105 g, 27.8 μmoles) in 3 mL of hexanes and 0.2 mL of $H_2PtCl_6 \cdot 6H_2O$ (20 nmoles) were brought to a reflux. Triallylsilane 0.136 g (0.89 mmoles, 32 equiv.) in 20 mL of hexanes was slowly added in and the solution was refluxed for 24 hours. Once cooled the solvent was removed on a rotary evaporator to yield a brown oil, 0.228 g. This was then further purified by flash column chromatography.

(156) G(5)3B

G(3)2B (0.100 g, 26.5 μmoles) in 3 mL of hexanes and 0.5 mL of $H_2PtCl_6 \cdot 6H_2O$ were set to reflux. A dropping funnel charged with triallylsilane 0.517 g (3.40 mmoles, 128 equiv.) in 60 mL of hexanes was slowly added over a 4 hour period. Reflux was continued for 24 hours total after which time the solution was extracted with 3 portions of ammonium chloride (20

mL). After drying with magnesium sulphate the solvent was removed to give a dark brown oil, yield 0.569 g. This was then further purified by flash column chromatography.

(157) G(7)3B

(156) (42 mg, 1.81 μmoles) in 3 mL of hexanes and $H_2PtCl_6 \cdot 6H_2O$ 0.4 mL (40 nmoles) was set to reflux. Triallylsilane 0.317 g (2.08 mmoles, 1152 equiv.) in 40 mL of hexanes was added in during a 16 hour period and the solution was refluxed for 36 hours in total. Once an aqueous extraction had been performed and the organic layer dried and then removed a dark brown oil remained, yield 0.359 g. Flash column chromatography was then used to purify this oil.

(158) G(>8)3B

G(3)2B (50 mg, 13.3 mmoles) together with $H_2PtCl_6 \cdot 6H_2O$ (0.8 mL, 80 nmoles) and triallylsilane 5.00 g (32.89 mmoles, 2473 equiv.) were dissolved into 15 mL of hexanes in a resealable tube. This tube was heated in an oil bath at 120 C for 48 hours after which the solvent was removed on a rotary evaporator. The dark brown oil that was isolated was very viscous, yield 4.62 g. Further purification was carried out using flash column chromatography.

(159) Addition of limited triallylsilane

G(3)2B (88 mg, 0.23 μmoles) together with $H_2PtCl_6 \cdot 6H_2O$ (0.2 mL, 20 nmoles) in 4 mL of hexanes were heated in a two-neck round bottomed flask. A solution of triallylsilane (71 mg, 0.47 mmoles, 20 equiv.) in 20 mL of hexanes was added dropwise over a period of 4 hours. The solution was then refluxed for a further 20 hours and solvent was removed on the rotary evaporator to give a brown oil, yield 0.150 g. Further purification was then attempted by flash column chromatography.

$Ge_2[(etSiMe)^1_2(prSiMe)^3_2{:}All]_6$ Hypercore

(160) G(5)3B

G(3)2B (0.280 g, 50 μmoles) in 3 mL of hexanes together with $H_2PtCl_6 \cdot 6H_2O$ 0.7 mL (70 nmoles) were heated to reflux. Triallylsilane 1.459 g (9.6 mmoles, 192 equiv.) in 80 mL of hexanes was slowly added into the refluxing solution by means of a dropping funnel. After 96 hours the reaction was stopped, filtered through a celite plug and solvent removed under reduced pressure to give a brown oil, yield 1.396 g. Further purification was carried out using flash column chromatography.

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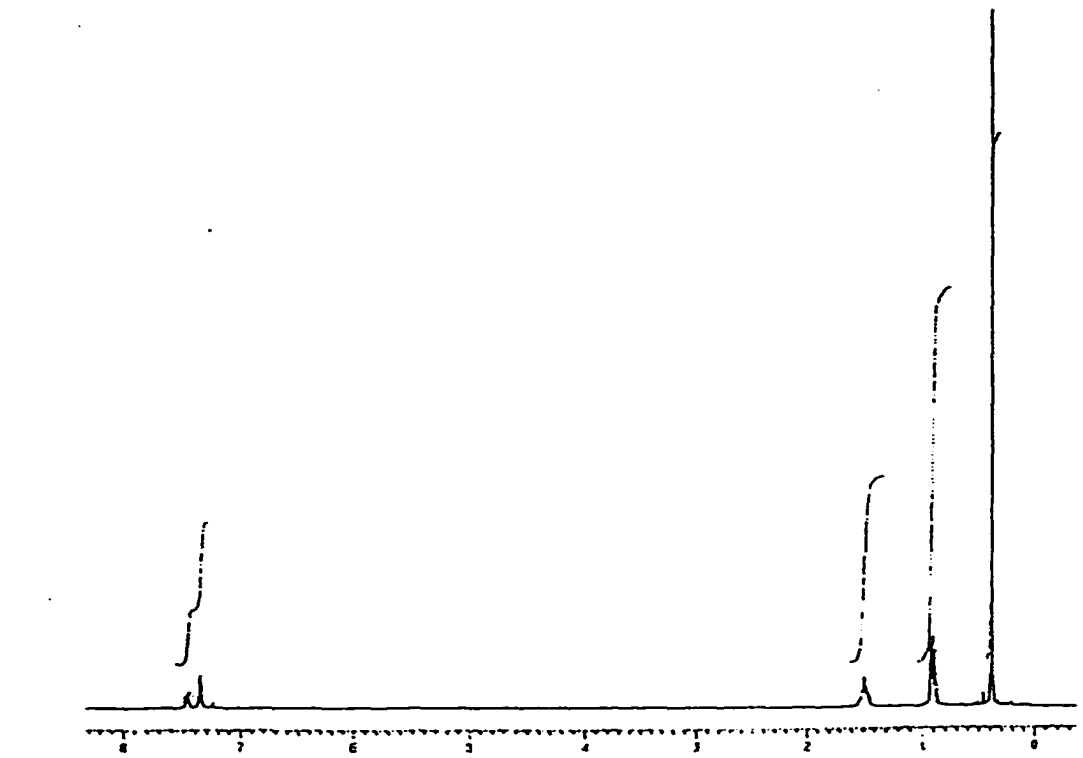
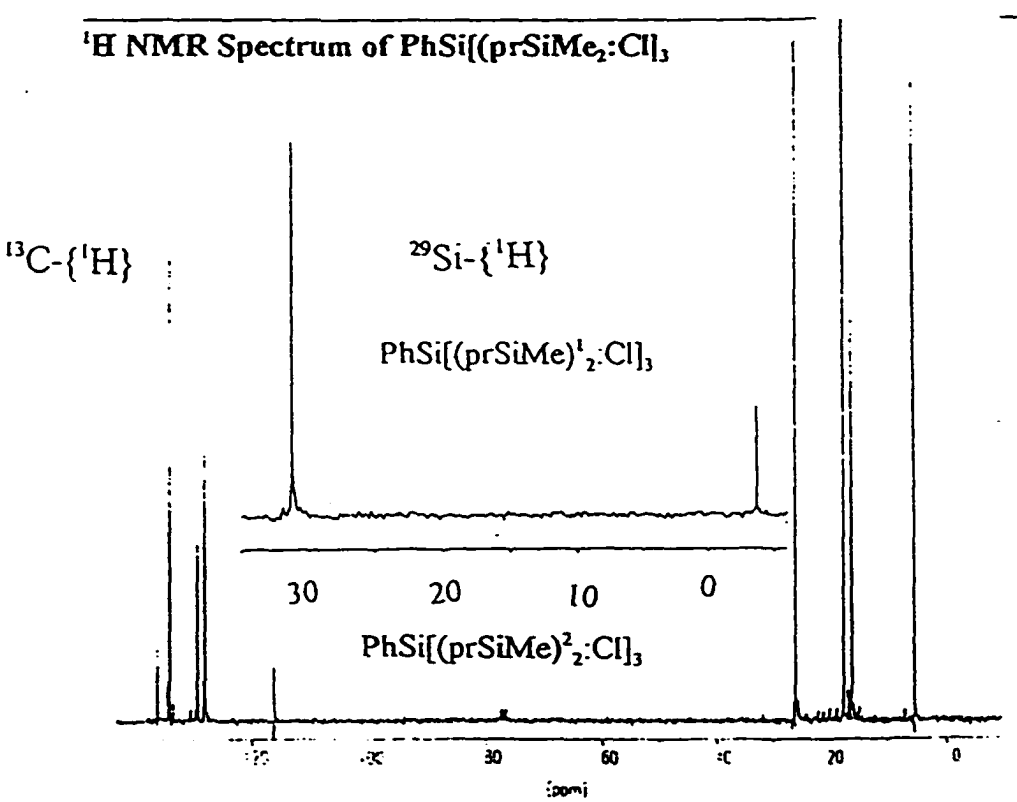
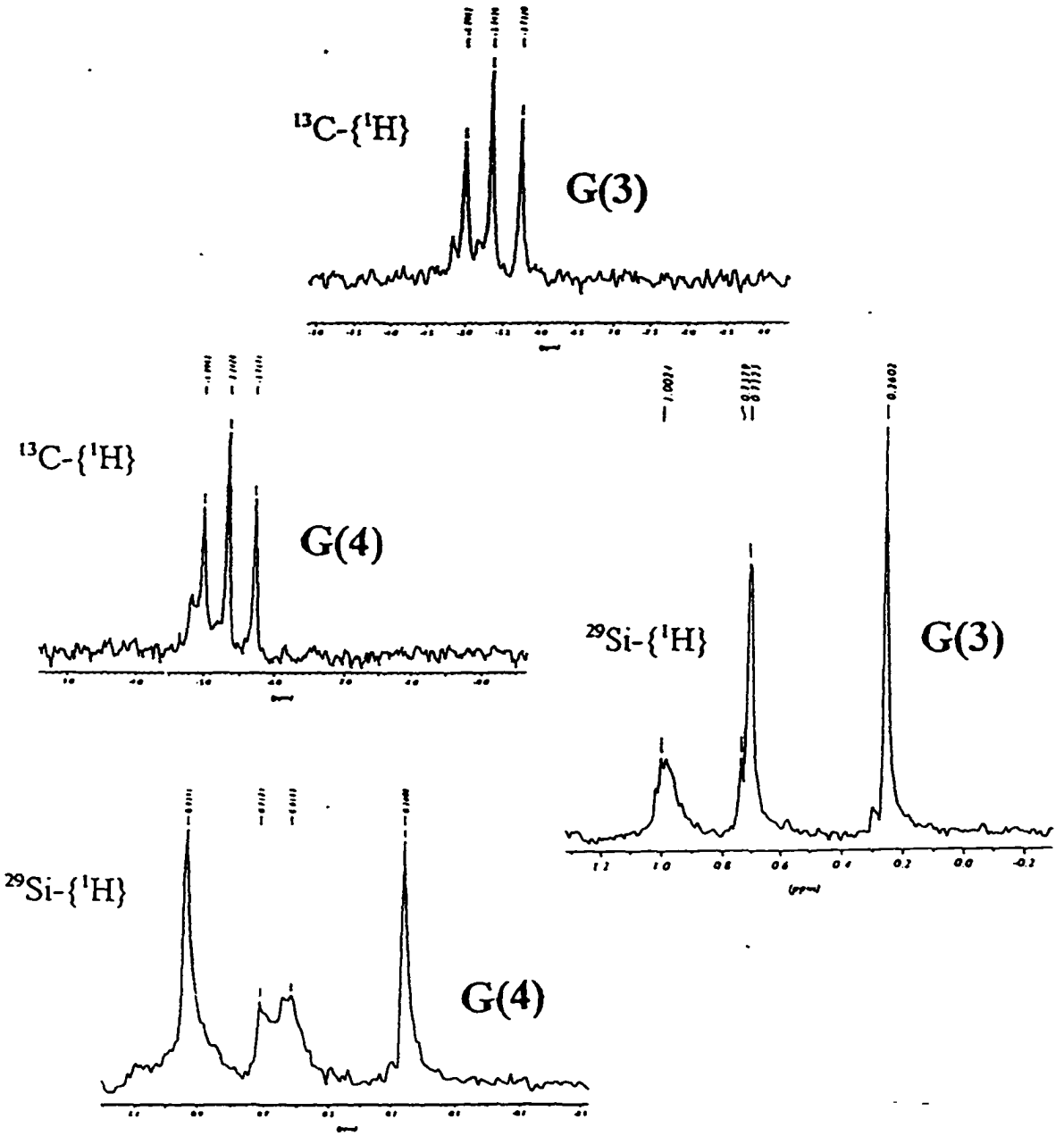
APPENDIX A

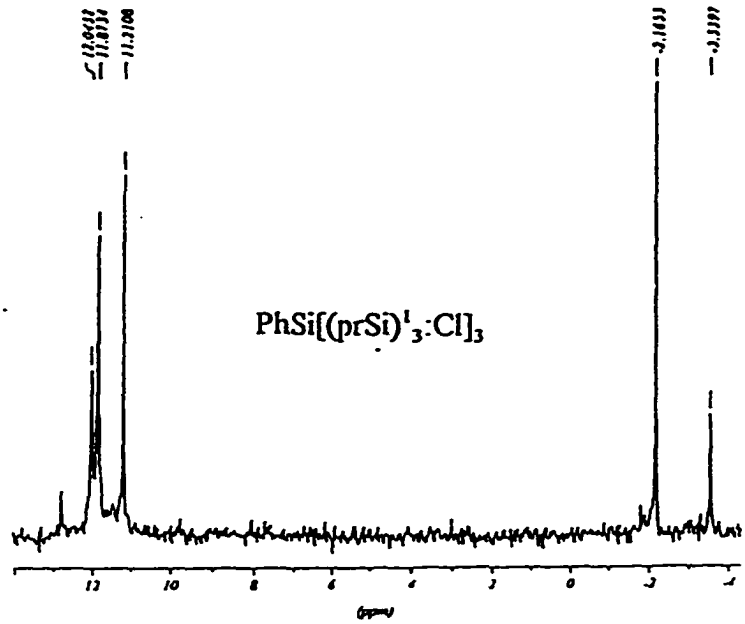


^{1}H NMR Spectrum of PhSi[(prSiMe$_2$:Cl]$_3$

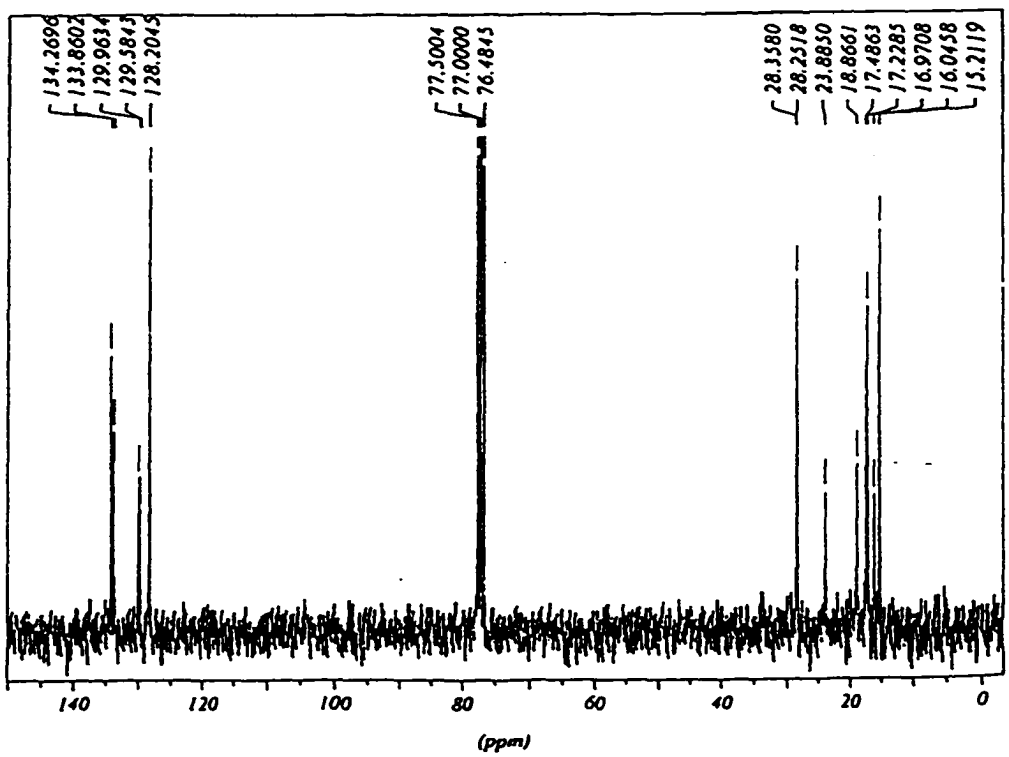




^{13}C and ^{29}Si NMR Spectra of PhSi[(prSiMe)$^{N}_{2}$:All]$_3$ Dendrimers a). N = 3 b). N = 4



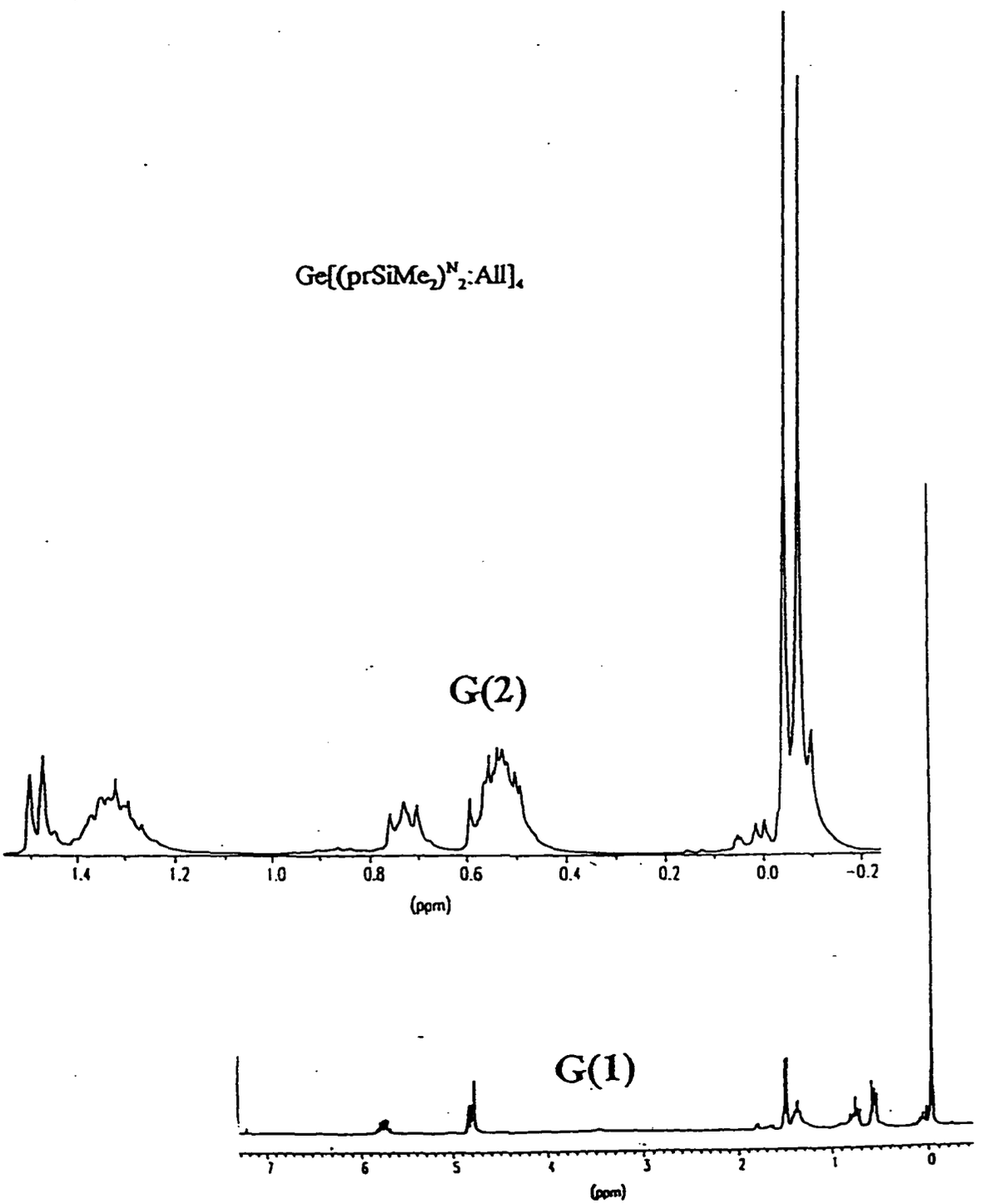
^{29}Si-{^{1}H} NMR Spectrum of Compound (20)

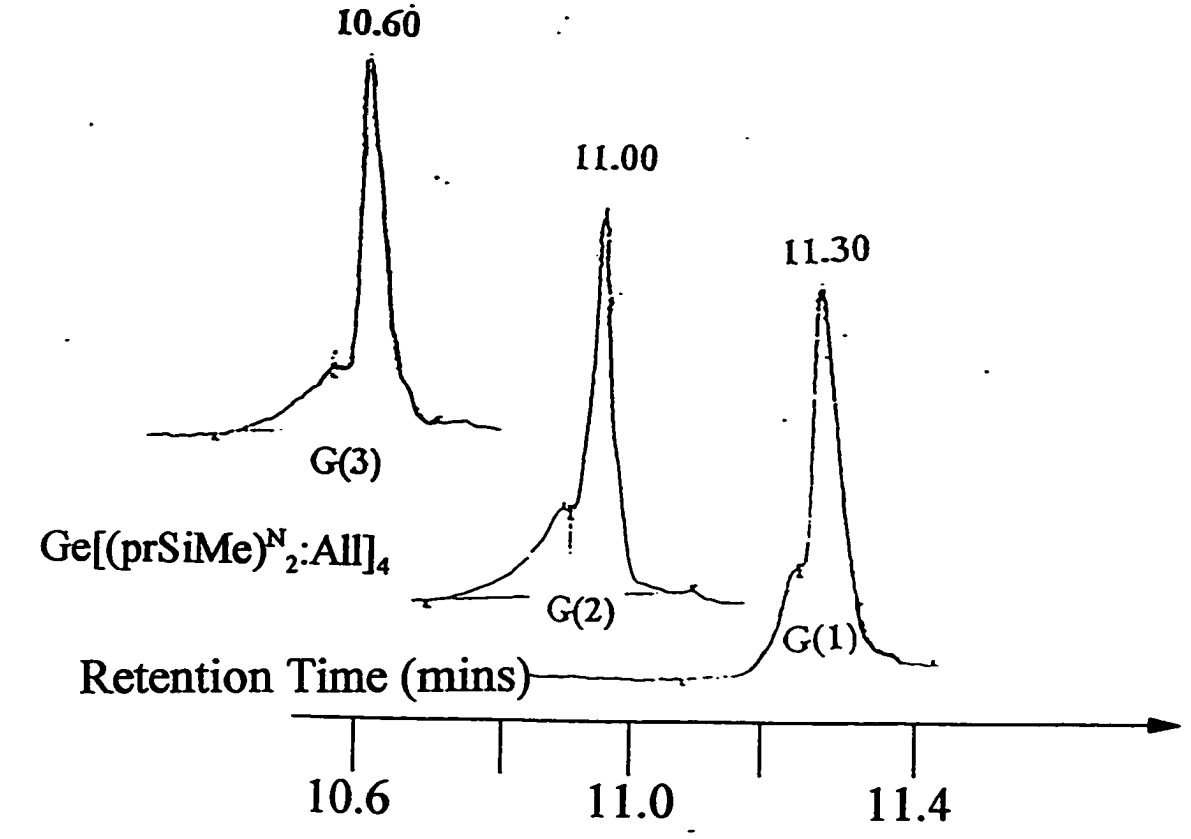


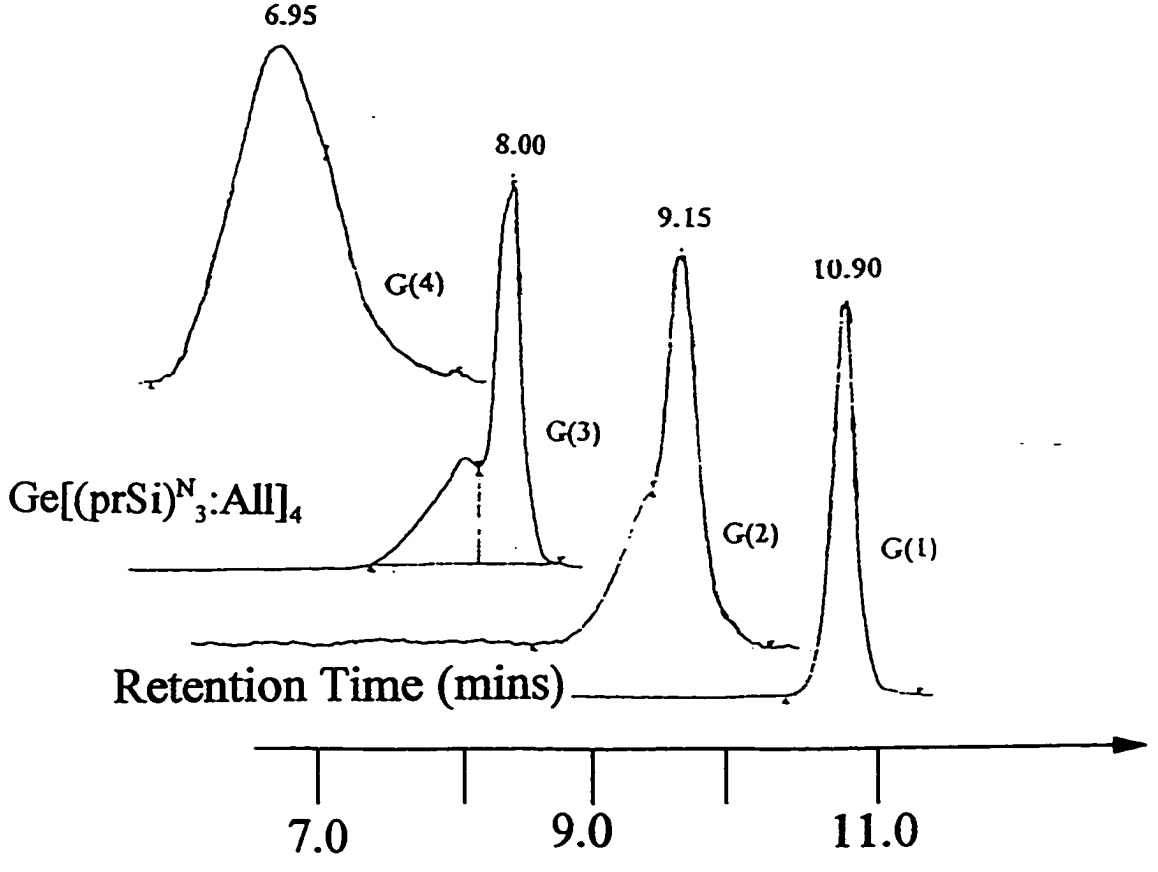
^{13}C-{^{1}H} NMR Spectrum of Compound (20)

APPENDIX B

$Ge[(prSiMe_2)^N_2:All]_4$




10.60
11.00
11.30
G(3)
Ge[(prSiMe)$^{N}_{2}$:All]$_4$
G(2)
G(1)
Retention Time (mins)
10.6
11.0
11.4


6.95
8.00
9.15
10.90
G(4)
G(3)
Ge[(prSi)$^{N}_{3}$:All]$_4$
G(2)
G(1)
Retention Time (mins)
7.0
9.0
11.0