Synthesis and Functionalisation of Organosilicon Dendrimers

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Thesis for PhD degree

Declarations

I, Pamela Ilene Coupar, hereby certify that this thesis has been composed by myself, that it is a record of my work and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

Signed   Date 4/5/2001

I was admitted to the Faculty of Science of the University of St. Andrews under the Ordinance General No. 12 on the 1st October 1996 and as a candidate for the degree of Ph.D. on the 1st October 1997.

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Abstract

This thesis describes the synthesis and attempted synthesis of various dendrimers using a variety of core molecules and branching molecules. Several different reactions were tried: hydrosilation, hydrobromination, Grignards, organolithiums, reduction, corner-capping and amination. Based on the knowledge gained from the synthesis of the dendrimers, some of them were then functionalised to be either silanols or aldehydes. Attempts to make silanols used either high dilution with acid or base or a catalytic reaction using palladium on charcoal. Two types of aldehyde synthesised were aromatic and aliphatic. The aromatic aldehyde was made via a hydrosilation reaction whereas the aliphatic dendrimer was made via a hydroformylation reaction. Attempts were made to synthesise carboxylic acids from the aldehydes using potassium permanganate. Incompletely condensed polyhedral oligomeric silsesquioxanes (POSS) molecules were synthesised. These molecules were corner-capped with either vinyl- or allyltrichlorosilane. Also mentioned are attempts to make mixed POSS species (POSS molecules with alternating R groups) via either homo- or heterofunctional means. Cubic silicates were also synthesised. Some cubic titanasiloxanes were made by corner-capping incompletely condensed POSS molecules with cyclopentadienyltitaniumtrichloride. Attempts were made to synthesis cubic titanasiloxanes using either homo- or heterofunctional means. Catalysis with some of the titanasiloxanes formed was tried. Also mentioned are attempts to synthesise porous polymers from some of the dendrimers that were made either by hydrosilation or hydrolysis. Characterisation was mainly done using ^{1}H and ^{13}C NMR, the polymers

were tested for porosity using multipoint BET and were also characterised using ^{13}C and ^{29}Si CP NMR. Two of the silsesquioxanes were characterised using X-ray crystal diffraction techniques.

Abbreviations used

CPA/Speier's catalyst	Hexaplatinic acid solution in propan-1-ol
Karstedt's catalyst	Platinium-divinyltetramethylsiloxane complex in xylene
LAH	Lithium Aluminium Hydride
THF	Tetrahydrofuran
POSS	Polyhedraloligomericsilsesquioxanes
NMR	Nuclear magnetic resonance spectroscopy
IR	Infra red spectroscopy
Cp	Cyclopentadienyl group
BuLi	Butyllithium
Tlc	Thin layer chromatography
CHN	Carbon hydrogen nitrogen
DMF	Dimethyl formamide
BET	Brunauer, Emmett and Teller isotherm
ETS	Engelhard Corporation Titanosilicates
JDF-L1	Jilin Davy Faraday Layered Solid Number 1
MFI	Mobil Five
HMS	Hexagonally ordered mesoporous silica
TS	Titanosilicate
TBHP	tert-butyl hydrogen peroxide
MMA	methyl methacrylate
2,6-DTBP	2,6-di-tert-butyl phenol

CP	cross polarisation
MAS	magic angle spinning

Acknowledgements

I would like to thank the following people: Emily and Professor Cole-Hamilton for their help with the hydroformylation reactions. Melanja Smith for help with the NMR spectra. The rest of the Morris group past and present plus my friends and family for their support and anyone else who I have forgotten to mention or who knows me.

The Story of the Stone by Cao Xueqin

Translated by David Hawkes, Chapter 2 p70

Bored by his enforced idleness, Yu-cun took to going for walks as soon as lunch was over whenever the weather was warm and sunny.

One day a desire to savour country sights and sounds led him outside the city walls, and as he walked along with no fixed destination in mind, he presently found himself in a place ringed with hills and full of murmuring brooks and tall stands of bamboo where a temple stood half-hidden among the trees. The walled approach to the gateway had fallen in and parts of the surrounding wall were in ruins. A board above the gate announced the temple's name:

THE TEMPLE OF PERFECT KNOWLEDGE

While tow cracked and worn uprights at the sides of the gate were inscribed with the following couplet:
(on the right-hand side)

As long as there is a sufficiency behind you, you press greedily forward.
(on the left-hand side)

It is only when there is no road in front of you that you think of turning back

'The wording is commonplace to a degree', Yu-cun reflected 'yet the sentiment is quite profound. In all the famous temples and monasteries I have visited, I cannot recollect having seen anything quite like it. I shouldn't be surprised to find that some story of spectacular downfall and dramatic conversion lay behind this inscription. It might be worth going in and inquiring.'

But when he went inside and looked around, he saw only an ancient, wizened monk cooking some gruel who paid no attention whatsoever to his greetings and who proved, when Yu-cun went up to him and asked him a few questions, to be both deaf and partially blind. His toothless replies were all but unintelligible, and in any case bore no relation to the questions.

Yu-cun walked out again in disgust. He now thought that in order to give the full rural flavour to his outing he would treat himself to a few cups of wine in a little country inn and accordingly directed his steps towards the near-by village. He had scarcely set foot inside the door of the village inn when one of the men drinking at separate tables inside rose up and advanced to meet him with a broad smile.

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Chapter 1
Background

In recent years, the chemistry of silsesquioxanes and dendrimers has been growing due to the potential uses of these molecules in catalysis (as supports) as well as other areas. For instance some metallosiloxanes have been used as either models of catalysts or as catalysts themselves as they mimic metals supported on silica e.g. the titanasiloxanes.

1.1 Dendrimers

1.1.1 History

Dendrimers are tree-like molecules, which were first suggested by Melville in 1944 but it was not until 1978 that Vogtle reported the first synthetic analogues. Since Vogtle synthesised his low molecular weight polyamine dendritic systems, which he referred to as "cascade molecules", the field has produced a variety of different systems including: arborols (trees with alcohol branches) (Newkome 1985) [1], organo-silicon dendrimers (Rebrov 1989) [2], hydrocarbon dendrimers (Moore 1991) [3], inorganic (Balzani 1992) [4] and organometallic (Astruc 1992) [5] dendrimers. The most characteristic features of dendrimers in contrast to linear and branched polymers are the absence of entanglements and the low solution and bulk viscosities, especially for higher generations that approach spherical geometry [6]. They have a very regular and controllable pattern of branching and are monodisperse i.e. all molecules have exactly the same molecular weight, structure and dimensions, unlike hyperbranched molecules or polymers [7]. More recently a dendrimer has been made on a cylindrical support [8].

1.1.2 Synthesis

There are two main ways of synthesising dendrimers and these are referred to as the divergent and convergent methods. There is also a combined method that uses the concepts of both of these methods [9].

1.1.2.1 Divergent method

The divergent method has been referred to as "genealogically directed synthesis", by Tomalia, since it transfers molecular level information from the initiator core to each generation [10]. This method of synthesis starts at the initiator core and is built up layer by layer, by using repetitive reaction steps that introduce new branching sites [11]. The process of growth is fully controlled by the core functionality and the functionality of the branching sites [11] (see Figure 1.1 for an example). To avoid loop or bridge formations in the dendrimer, a very high excess of reagents is needed [11]. The layers are called generations and there is a limit to the number of these generations described by the De Gennes dense-packing model. The De Gennes model states that after a certain generation surface congestion occurs and causes defects.

$$A_Z = A_d/N_Z \ \alpha \ r^2/N_cN_bG$$

Where A_Z is the surface area per terminal group

z is the number of terminal groups

A_d is the total surface of the tree

N_Z is the number of surface groups per generation

r is the radius of the tree

N_c is the number of core branches

N_b is the number of branches at each generation

and G is the number of generations

Since $A_Z \ \alpha \ 1/G$, A_Z decreases as the number of generations G increases. Generations that occur after the "dense-packed" generation (when A_Z reaches the cross-sectional area corresponding to the van der Waals radii) have defects [9].

1.1.2.2 Convergent method

The convergent method was developed independently by Hawker and Frechet and by Miller and Neenan. It involves two stages, repeated coupling of protected/deprotected branch cells to produce a focal point functionalised dendron followed by a divergent core anchoring step to produce various multi-dendron dendrimers [10] (see Figure 1.2 for an example).

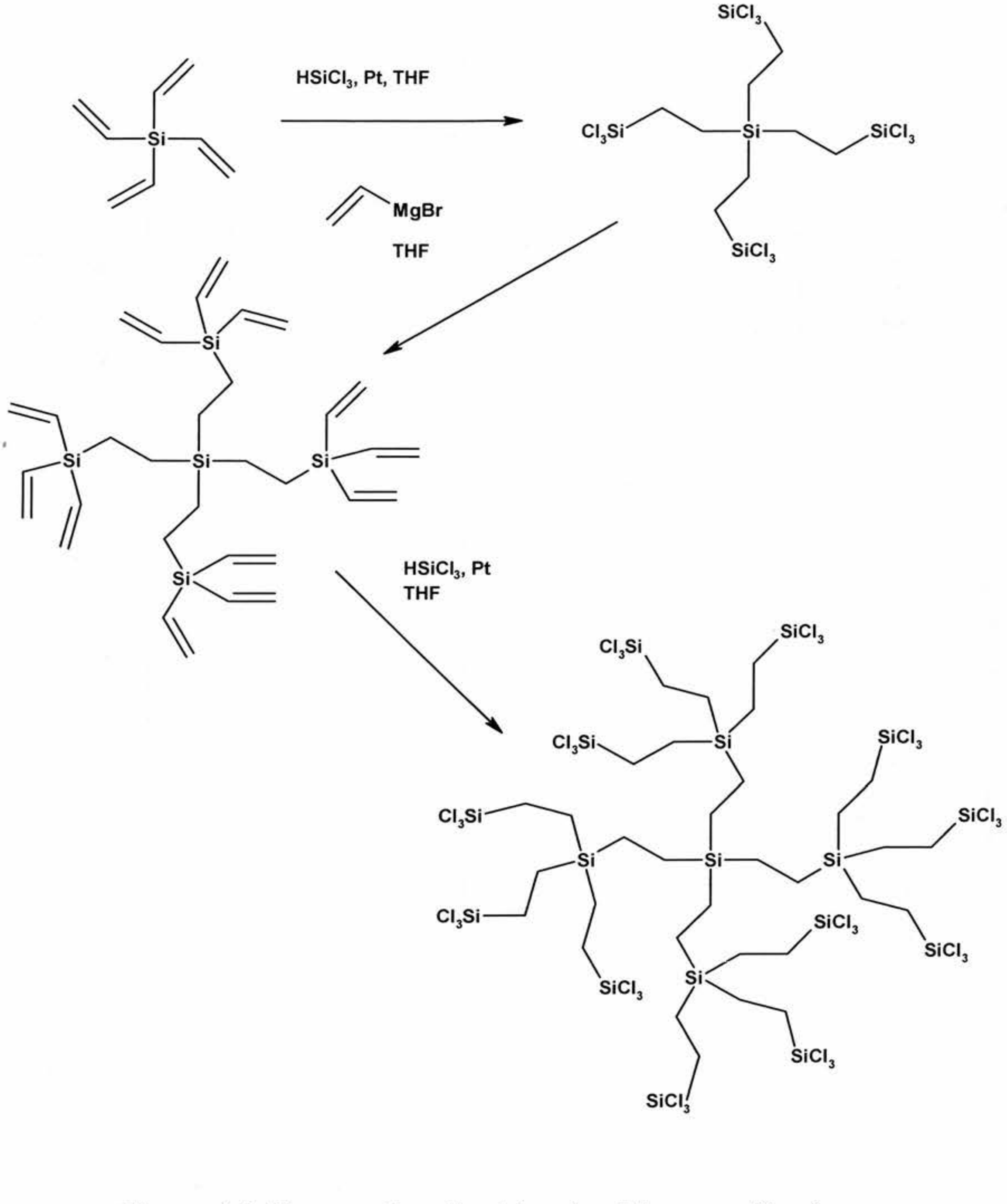

Figure 1.1 Divergent method for dendrimer synthesis

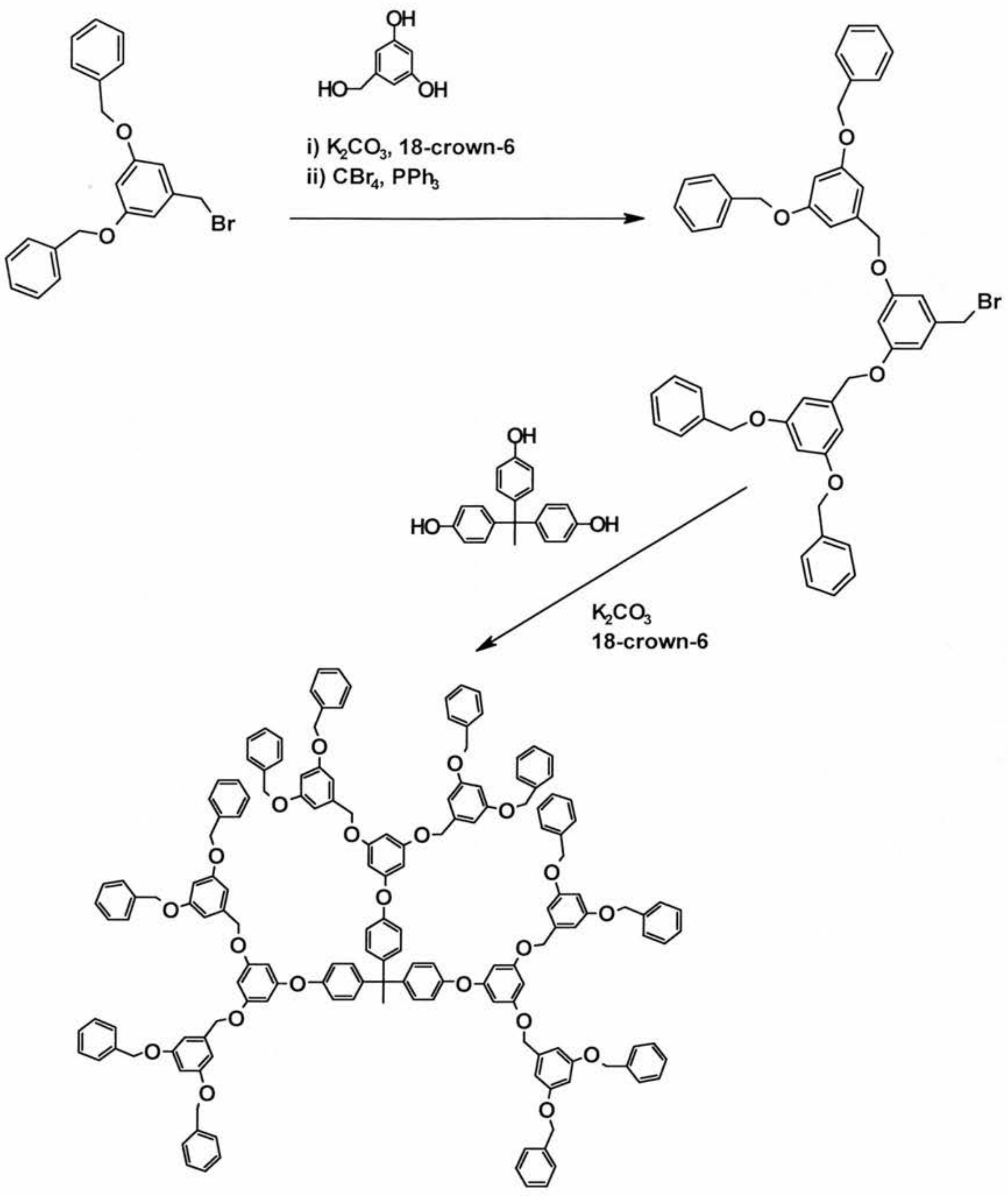

Figure 1.2 Convergent method for dendrimer synthesis

A comparison of the methods shows that in the divergent approach the dendrimer grows layer by layer from the "inside out", while, in essence, the convergent approach is the reverse: the dendrimer appears to grow "outside in" [7]. In the divergent approach the number of generations is restricted by De Gennes. The convergent approach also suffers from steric hindrance, at the focal point (as opposed to the surface c.f. the divergent method) if the dendrons are large enough this results in low reactivity [11]. It is important in both methods that all the reactions and transformations proceed with very high selectivity and yield [7].

1.1.3 Uses

Dendrimers have been utilised in the fields of catalysis, biology and also as viscosity modifiers.

1.1.3.1 Catalysis

The advantages of having dendrimers with a catalytic function are that the dendrimer can be covered with many catalytic sites and therefore could induce a large number of catalytic reactions. Since dendrimers can be designed to be soluble they have some advantages of homogeneous catalysts, e.g. faster kinetics, and they have the added bonus of being large enough to be filtered out by ultrafiltration and hence used again [12].

Silane dendrimers functionalised with aryl nickel(II) complexes have been effectively used in catalysing the Kharasch addition of polyhalogenalkanes to olefinic double bonds (see Figure 1.3). The catalytic sites are hydrophilic, and this causes easier separation and recovery of the catalyst. The organometallic sites are on the edge of the dendrimer and have structures that are consistent with the monomolecular complexes that can be used for this type of reaction. The structure of the organometallic portion is known to be highly effective for this type of reaction. Using dendrimers as a support for the aryl nickel(II) complex has the advantage of minimised leaching of the catalyst. The catalytic activity using the dendrimer catalyst is 20 to 30% less than that of the monomeric organometallic complexes but the catalyst recycling possibilities may make up for the decrease in activity. The optimum catalytic performance may be improved with other dendrimer ligands [13a]. The reaction produces a clean regiospecific formation of the 1:1 addition product without polymerisation of the alkene or production of C_2Cl_6 from CCl_3 radical dimerisation [13b]. Small organophosphine dendrimers containing palladium have also been used to catalyse the electrochemical reduction of CO_2 with rates and selectivities similar to monomeric catalysts [14].

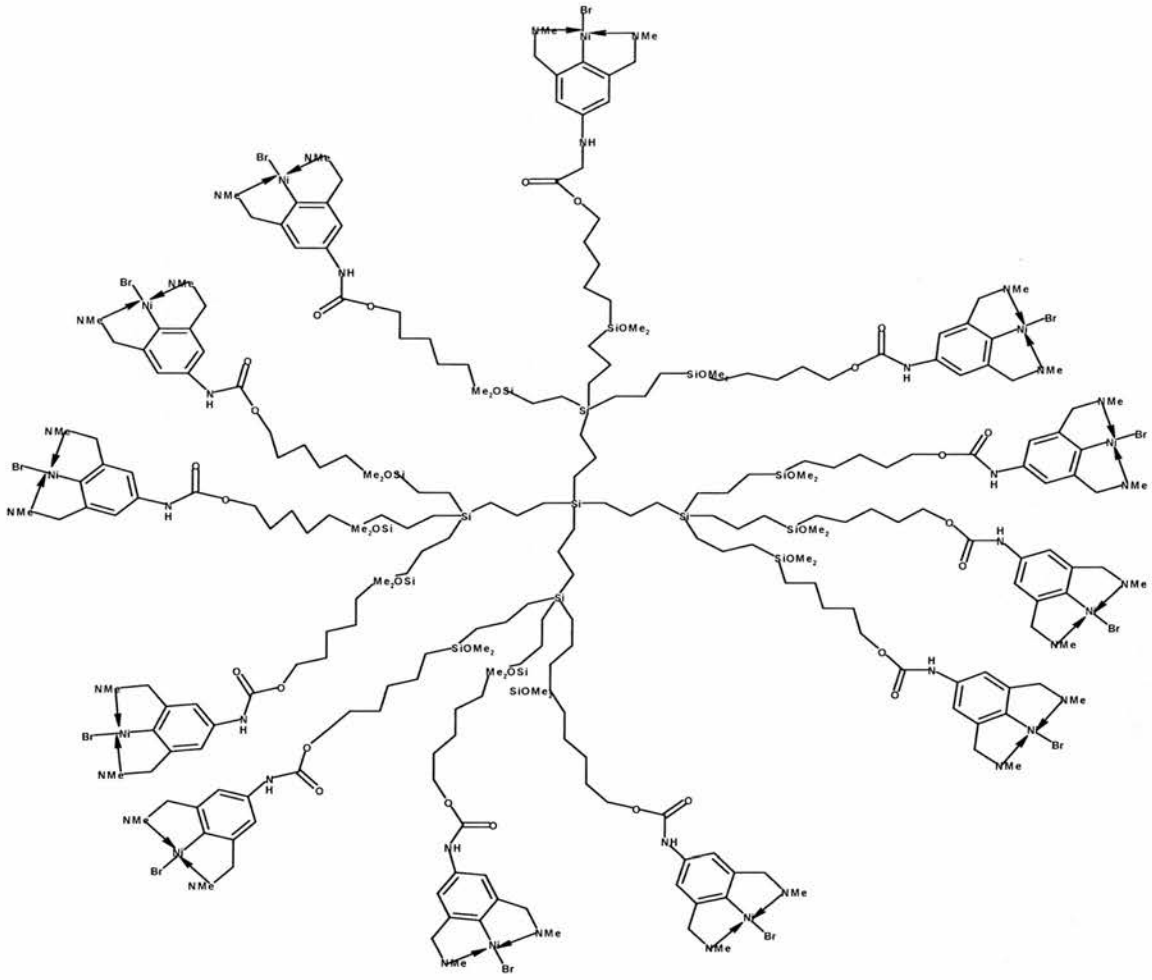

Figure 1.3 Polysilane dendrimer containing 12 diaminoaryl complexes

Dendrimer catalysts have been prepared where the catalytically active site is at the focal point of the dendrimer as opposed to being on the surface. The asymmetric dendrimers produced catalysed the enantioselective diethylzinc addition to benzaldehyde with the corresponding secondary alcohol being produced in high yields with good enantioselectivity [15]. Also biomimetic catalysis has been found with dendrimers functionalised by amine surface groups for aminolysis of phenyl esters (as in microgels [9]).

1.1.3.2 Biology

Dendrimers have been suggested as biomimics and models for certain biological species. Dendritic porphyrins have been suggested as models for electron transfer proteins like cytochrome c [16]. A variety of sterically hindered faced metalloporphyrins were designed to mimic the function of haemoproteins and chlorophylls. Later the models for these molecules suggested the importance of isolation of the metalloporphyrin nucleus for realising certain biological functions. So better models were porphyrins covalently encapsulated into a huge dendritic cage [17].

The surface behaviour of dendrimers can be compared to that of vesicles and viruses. Small viruses have many identical protein groups that are symmetrically located around their RNA and are responsible for their function [9].

Certain starburst dendrimer families mimic either regular or inverse micelles, depending on the compatibility of the dendrimer surface with water. Dendrimers also mimic certain properties of liposomes [18]. A water-soluble dendrimer with a thiosialoside surface can mimic the effect of some antibodies of glycoprotein type in order to increase the inhibiting capacities of the α-sialoside group against the cold virus [9]. It is conceivable that dendrimers could mimic the functions of large biomolecules in nature, including enzymes, antibodies, DNA, RNA and viruses [12].

Dendrimers may become valuable in gene therapy, for the transport of DNA into cells. Tomalia made dendrimers that resembled clusters of proteins called histones. In the human body, nuclear DNA is found wrapped around such clusters. The dendrimers were so close in shape and size to a histone cluster that DNA wrapped around them just as it does around the natural protein complex. Since the dendrimer's structure can be designed to home in on specific target cells, by carefully selecting the substances added to the dendrimer surface, the dendrimer-DNA combination can be directed towards specific types of cells. Current vehicles for delivering DNA are viruses but these trigger off the immune system whereas dendrimers do not [18]. Antibodies can also be delivered in this manner [18]. Polylysine dendrimers have been used as scaffolding for the presentation of certain antigen structures and could lead to new synthetic vaccine strategies, by growing appropriate polypeptide sequences upon a dendrimer scaffold [18].

Due to the biocompatibility as well as the recognition of cells, dendrimers have been used to detect and quantify viruses such as AIDS [9]. Dendrimers can also encapsulate smaller molecules and pH-dependent release of guests has been demonstrated indicating a potential use for drug release or targeting [9]. Use as fluorescent markers for pores in the nanometer range as well as the isolation of molecules to study their photochemistry and photophysics is a possibility for the dendrimers that can encapsulate smaller molecules [19]. Dendrimers have been used as linker molecules to radiolabel antibodies [9].

Dendrimers could also be used to detect dangerous biological or chemical agents in the environment, since catalytic and biosensory agents can be attached to the dendrimer surface [12].

1.1.3.3 Viscosity Modifiers

Dendrimers have properties which make them useful as viscosity modifiers in paints i.e. they can exhibit higher concentrations of functional groups, they can be less sensitive to degradation by shearing which is also useful in enhanced oil recovery and they have relatively low intrinsic viscosities even at high molecular weight [20].

1.1.3.4 Other

Dendrimers could be used as chemical sensors. A functionalised dendritic molecule that is adsorbed to a surface could be the basis of a sensor. The molecule's interaction with a chemical species in solution could be designed to trigger a change in a measurable property, such as surface conductivity or refractive index. The target application for this kind of work is in signalling application for fiber-optic communication systems [21].

Other applications forseen include; nanoscale reactors, magnetic resonance imaging agents, nano-antennae and nano-scope building blocks for more complex megamolecular structure, molecular weight or size standards, as cores for star-branched polymers, as X-ray beam scattering materials, and, in general, as materials with new and improved properties [7,22]. Applications have also been sought in agrochemistry, photocopier toners, imaging radiation therapy, anticancer properties, with potential applications in new polymers and adhesion [9].

Liquid crystal formation of highly branched spherical shaped polymers has been reported as well as luminescent and redox-active arborols [23, 24].

The homogeneity of symmetrical branch junctured dendrimer surfaces provides the unique opportunity to study the effect of congestion surface stoichiometry, reaction kinetics, surface cooperativity and surface charge repulsion [18].

Dendrimers are very versatile as well as very applicable molecules and should continue to engage the interest of research groups all over the world.

1.2 Silsesquioxane chemistry

1.2.1 History

Silsesquioxanes (have the molecular formula $(RSiO_{1.5})_n$) have been known since the 1870s when phenylsilanetriol condensation products were treated with alkali to produce soluble, relatively low molecular weight materials having the composition $(C_6H_5SiO_{1.5})_x$ [25]. The structures of silsesquioxanes can be random structure, ladder structure, cage structure, or partial cage structure [26].

In 1946, silsesquioxanes were prepared by hydrolysis of organotrichlorosilanes, but due to the insolubility of the compound, structural analysis was held up. Since then, organosesquioxane structures that have been defined crystallographically (R = Me, Et, Ph, $PhCH_2$, vinyl, allyl) were found to be analogous octameric species [27].

In 1959 the first hydridospherosiloxane (aka hydrosilsesquioxane) was synthesised by Muller, Kohne, and Sliwinski (<1% yield from $HSiCl_3$) and shown to be O_h - $H_8Si_8O_{12}$ (see Figure 1.4a). An improved synthesis of the compound was reported in 1970 by Frye and Collins (13% yield from $HSi(OCH_3)_3$). They also reported a synthesis that yielded a mixture of hydridospherosiloxanes in variable yields from $HSiCl_3$. In 1987, Agaskar, Day and Klemperer reported a modification of this procedure that gave more reproducible results and a purification procedure that produced gram quantities of four pure hydridospherosiloxanes, O_h - $H_8Si_8O_{12}$, D_{5h} - $H_{10}Si_{10}O_{15}$ (see Figure 1.4b), D_{2d} - $H_{12}Si_{12}O_{18}$ and D_{3h} - $H_{14}Si_{14}O_{21}$ [28]. Whilst this procedure improved the separation of the hydridospherosiloxanes, it did not change the method which formed the molecules [29].

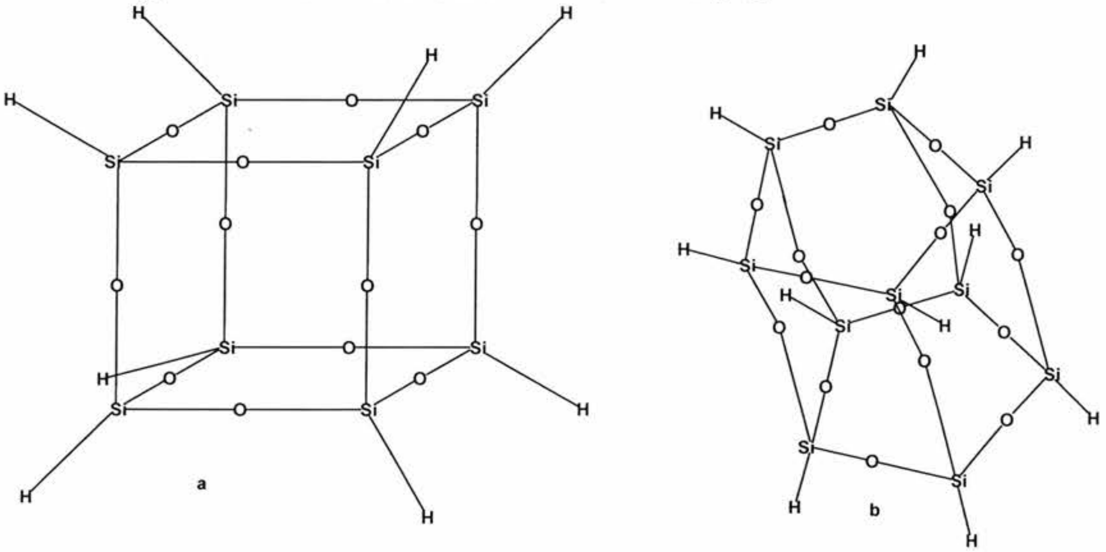

Figure 1.4 Diagram of hydridospherosiloxanes, (a) O_h - $H_8Si_8O_{12}$ (b) D_{5h} - $H_{10}Si_{10}O_{15}$.

In 1965, Brown and Vogt prepared incompletely condensed polyhedral oligomeric silsesquioxanes (POSS) molecules with R= c-C_6H_{11} by the kinetic hydrolytic condensation of cyclohexyltrichlorosilane (cy$SiCl_3$) in aqueous acetone [30]. This produced two different incompletely condensed POSS (polyhedral oligomeric silsesquioxanes) species (see Figure 1.5).

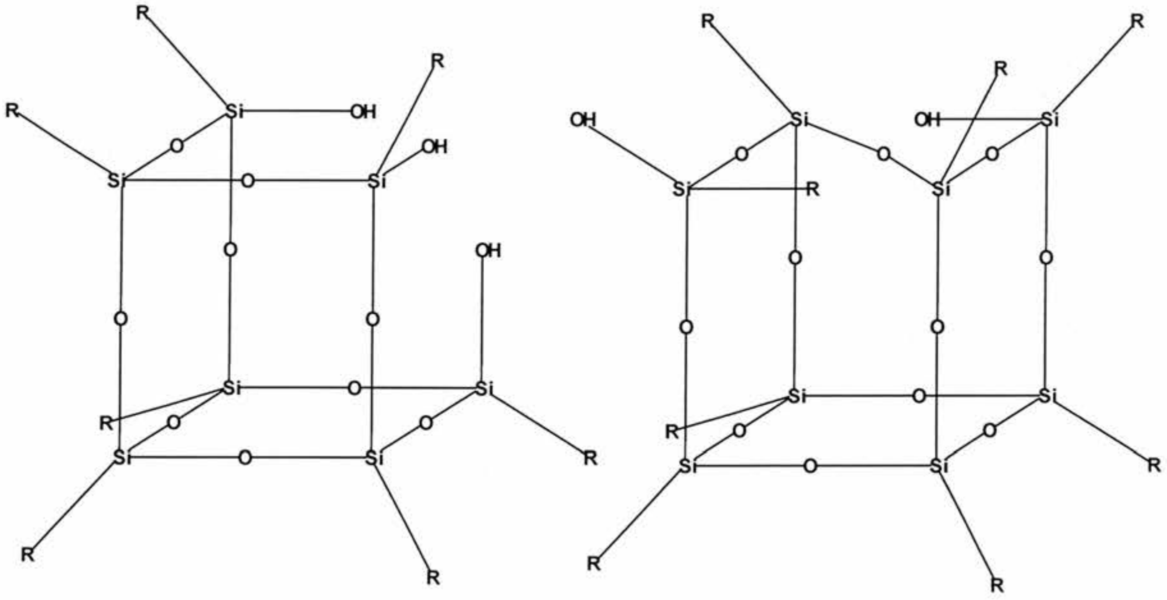

Figure 1.5 Diagram of the incompletely condensed POSS molecules formed from the kinetic hydrolytic condesation of cy$SiCl_3$.

In the early 1990s three-dimensional metallasiloxanes have been produced from silanetriols [31]. Metallasiloxanes are siloxane molecules with metal atoms incorporated into the framework i.e. they contain some Si-O-M bonds. They can be built to have alternative Si-O-M bonds or an incompletely condensed silsesquioxane can be "corner capped" with a metal atom (i.e. a metal atom can be placed in the empty vertex of an incompletely condensed POSS molecule) [31].

More recently, work has been carried out to use silsesquioxanes as dendritic cores. Feher et al. reported the synthesis of amine and ester substituted silsesquioxane frameworks that could be used as cores for starburst dendrimers [32]. Morris et al used T_8 vinyl POSS to grow dendrimers by the divergent synthesis method, using alternating steps of hydrosilation and Grignard reactions [33].

1.2.2 Synthesis

Synthetic methods for the preparation and isolation of both completely and incompletely condensed POSS molecules rely upon the manipulation of a variety of empirical reaction variables [34]. The reactions that make POSS molecules also produce a variety of other silsesquioxanes, which makes isolation of the molecule required very important. Hydrolytic condensation of trifunctional monomers $XSiY_3$, where X is a chemically stable organic group and Y is a highly reactive group, such as Cl or alkoxy, is the most common way for forming POSS molecules. These reactions depend on: the concentration of initial monomer, the nature of the solvent, the character of the substituent X in the initial monomer, the nature of the functional group Y in the initial monomer, type of catalyst employed, temperature, rate of the addition and quantity of water added and the solubility of the POSS molecules formed [35]. The formation of the POSS molecules is a multi-step process involving the formation consecutively of linear, cyclic, polycyclic and finally polyhedral siloxanes and chain growth is random [36].

1.2.2.1 Full Cages

The POSS molecule cages are denoted by a letter and a number. With silsesquioxanes the letter T is used as T denotes the type of silicon present. The number after the T tells how many of this type of silicon are present in the molecule. T denotes that the silicons are tertiary in nature i.e. each silicon is attached to three oxygens. Other letters used to describe the other types of Si-O building blocks are Q, D, M. The letter Q means that the silicon is attached to 4 oxygens and the types of molecules with mostly this arrangement are called silicates. D indicates that the silicons are connected to 2 oxygens and referred to as siloxanes, whilest the M denotes silicon only attached to 1 oxygen. The formula also denotes whether the POSS molecule is completely or incompletely condensed, by declaring if there are any hydroxyl groups present. If there are hydroxyl groups present then the POSS molecule is incompletely condensed.

1.2.2.1.1 Synthesis of T_6 (Figure 1.6)

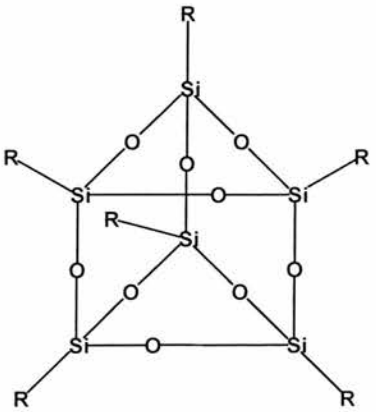

Figure 1.6 Structure of T_6 silsesquioxane

In 1955, Sprung and Guenther synthesised the first T_6 compounds $Me_6Si_6O_9$ and $(C_2H_5)_6Si_6O_9$ [36-38]. The homologous compounds $(C_7H_{15})_6Si_6O_9$ [39,40], $(C_8H_{17})_6Si_6O_9$ [39,41], $(I\text{-}C_9H_{19})_6Si_6O_9$ [39,40], $(C_6H_{11})_6Si_6O_9$ [30,42] and $(C_6H_5)_6Si_6O_9$ [43,44] were synthesised in subsequent years by the hydrolysis of the corresponding $RSiX_3$ monomers. In 1970, Smolin [45] was able to synthesise and determine the structure of a T_6 molecule with $R=O^-$ (see Figure 1.6) by reacting an ethylenediamine solution of nickel hydroxide with a 2.5% solution of silicate in ethylenediamine.

(R = c-C_6H_{11} – cyclohexyl, see Figure 1.6)

The molecule is formed as a minor product in the reaction where water is carefully added to a solution of $CySiCl_3$ in acetone and allowed to stand at room temperature. After 12 weeks 40% of the product is T_6. T_6 can be isolated by stirring the crude product mixture in 5 times its weight of pyridine then collecting the solid on a medium sintered glass funnel and washing with pyridine, then drying overnight. The reaction that forms the POSS molecules continues to precipitate the major product ($T_7(OH)_3$) for at least 3 years but useful quantities can be obtained in a few weeks by performing the reaction on a large scale [30].

(R = t-hexyl, see Figure 1.6)

This was synthesised by the following method; (1,1,2 - Trimethylpropyl)silanetriol (which the authors of the paper made), dicyclohexylcarbodiimide and dimethyl sulfoxide were heated to 120°C for 72 hours. Benzene was added to the mixture and the mixture was filtered. The filtrate was washed with water and the aqueous phase was extracted three times with hexane. The combined organic phase was dried and evaporated. The resulting solid was triturated with acetone to give the product [46].

(R = t-Butyl, see Figure 1.6)

This was synthesised by the following method; $t\text{-}Bu_2Si_2O(OH)_4$, dicyclohexylcarbodiimide and dimethyl sulfoxide were heated to 130°C for 72 hours. The reaction mixture was poured in hexane and water and separated. The organic phase was washed three times with water and then dried and evaporated. The resulting semisolid was triturated with acetone to give the product [46].

1.2.2.1.2 Synthesis of T_8 (Figure 1.7)

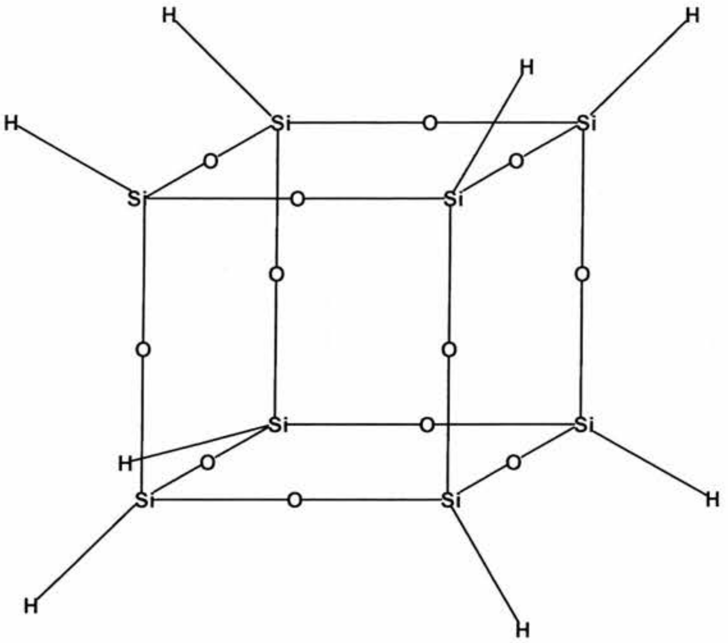

Figure 1.7 Structure of T_8 silsesquioxane

The first synthesised T_8 structure was $Me_8Si_8O_{12}$ [38,47-50] by Scott [50], but since then many more T_8 structures have been synthesised including C_2H_5 [36,37,47,49,51-53], C_3H_7 [47,49], $CHMe_2$ [49], C_4H_9 [47,49], C_5H_{11} [54], C_6H_{13} [39-41], i-C_9H_{19} [41], C_6H_{11} [47,55], 1-$C_{10}H_7$ [44], 2-C_4H_3S [56] and aryl substituents including C_6H_5 [25,42, 49, 54, 57] and 4-MeC_6H_4 [57], have all been synthesised. Silicates with saturated alkyl groups are chemically quite inert species whereas compounds with R=H [37, 58, 59] or vinyl [28, 60, 61] have the capacity for further reaction.

(R = H, see Figure 1.7)

This was prepared by Frye and Collins by reacting trimethoxysilane in a mixture of acetic acid, cyclohexane and hydrochloric acid [26].

(R = C_6H_5 – phenyl, see Figure 1.7)

This product precipitated when a mixture of phenyltrichlorosilane hydrolysate, KOH, ethanol, ether and benzene were allowed to stand [25]. Also the hydrolytic condensation of $RSiCl_3$ (R=benzyl, m-tolyl-1,3,5-dimethylphenyl) gives good yields of the corresponding octameric aryl silsesquioxanes. The catalytic hydrogenation of aryl POSS gives the corresponding aliphatic silsesquioxanes [62].

1.2.2.1.3 Synthesis of T_{10} (Figure 1.8)

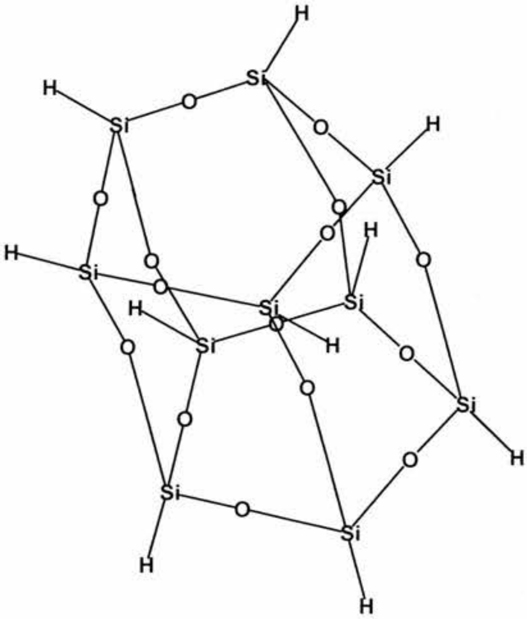

Figure 1.8 Structure of T_{10}

Only a few T_{10} silicates have been prepared and characterized i.e. $H_{10}Si_{10}O_{15}$ [28,61], Me_{10} Si_{10} O_{15} [47, 63], $(C_2H_5)_{10}$ $Si_{10}O_{15}$ [51, 53, 64], $(I\text{-}C_9H_{19})_{10}Si_{10}O_{15}$ [41], $(CH_2{=}CH)_{10}Si_{10}O_{15}$ [59], $(C_6H_5)_{10}Si_{10}O_{15}$ [25, 57]. In 1975 Hoebbel [65] found the silicate unit $\{Si_{10}O_{25}{}^{10-}\}$ in solution and made the corresponding trimethylsilylester [65] via the method of Gotz and Masson [66].

(R = H, see Figure 1.8)

There is no easy one-pot synthesis known for the preparation of $H_{10}Si_{10}O_{15}$. Its preparation is always accompanied by major quantities of $H_8Si_8O_8$ and higher silsesquioxanes [28, 61]. Frye and Collins were the first to obtain a soluble hydridosilsesquioxane containing $T_{10\text{-}16}$ oligomers in a practical yield. They prepared the oligomer by slowly adding a benzene solution of trichlorosilane to a mixture of benzene, concentrated sulfuric acid and fuming sulfuric acid [26].

1.2.2.1.4 Other silsesquioxanes

Higher silsesquioxanes exist e.g. dodecasilsesquioxane has two isomers and the possibilities for isomeric complexity increase sharply for the higher silsesquioxanes $(RSiO_{1.5})_{14\text{-}16}$. Reactions of these molecules are sparse. They are prepared by hydrolysis of their corresponding trifunctional monomer $RSiY_3$ (Y=Cl, CH_3COO). $Si_{12}O_{18}Ph_{12}$ can be hydrogenation to $Si_{12}O_{18}(c\text{-}C_6H_{11})_{12}$ [67]. Silylation of $H_{12}Si_{12}O_{18}$ and the two (D_{3h}- and C_{2v}-) isomers of $H_{14}Si_{14}O_{21}$ using the $Me_3NO/CSiMe_3$ reagent yields the new trimethylsilylated cages $[Si_{12}O_{18}](OSiMe_3)_{12}$, $D_{3h}\text{-}[Si_{14}O_{21}](OSiMe_3)_{14}$ and $C_{2v}\text{-}[Si_{14}O_{21}](OSiMe_3)_{14}$.

Also there exists silsesquioxanes that have an extra vertex present in their framework which have been obtained as side products in the synthesis of other silsesquioxanes. However, they appear to be as yet totally uninvestigated [68].

1.2.2.2 Partial Cages

1.2.2.2.1 Synthesis of $T_7(OH)_3$ (Figure 1.9)

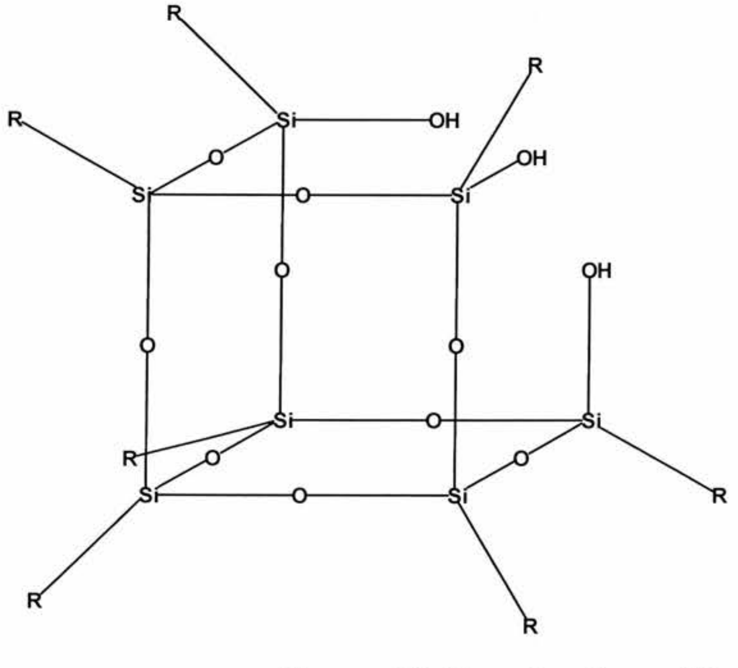

Figure 1.9 The structure of $T_7(OH)_3$

(R = c-C_6H_{11} – cyclohexyl, see Figure 1.9)

This product is the major product of the reaction where water is carefully added to a solution of cy$SiCl_3$ in acetone and allowed to stand at room temperature. It is separated from the other two minor products of the reaction by stirring in 5 times its weight of pyridine, filtering through a medium sintered glass funnel, pouring into 5 times its volume of ice cold aqueous HCl, filtering, stirring in an excess of water, filtering and washing with copious amounts of water, drying overnight, dissolving in a minimum amount of hot diethyl ether, filtering and then the volume of solution is reduced whereby the product wanted precipitates out. After 12 weeks 45% of the product is T_7, further filtrations after the same time has elapsed give 62% of T_7 and 77% of T_7 respectfully [30].

(R = c-C_5H_9 – cyclopentyl, see Figure 1.9)

This product is formed when water is cautiously added with vigorous stirring to a solution of c-$C_5H_9SiCl_3$ and acetone and refluxed for several days. It is filtered and the filter cake is stirred in acetone, filtered and dried. Next the crude product is suspended in 20 times its weight of pyridine and stirred overnight then filtered again. The solution is then poured into an equal volume of concentrated HCl mixed with crushed ice. The product is collected on a Buchner and washed with copious amounts of water and dried overnight [69].

(R = c-C_7H_{13} – cycloheptyl, see Figure 1.9)

This product is produced when distilled water is added cautiously with vigorous stirring to a solution of c-$C_7H_{13}SiC_{l3}$ in acetone. The solution is refluxed for 3 days, before being cooled giving a white gelatinous precipitate that is triturated with acetone and filtered. The filter cake is washed with acetone and air-dried. The minor product formed in this reaction is removed by extraction with CH_2Cl_2 and the product $T_7(OH)_3$ is re-crystallised from hot $CHCl_3$ [69]. There is also a room temperature version that produces this product with a longer reaction time.

1.2.2.2.2 Synthesis of $T_8(OH)_2$ (Figure 1.10)

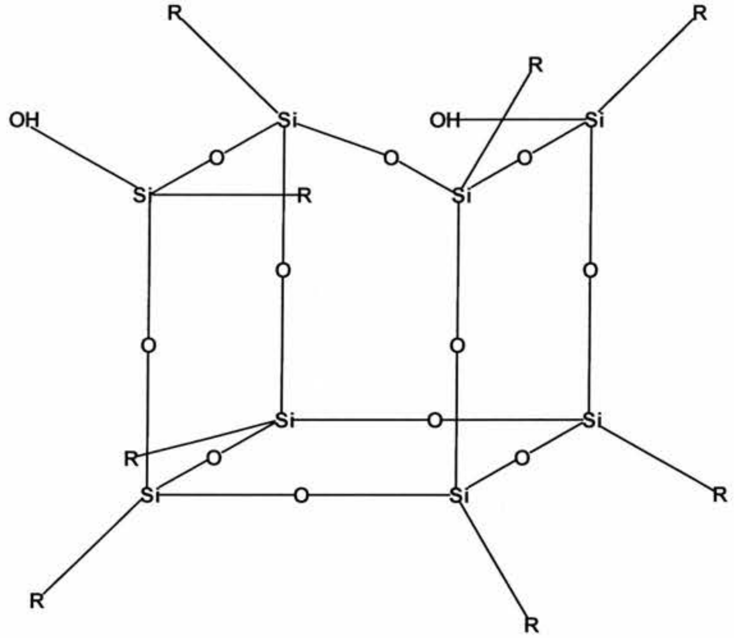

Figure 1.10 The structure of $T_8(OH)_2$

(R = c-C_6H_{11} – cyclohexyl, see Figure 1.10)

This is the other minor product of the reaction involving the production of T_6 and $T_7(OH)_3$. After $T_7(OH)_3$ is filtered off, the remaining solution is evaporated to dryness and then re-crystallised from a minimum amount of hot chloroform [30].

1.2.2.2.3 Synthesis of $T_6(OH)_4$ (Figure 1.11)

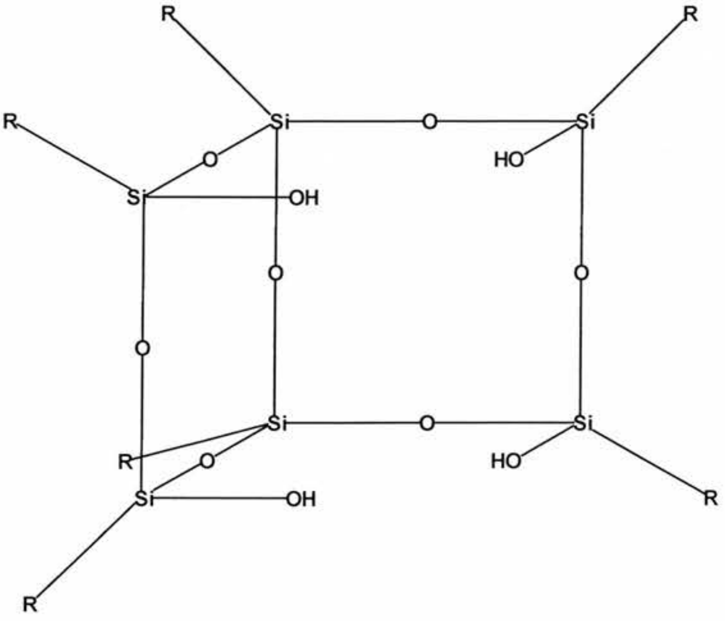

Figure 1.11 The structure of $T_6(OH)_4$

(R = c-C_7H_{13} – cycloheptyl, see Figure 1.11)

This product is produced as the minor product in the formation of $T_7(OH)_3$. The room temperature reaction gives a better yield to this product i.e. 7%. Water is added cautiously with vigorous stirring to a solution of c-$C_7H_{13}SiCl_3$ in acetone in a bottle. The bottle is sealed with a screw cap and allowed to stand at room temperature. A white precipitate forms after 24 hours and is accompanied by gel formation after 1 week. The solution is decanted after 6 weeks to leave a gelatinous white solid, which is triturated with acetone and filtered. The filter cake is washed with acetone and air-dried. $T_6(OH)_4$ is extracted from the powder with CH_2Cl_2. The extracts are carefully layered with acetone to slowly crystallise the product [69].

1.2.3 Possible Applications of POSS species

1.2.3.1 Catalysis

1.2.3.1.1 Models of catalysts

Polyhedral organosilsesquioxanes can be used to model silica surfaces, information has been gained on reaction pathways, for instance, surface sites possessing three (or more) adjacent siloxy groups may play an important role in the chemistry of silica and silica-supported catalysts [70]. Modified silica surfaces are also known to be useful in ion collection, drug delivery agents, silane coupling agents, heterogeneous hydrogenation catalysts [71], inorganic polymer fillers [71], SiO_2 films used in semiconductor technology [73, 74], in the deposition of dielectric, semi-conducting and metallic layers, as volatile element-organic compounds (EOCs) [75, 76] and they have been used extensively as the stationary phase in chromatography [77, 78]. Metallasiloxanes are good models for metals supported on silica since they are structurally similar to the surfaces and they have been found to mimic the role of these catalysts. Hence they are useful in unravelling the reaction mechanisms for such catalytic conversions [31]. $H_8Si_8O_{12}$ has also revealed important information on the mechanism of substitution reactions at silicon [27].

Corner capping of incompletely condensed POSS molecules with metals, and other metallasiloxanes have become good models for homogeneous and heterogeneous catalysts. They model metal oxides and transition metal complexes supported on silica as well as monomeric homogeneous catalysts [79, 80]. Also the metals in the metallasiloxanes make them more thermally stable [81]. Since Feher placed a zirconium atom into the corner of a POSS molecule it seems that the size of the metal is not important [82]. Lanthanides have also been placed into the corners of POSS molecules [83].

Mo corner capped POSS molecules have a catalytic function since they catalyse olefin metathesis. It may even be possible to make a chiral chelating silsesquioxane to effect stereospecific metathesis reactions including ring-opening metathesis polymerisation [84]. Cr- and V- containing silsesquioxanes were prepared by reacting CrO_3 and $(n\text{-}PrO)_3VO$ with the incompletely condensed POSS molecules; they had no catalytic function but were good models for the catalysts of olefin polymerisation [26]. Later Feher managed to make the vanadium-containing silsesquioxanes catalyse ethylene polymerisation by ensuring that there was more vanadium-POSS monomer present in solution than vanadium-POSS dimer [85]. The vanadium-POSS monomer is catalytic but the vanadium-POSS dimer is more thermodynamically stable. The vanadium species was a good model, since the predominant vanadium species on silica is apparently a three-legged complex [86].

Ti- containing silsesquioxane has been prepared that can catalyse the epoxidation of alkenes by tert-butyl hydroperoxides. It can catalyse the somewhat difficult epoxidation of oct-1-ene very effectively [87].

1.2.3.1.2 Comparison to zeolites

Soluble aluminosiloxanes have been made which might serve as model compounds for many naturally occurring insoluble, ionic aluminosilicates (zeolites) [88]. Other models use anionic aluminosilicates, reacted from $LiAlH_4$ or $NaAlEt_2H_2$, as models for both natural and synthetic zeolites that contain alkali metal counterions in additon to the anionic aluminosilicate framework. The observed square-pyramidal geometry around the Na^+ in these aluminosilicates is very similar to the coordinated geometry of Na^+ in the sodium zeolite A [31].

Cage-shaped hydridosilasesquioxanes of the general formula $(HSiO_{1.5})_{2n}$ n=2,3 etc are appealing molecules for studying structural, electronic, and vibrational properties of silicon dioxide cage structures. Some of them maybe considered as molecular models of the building units found in infinitely extended zeolite and silicate frameworks. The molecules are suited as models for studying pore-opening vibrations, which are believed to play an important role in the dynamics and the transport in zeolites [89].

$H_8Si_8O_{12}$ and $H_{24}Si_{24}O_{36}$ can be related to the structure of zeolite A. Since $H_{24}Si_{24}O_{36}$ bears the structure of the sodalite cage, it maybe used as a link to the many zeolites in which this structure is present. I_h - $H_{20}Si_{20}O_{30}$ and O_h - $H_{24}Si_{24}O_{36}$ are parts of many silicates and zeolites and present models for many silicates and extended microporous materials [89]. Metallasilsesquioxanes (containing 3 titaniums) have been used to model metal-incorporated silica structures and metal-doped zeolites [79]. Since lanthanoid-doped zeolite catalysts are of considerable technical importance, yttrium and neodymium corner capped incompletely condensed POSS molecules have been made to model these systems [83].

An aluminosiloxane POSS molecule with cobalt carbonyl clusters attached to the Si was made to resemble a modified zeolite. This POSS molecule carried out a hydroformylation reaction showing high regioselectivity. By suitable modifications this synthetic path should prove appropriate for the design of a new generation of hydroformylation catalysts [81].

1.2.3.2 Thermal stability

In polymers, POSS units can be either of main chain (bead), side chain (pendant), or chain terminus groups depending on their functionalities [34]. The incorporation of POSS molecules into polymers and polymeric materials enhances their resistance to combustion and may also improve resistance to oxidation and degradation [34]. POSS molecules also have high temperature stability in air and good adhesion to a number of substrates. POSS molecules that have a metal in the siloxane framework have high thermal stability and conducting properties, and this would be useful incorporated into a polymer backbone [31]. Polymers have been synthesized containing ferrocenyl and silsesquioxane components [90].

1.2.3.3 Hard Blocks

The POSS component in linear systems is anticipated to behave similarly to that of a conventional hard block in hydrocarbon based polymers. Through variation of the amount of hard block and soft block incorporated into a particular copolymer, physical properties such as thermoplasticity and elasticity should be attainable in POSS-based polymers. The rigidity and mass of the POSS segment is also expected to reduce intra and inter molecular chain motions [34]. The POSS segment was found to act as a hard block and the properties observed spanned the range from non-meltable, brittle plastics to flexible thermoplastics [34].

1.2.3.4 Dentist filling material

Currently there is work being carried out in this area by Laine et al and they are trying to make new white filling material using POSS molecules. The problem with the existing polymer is that it does not adhere to the tooth well. Laine et al. are trying to functionalise four corner Si atoms in a T_8 molecule. All eight corners have been previously reacted [91] but Laine only needs four corners which is harder to accomplish [92]. Laine only needs four functional corners, since these will have to be polymerized by UV light that will attach the molecules to each other as well as the tooth. In addition, POSS molecules show excellent adhesion to a wide variety of surfaces, including dentin, and are extremely abrasion resistant. Therefore, hybrid copolymers of LC units and silsesquioxane units offer the opportunity to create single-phase copolymers that will have good-to-excellent adhesion, abrasion, resistance and high processability.

1.2.3.5 Others

POSS molecules have been suggested as nonchelating ligands, precursors to silica surfaces and interfaces, precursors to silicates, polymerisable reagents [93], protective coatings for electronic devices and other substrates and as precursors for ceramic coatings, foams, fibres and articles [94]. Functionalised derivatives of T_8 could be used as surfactants, antifoaming agents, cross-linking agents and ionophores [95].

Hydriosilsesquioxanes can be converted to silica coating for application in environmental protection and as the interlayer dielectic for integrated circuits [26] and as photoresists [27].

Phosphine substituted silsesquioxane frameworks could be used as rigid spacers to connect phosphine complexes of the late transition metals [96].

Many of the silylated spherosilicates offer the interesting possibility to become precursors of organolithic macromolecular materials [93].

T_8 silsesquioxane with liquid crystals attached to all eight silicons has been made and this combines the properties of low molar mass liquid crystals, for example low viscosity and fast response to external stimuli, with those of polymers, for example mechanical stability and robustness [97].

Several highly functionalised spherosilicates and silsesquioxanes are being used to help elucidate the mechanistic details of the sol-gel process [93].

1.3 Titanosilicate Chemistry

1.3.1 History

During the early 1980s a breakthrough was made in asymmetric epoxidation by Sharpless. He treated a mixture of commerically available titanium tetraisoproxide, tert-butyl hydroperoxide and diethyl tartrate with allylic alcohols. Prior to this discovery other transition metals had been tried (ie V and Mo) which gave a small percentage of enantiomeric excess (e.e.) [98].

In 1986, Sharpless had improved his catalyst by adding molecular sieves (zeolites with a pore size of 0.3 and 0.4 nm) that removed water during the reaction. This enabled him to use catalytic amounts, instead of stoichiometric amounts, of the titanium tartrate catalyst. It also improved the enantioselectivity (90-95% e.e.) compared to the same amount of catalyst without zeolite (39-80% e.e.) with only 50-60% conversion [99]. The 1990s have seen even bigger breakthroughs in this field with Jacobsen's manganese complexes of chiral Schiff bases. These molecules catalyse the epoxidation of alkyl- and aryl- substituted olefins with the highest enantioselectivities reported to date for non-enzymatic catalysts [100] and also for cyclic and acyclic trisubstituted olefins as substrate [101].

In 1983, titanosilicate-1 (TS-1) was synthesised by Enichem in Italy. It was found to be a catalyst for a variety of organic molecules using hydrogen peroxide as the oxidant. It is a ZSM-5 type molecular sieve with a MFI (Mobil Five) topology [102]. The problem with TS-1 is that it is a microporous crystalline titanosilicate and cannot catalyse molecules larger than its pore size of 0.6 nm (this is also an advantage in certain cases) [103].

TS-1 is unusual as a catalyst due to the by-product of oxidations using hydrogen peroxide being water, which is detrimental to conventional Ti-based catalysts. The hydrophobic nature of TS-1 favours diffusion of nonpolar substrates to the active site. Since the micropores are hydrophobic, they are believed to exclude water from the internal cavities and thus protect the active site from deactivation. The Ti atoms in TS-1 are tetrahedrally coordinated. Other first generation titanosilicates include TS-2 that has a pore size of the same order as TS-1 and has the topology of MEL zeolite. There is also Ti-ZSM-48 that is a ZSM-48 type molecular sieve [102].

Next was the development of Ti-doped zeolite β (Ti-β). This is a high silica zeolite (little or no Al i.e., 0.01%) with a three-dimensional pore system containing 12 membered ring aperatures with a pore size of the order of 0.7 x 0.7nm. Ti-β has high reactivity in aprotic solvents (unlike TS-1 and TS-2) and the large pore size makes it suitable to catalyse branched and cyclic alkenes. Higher selectivity and activity is observed using organic hydroperoxides as oxidants [102].

There is also an aluminium containing Ti-Al-β zeolite. These have Brønsted acid sites (the protons associated with the Al centres catalyse the ring opening of the epoxides) that react with the epoxides, and produce side products such as diols, aldehydes and ketones. The use of a basic solvent reduces these side reactions by poisoning the acidic centres [102].

In 1989, a family of microporous titanosilicates (generically denoted ETS standing for Engelhard Corporation Titanosilicates) was discovered in which Ti^{4+} are octahedrally coordinated. The structure of these compounds proved elusive as they were highly disordered but ETS-10 has now been solved (it contains 12 membered rings) [104]. The Ti^{4+} ions have an octahedral arrangement of O^{2-} ions, linked to the Si^{4+} (tetrahedral) ions through corner-sharing of O^{2-} ions. The net negative charge of the frameworks is compensated by Na^+/K^+ counterions. ETS-10 is a large pore hydrophilic molecular sieve whilst ETS-4 is a small pore molecular sieve whose structure matches that of the mineral zorite [102].

More recent has been the synthesis of the mesoporous siliceous materials (M41S) that are classified in three groups depending on their geometry: Ti-HMS (hexagonally ordered mesoporous silica), MCM-41 (hexagonal) and MCM-48 (cubic). The pore size in these materials varies from 1.6 to 10nm. This class of compounds can oxidise large alkenes [102].

Thomas et al and Pang et al have recently synthesised a novel layered titanosilicate of composition $Na_4Ti_{12}Si_8O_{22}.4H_20$. This compound named JDF-L1 (Jilin Davy Faraday Layered Solid Number 1) contains five coordinate Ti atoms in a noncentrosymmetric tetragonal layered structure. This is the first synthetic zeolite type material with pentacoordinate Ti. In nature there is only one mineral with pentacoordinate Ti and that is fresnoite [105]. Each titanosilicate layer is made up of small cage-type units, each of which contains 8 tetrahedral SiO_4 units and one square pyramidal TiO_5 polyhedron. Two of the layers are separated by a layer of Na^+ ions. The interlayer distance of 1.07nm can almost be tripled (to 2.97nm) by replacing the layer of Na^+ ions by amines such as monoprotonated nonylamine. JDF-L1 has properties analogous to those of aluminosilicate clays [106]. JDF-L1 in its "as prepared state" is inactive as a catalyst but when treated with dilute hydrochloric acid and aqueous hydrogen peroxide yields a catalytic material [102].

1.3.2 Synthesis

The titanosilicates are all synthesised using templates. The template is either a primary or a quaternary ammonium ion. The silicon and titanium sources are added to the previously dissolved, in solvent or acid, template. The reaction mixture is then vigorously stirred at either ambient or high temperatures. The product is filtered, washed and dried thoroughly and then calcinated at high temperatures to remove the organic template.

1.3.2.1 First generation titanosilicates

TS-1 has been synthesised by three methods. The first procedure employs silicon and titanium alkoxides as the source of Si and Ti, the second method involves an additional step for the formation of peroxytitanates by the reaction of aqueous hydrogen peroxide with a second aqueous solution containing hydrolysed titanium alkoxide. The third method uses co-precipitated amorphous TiO_2-SiO_2 in an aqueous solution of tetrapropyl ammonium hydroxide. The synthesis is carried out in the absence of alkali metal cations under nitrogen. Precautions are necessary to avoid precipitation of TiO_2 as a separated phase, which often acts as a catalytic poison in the subsequent oxidation reactions [102].

TS-2 can be prepared by similar methods to TS-1. In the case of the co-precipitation of TiO_2-SiO_2, tetrabutyl ammonium hydroxide is used as the structure directing agent for the MEL structure (instead of the tetrapropyl ammonium hydroxide as is used in the TS-1 synthesis). Ti-ZSM-48 is prepared by employing a TiO_2-SiO_2 co-precipitate and 1,8-octadiamine as the structure directing agent [102].

1.3.2.2 Ti-doped zeolite β

Ti-β is synthesised by mixing TiO_2, SiO_2, tetraethyl ammonium hydroxide, and hydrogen peroxide, followed by heating. Aluminium-containing Ti-β (Ti-Al-β) is synthesised from a mixture of tetraethyl orthotitanate, tetraethyl ammonium bromide, and silica, to which aqueous aluminium nitrate is added as the Al source. In the established synthesis, Ti-β crystallises with some Al as a framework constituent. This leads, after calcinations, to the presence of acid centres that while being useful for bifunctional acid/redox catalytic processes, have a detrimental effect on the activity and selectivity of the epoxide during the oxidation of alkenes with hydrogen peroxide. A new, reproducible procedure based on a seeding technique, afforded very high yields of Al-free Ti-β oxidation catalyst. The organic additive that directs crystallisation was tetraethylammonium hydroxide. No MTW, MFI, cristobalite or any other impurities were found in these synthetic conditions [107].

1.3.2.3 ETS-10

The synthesis of ETS-10 was carried out initially by using sodium silicate, sodium hydroxide, potassium fluoride, $TiCl_3$, NaCl, and an ETS-4 seed. However, the use of $TiCl_3$ as the titanium source gives rise to an ETS-4 impurity. The use of a cheaper titanium source such as $TiCl_4$ resulted in thermally stable ETS-10 free of ETS-4. The use of $TiCl_4$ as the source of Ti produces highly crystalline and pure ETS-10 samples within 16 hours. 4-10 days is normally required for ETS-10 but has ETS-4 impurities. In the new synthesis, highly crystalline nearly uniform cuboids of <1µm can be obtained without any detectable impurity of ETS-4 [108].

Very recently, a new method that employs a TiO_2/anatase/rutile mixture as the titanium source has been reported. Here TiO_2 is polydispersed in water to which NaOH, KF, and collidal silica are added. Vigorous mixing and heating yields ETS-10 [109].

1.3.2.4 M41S

The M41S class of catalysts are prepared by hydrogel impregnation of the precipitates with organic compounds. The gel is prepared by hydrolysis of the starting materials, before it is stored under hydrothermal conditions at 373K in a static Teflon bottle for 10 days, to form the mesoporous material [110]. Ti-HMS is synthesised by acid hydrolysis of tetraisopropyl orthotitanate and tetraethyl orthosilicate with dodecylamine as template, followed by heat treatment. Ti-MCM-41 is synthesised by a similar procedure, with a quaternary ammonium bromide as the structure templating agent. Large pore (mesoporous) silica-based molecular sieves have been prepared recently by Kresge et al [111] and Kuroda et al [112]; the former used a templating approach in which the formation of an inorganic mesoporous structure is assisted by self organisation of surfactants, the latter involved topochemical rearrangement of a layered silica precursor. Hexagonal mesoporous titanosilicates with textural mesoporosity, Ti-MCM-41 and Ti-HMS, can be prepared at ambient temperature by electrostatic and neutral assembly processes, respectively [113]. A titanium containing mesoporous material with a cubic structure, MCM-48, can be synthesised by a two-stage hydrolysis method using tetraethyl orthosilicate and tetrabutyl orthotitanate. MCM-48 may have several advantages over MCM-41, MCM-48 has three dimensional channels which should be more resistant to blockage by extraneous materials than the MCM-41's one dimensional channels [102].

In all the above cases, either Ti alkoxides are treated with silicon compounds, or TiO_2 is mixed with silica. The zeolite type compound is then prepared directly. A new method of introducing Ti centres into a zeolite type framework is by grafting titanium based organometallic compounds into the pores of MCM-41 (as the pores are large enough for this to occur). The material is prepared by diffusing a solution of $[Cp_2TiCl_2]$ in chloroform into the mesopores, followed by treatment with Et_3N to activate the Si-OH groups of the silica walls to form Si-O-Ti linkages. The final catalyst is obtained on the removal of the cyclopentadienyl groups by calcination at 550^{o}C [114].

1.3.2.5 JDF-L1

JDF-L1 is prepared by mixing tetrabutyl orthotitanate, aqueous ammonia, aqueous hydrogen peroxide, tetrabutyl ammonium bromide and fumed silica. The mixture is stirred for several hours and then heated for 10 days under pressure. After filtration, washing with distilled water and drying, a mircocrystalline powder is obtained that is known as "JDF-L1 in as prepared state". In this state JDF-L1 is inactive as a catalyst for alkene epoxidation. However, treatment with dilute hydrochloric acid and aqueous hydrogen peroxide yields the catalytic material [102].

1.3.3 Applications

Open structure meso- and microporous crystalline silicas in which some of the Si(IV) ions have been isomorphously replaced by Ti(IV) ions are often very good catalysts and of prime significance in the petrochemical industry. One of the most widely known is TS-1 for the catalytic conversion of phenol to hydroquinone and the epoxidation of styrene [105]. Interest in titanium containing micro- and mesoporous silicate molecular sieves stems not only from their catalytic performance for the oxidation of organic compounds under mild conditions, but also for their ion-exchange properties [115].

1.3.3.1 First generation titanosilicates

TS-1 catalyses the oxidation of unsaturated hydrocarbons with aqueous hydrogen peroxide (for example the epoxidation of alkenes), oxidation of alcohols to ketones, hydroxylation of aromatic hydrocarbons and the conversion of amines into oximes, the oxyfunctionalisation of alkanes, sulfoxidation of thioethers, as well as the selective oxidation of aniline to azoxybenzene using hydrogen peroxide as oxidant.

Alkanes are, to all intents and purposes, chemically inert and so the introduction of functional groups into them by oxidation has tended to require severe and unselective conditions. TS-1 is able to activate secondary and tertiary carbon atoms in alkanes, so that they maybe oxidised to alcohols and subsequently to ketones using aqueous hydrogen peroxide. The catalyst has low regioselectivity for alcohol formation but high reactant selectivity in the formation of ketones [116].

TS-1 is an effective catalyst for the epoxidation of lower olefins, such as propylene. The reaction is carried out with 30% aqueous hydrogen peroxide, under mild conditions (40°C) in methanol as solvent [117].

The activity of TS-1 arises from the presence of isolated Ti centres in the silicalite framework. These are capable of undergoing a facile coordination change and forming an active peroxo-titanium complex [113] (see Figure 1.12).

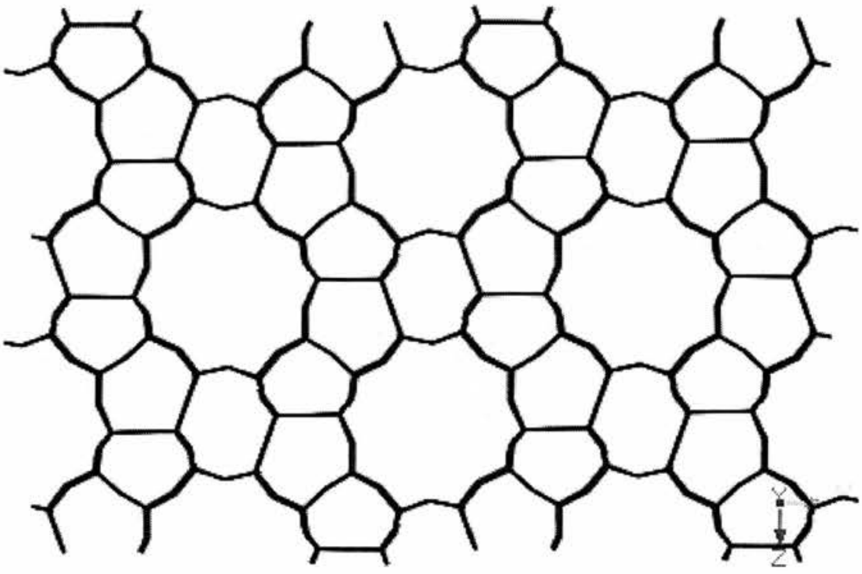

Figure 1.12 Framework structure of TS-1 (the MFI zeolite structure) showing the channels

The oxidation of aniline to nitrosobenzene with a selectivity >73% has been achieved using TS-1, and aqueous hydrogen peroxide as oxidant at 273K in a batch reaction. Homogeneous catalysts give more than 80% yields of nitroso compounds in this reaction, but the use of titanium silicate molecular sieves provides a better alternative to the problems of catalyst recovery, requirement of a stoichiometric amount of the homogeneous catalyst, separation of the products and the corrosive nature of the catalyst etc, caused by the homogeneous system. All liquid phase oxidations over TS-1 were carried out at either room temperature or reflux. Temperature affects which product is formed: high temperature favours azoxybenzene, whereas low temperature affords nitrosobenzene [118]. This effect could be due to the highly reactive nitrosobenzene being converted to azoxybenzene at higher temperatures. This could occur by either the condensation of the primary intermediate, phenylhydroxylamine, with nitrosobenzene or by the condensation of nitrosobenzene with un-reacted aniline which leads to the formation of azobenzene which is further oxidised to azoxybenzene [118].

1.3.3.2 Ti-β

Ti-β shows high reactivity in aprotic solvents such as acetonitrile. The Ti-β zeolite framework is hydrophilic, and the large pore size makes this material suitable for branched and cyclic alkenes. Also higher selectivity and catalytic activity are observed with organic hydroperoxide oxides as oxidants. Titanium substituted zeolite β (Ti-Al-β) catalyses the epoxidation of oct-1-ene with tert-butyl hydrogenperoxide (TBHP); with high selectivities to epoxide (92-100%) when the Brønsted acid sites are neutralised by ion exchange with alkali or alkaline earth metal ions i.e. when reacted with a base [117].

Al-free Ti-β zeolite shows enhanced activity and selectivity to the epoxide in the oxidation of alkenes with hydrogen peroxide in protic solvents with respect to the previously reported Ti-Al-β sample. It is the only Ti containing zeolite with three dimensional pore system of 12 membered ring channels. It is more active than the medium pore TS-1 for oxidation of cyclic and branched alkanes and alkenes with aqueous hydrogen peroxide. It shows high selectivity and activity when using organic hydroperoxides as oxidants. These are important when the desired selectivity during the oxidation process requires absence of water.

When hex-1-ene epoxidation with hydrogen peroxide was used as a test reaction, it was found that as Al content decreases, selectivity to the epoxide increases. This is due to the decreasing concentration of strong acid centres catalysing the opening of the epoxirane ring to yield the methyl glycoether by addition of one molecule of methanol (solvent). Very high efficiency for hydrogen peroxide utilisation (selectivity >95%) is obtained on Al-free Ti-β. It was found that sites other than bridging hydroxyl groups are able to catalyse the opening of the oxirane ring (could be Si-OH groups and /or centres related to framework Ti) [107]. It is shown that the Al-free Ti-β produced an enhanced activity and a much higher selectivity to the epoxide during the oxidation of alkenes in the presence of hydrogen peroxide.

1.3.3.3 ETS-10

ETS-10 is a large pore hydrophilic sieve, it is also used as a large pore molecular sieve for adsorption and ion exchange. As a result of the octahedral coordination of the Ti^{4+} ions, there is a net negative charge of two units associated with each Ti^{4+} ion, this charge is compensated by alkali-metal ions (Na^+/K^+) [108]. The double negative charge makes ETS-10 a highly hydrophilic molecular sieve with a large sorption capacity for polar molecules. This makes it eminently suitable as an adsorbant.

1.3.3.4 M41S

Due to their mesoporosity and the easy access to the catalytically active sites, this class of compounds has an advantage in selective oxidation of large alkenes. These catalysts have already shown good catalytic ability in the oxidation of large molecules such as norbornene in the presence of bulky oxidants i.e. TBHP. These materials show selective catalytic activity towards the oxidation of 2,6-ditertbutyl phenol to the corresponding quinone and the conversion of benzene to phenol [103]. Such reactions were not possible with first generation TS-1 catalysts due to the small pore size.

All mesoporous molecular sieves exhibit catalytic activity superior to that of TS-1 for the liquid phase peroxide oxidations of methyl methacrylate (MMA), styrene, and 2,6-di-tert-butylphenol (2,6-DTBP). The exceptional catalytic activity in the case of Ti-HMS, especially towards larger substrates, is attributable to the small crystallite size and complementary textural mesoporosity that facilitates substrate access to framework Ti sites. However, the recently reported hexagonal mesoporous silica molecular sieves prepared by electrostatic and neutral surfactant templating pathways offer promising opportunities for the prepartion of large pore TS-1 analogs capable of transforming larger organic molecules.

The difference between the mesoporous molecular sieve catalysts and microporous TS-1 increases with increasing substrate size. The activity difference is small for the relatively small MMA molecule, but as the substrate becomes larger, as in styrene and especially 2,6-DTBP, the difference in activity becomes much more pronounced. This result is not surprising given the much more accessible Ti-active centres embedded in the larger mesopore size frameworks of Ti-MCM41 and Ti-HMS [113].

The oxidation of cyclododecene (cis/trans = 75/25) was performed using Ti-MCM-41, TS-1 and amorphous TiO_2-SiO_2 with hydrogen peroxide or TBHP as the oxidant at 323K [110]. Cyclododecene was epoxidised to cyclododecene oxide with either THBP or hydrogen peroxide on Ti-MCM-48 and Ti-MCM-41. Preference for the epoxidation of trans isomer was obtained for both oxidants. Ti-MCM-48 has been found to be more active than Ti-MCM-41 in the epoxidation of bulky alkenes using hydrogen peroxide (bulky molecules which cannot enter TS-1, TS-2 and Ti-β). Ti-MCM48 was also applicable for the epoxidation of other alkenes i.e. pent-2-en-1-ol. The high reactivity of pent-2-en-1-ol compared to cyclododecene maybe ascribed to enhancement by the OH group [110].

Ti-, V-, Cr-, Mo-, and Mn- substituted hexagonal mesoporous silica prepared at ambient temperature by electrostatic ($S^+X^-I^+$) and neutral (S^oI^o) surfactant templating pathways are catalytically active for peroxide hydroxylation of benzene to phenol in the absence of a solvent. At high conversions, the titanium and vanadium derivatives of MCM-41 are more active for benzene hydroxylation than the HMS analogues. Nevertheless, benzene in the absence of a solvent can be oxidised primarily to phenol by transition metal substituted MCM-41 and HMS catalysts, provided that the conversions are kept sufficiently low to avoid oxidation to complete mixtures [119]. Exposure of the catalyst to atmospheric conditions does not deactivate it [120].

The Ti grafted MCM-41 epoxidises cyclohexene in the presence of tetrabutyl peroxyhydroxide giving 50% olefin conversion with 95% selectivity for epoxide formation. Inorganic microporous framework solids such as zeolites are of considerable technological importance as shape selective catalysts, ion-exchange materials and molecular sieves [104]. Grafting metallocene complexes into mesoporous silica produces highly selective catalysts. It is a shape selective catalyst with a large concentration of accessible, well spaced and structurally well defined active sites. Specifically the attachment of a titanocene-derived catalyst precursor to the pore walls of MCM-41 produces a catalyst for the epoxidation of cyclohexene and more bulky cyclic alkenes. Ti-MCM-41 can be shape selective whereas silica gels can never be shape selective. It has a high catalytic performance [114]. During use, the catalyst is rapidly deactivated, it can be regenerated by calcination at 550°C and the titanium in the regenerated catalyst has been shown to be identical to the titanium in freshly prepared catalyst (by X-ray absorption spectroscopy).

1.3.3.5 JDF-L1

After treatment with hydrochloric acid and hydrogen peroxide the material can catalyse phenol and 1-naphthol to the corresponding quinones (hydrogen peroxide is used as oxidant, and acetone as solvent). JDF-L1 is a fine catalyst for low temperature oxidations [106]. These results indicate that the material should have useful catalytic, intercalation and ion-exchange properties analogous to those of aluminosilicate clays. It converts phenol to quinone with 100% selectivity. The conversion is 20% complete after 2 hours at 60°C, whereas as-prepared JDF-L1 and powdered TiO_2 in the form of anatase are totally inactive [105].

1.4 Aims and Objectives

The aims of this project are to synthesise novel organosilicon dendrimers using various sizes of molecular cores. To functionalise the exteriors of the dendrimers in order to render them suitable for use as catalyst supports. To optimise these synthetic routes and to fully characterise the resulting materials.

The rest of the thesis will be organised as follows. Chapter 2 describes the hydrosilation reaction and Grignard reactions that were used in growing dendrimers using the divergent synthesis. Hydrosilation reaction was used in attempts to make functionalised branch ends i.e. phenol groups or ethoxy groups. The reduction of Si-Cl groups to Si-H groups is described. Hydrobromination is another reaction described as it was used on vinyl groups to provide a possible route by reacting them with amines. Organolithium reagents were tried as a different way of functionalising the Si-Cl branch ends.

Chapter 3 deals with the synthesis of silanols and aldehydes. Attempts to make silanols used three different reactions: base attack on Si-Cl groups, acid attack on Si-OMe groups and a catalytic reaction using Pd/C on Si-H groups. Aromatic as well as an aliphatic aldehyde were synthesised. The aromatic aldehyde used bromobenzaldehyde as one of the starting reagents. The bromobenzaldehyde has its aldehyde functionality protected before it is converted into a silane and hydrosilated onto a core molecule. The final dendrimer is then deprotected. The aliphatic aldehyde was made using a catalytic reaction of syngas with a rhodium catalyst on a vinyl core molecule.

Chapter 4 is concerned with the synthesis of partial and fully condensed POSS molecules. Chapter 5 outlines attempts to synthesis titanasiloxanes. Chapter 6 outlines the attempts to make porous dendrimers using either the hydrolysis reaction or the hydrosilation reaction.

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Chapter 2
Dendrimer synthesis and functionalisation

2.1 Aims and objectives

The aims of this project were to synthesise novel organosilicon dendrimers using various sizes of molecular cores. To functionalise the exteriors of the dendrimers in order to render them suitable for use as catalyst supports in the future. To optimise these synthetic routes and fully characterise the resulting materials.

Very little was known about functionalising carbosilane dendrimers prior to the start of the PhD work. Since this is a relatively new area of work, a scatter-gun approach of trying a large number of reactions was deemed as being the best way to attempt to collect evidence quickly as to which types of reaction would be best suited to be followed up.

The dendrimers were made using the divergent method of synthesis. The main disadvantage of this method is the need for repetitive modification/purification/re-modification steps in order to build out the required number of generations. For a successful dendrimer synthesis, the conversion efficiency of the reaction must be extremely high to ensure that all chain ends, or as many as possible, have reacted to form the desired product. Preferably, there must then be an easy method available to purify the product. Even when seemingly suitable synthetic methodologies are available in the literature, the unusual properties of the dendrimer cores, such as their very high steric bulk, means that it is very hard to predict which of the reactions are going to be suitable for dendrimer synthesis. The goal of this first piece of work in the thesis was then to undertake a large number of reactions using the dendrimer cores shown in section 2.2.1, and to ascertain which were suitable for further study. The criterion used for this assessment were

(a) evidence from crude NMR spectra of a high yield reaction having taken place
(b) contamination of the mixture with by-products was low with a need for only facile purification procedures.

Because of these rather tight criteria, many reactions have been discarded after a small number of attempts. This is not to say that a number of these reactions would not be suitable given further study. However, a pragmatic view was taken that it was unlikely that the correct conditions for any reaction would be found in one or two attempts unless that reaction had a fairly wide range of conditions under which it would be successful. Those where the reactions worked in the first couple of tries were then thought of as 'facile' reactions. It is these reactions that were chosen as suitable ones for further study in the following chapters. This chapter therefore contains a large number of reactions that have been deemed 'failures' under the criteria outlined above. These reactions have been included to illustrate the strategy of the approach, and many of the products have not been characterised fully.

Defects can occur when dendrimers are grown. Defects that have been detected include branch defects, intramolecular looping, intermolecular bridging, intermolecular looping and intermolecular bridging and looping [1]. 13C NMR is considered to be a good technique to investigate branch defects whereas Time of flight (TOF) matrix-assisted desorption ionisation (MALDI) is a good technique for other types of defect. Any defects that were discovered during the work would be minimised as much as possible by varying the experimental conditions of the reaction.

The two basic reactions used in growing the dendrimers were hydrosilation followed by functionalisation using a Grignard reagent. These two reactions have been shown to be successful in preparing carbosilane dendrimers based on tetravinylsilane core molecules [2,3]. The first aim of this work was to extend the hydrosilation and

Grignard derivatisation steps and show that they are general reactions that can be used for a large number of silane, silsesquioxane and siloxane core molecules under similar conditions to those previously reported. These methods produce dendrimers with either –Cl or –vinyl functionality. A range of other reactions was then used in an attempt to functionalise the branch ends with different functional groups. For example, dendrimers with chloride branch ends could be reacted with organometallic reagents, reduced with LAH or used in corner capping type reactions. Other reactions were tried on some of the products to functionalise them further i.e. amination and ether cleavage using borontribromide.

2.2 Results and discussion

2.2.1 Hydrosilation

Hydrosilation is the addition of hydrogen and silicon across a double bond and requires a platinum catalyst. Under the right conditions, addition occurs primarily at the α carbon, which is why it is used very frequently in building up dendrimers using the divergent synthesis [2 - 6]. The platinum catalysts used are Speier's catalyst, also known as CPA (chloroplatinic acid, H_2PtCl_6) and Karstedt's catalyst (a divinyldisiloxane platinum complex, see Figure 2.1). Platinum on activated carbon is used as a catalyst by one of the groups as the catalyst for hydrosilation [5].

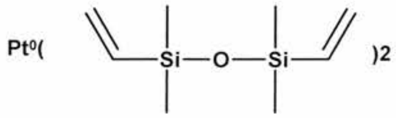


Figure 2.1 Karstedt's catalyst

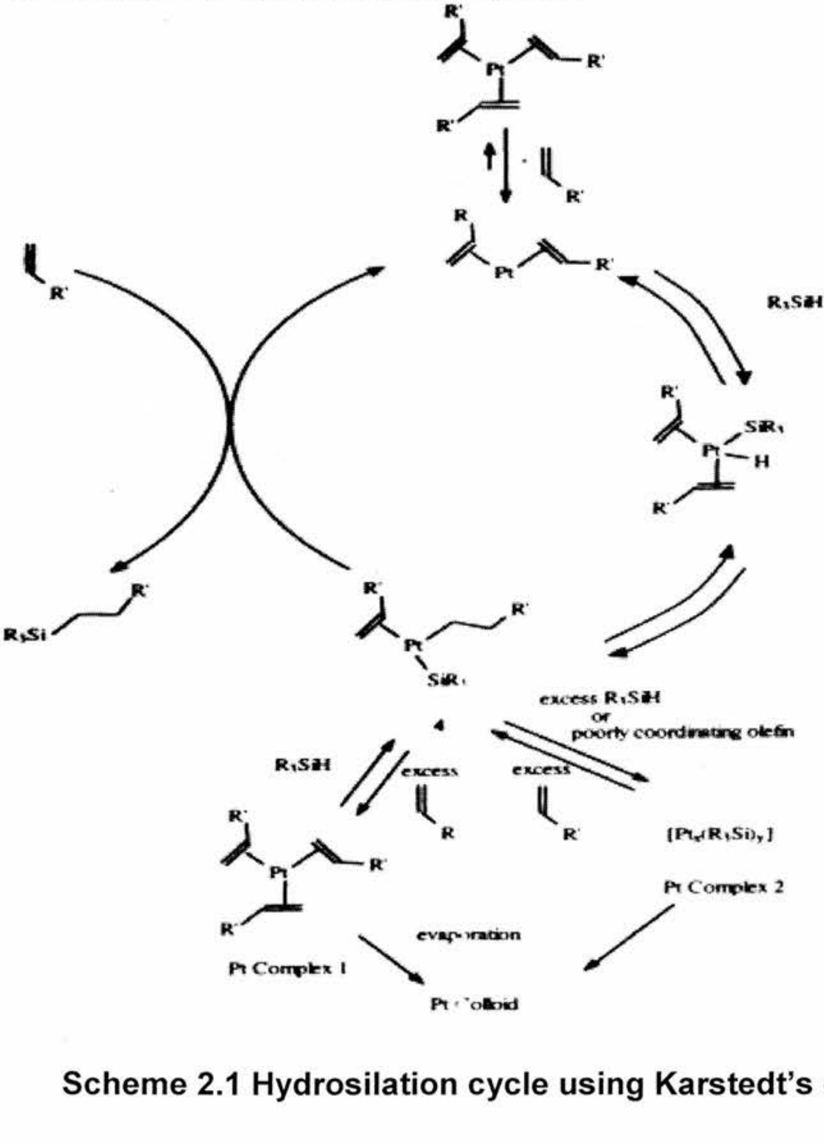
The main differences between the Karstedt's and Speier's catalysts are the oxidation states of the platinum i.e. in Speier's catalyst, the oxidation state of Pt is 2 whereas in

Karstedt's catalyst, the oxidation state is 0, also CPA is acidic whereas Karstedt's catalyst is not.

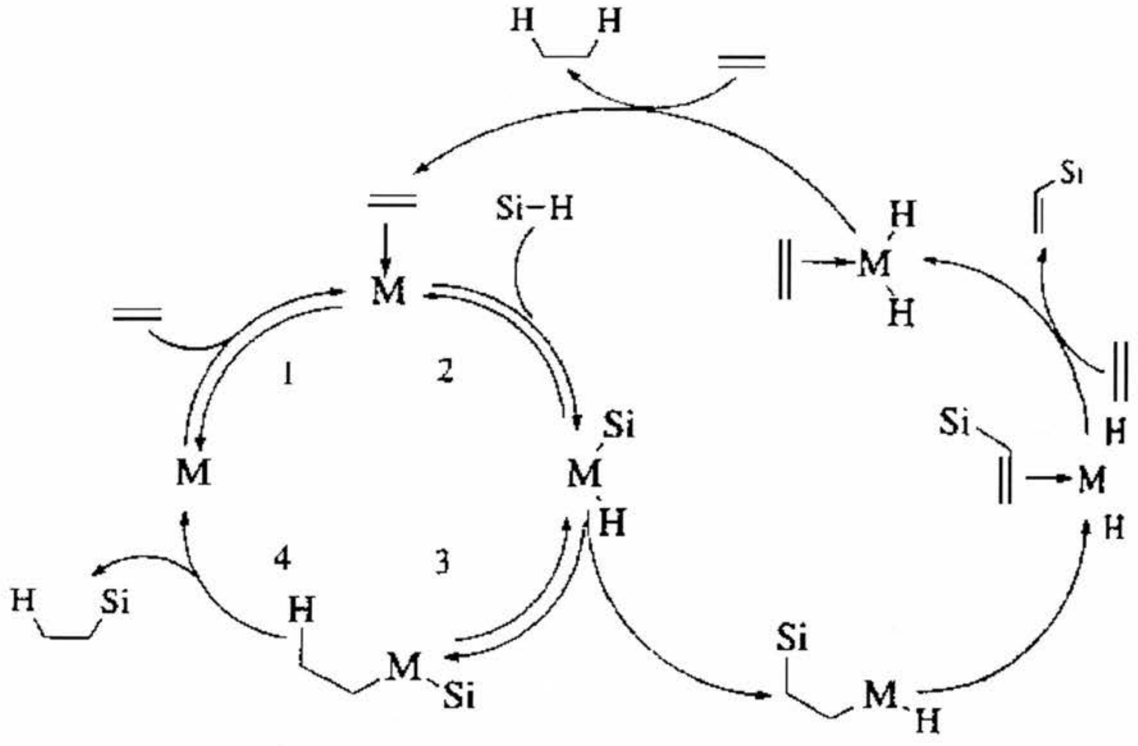
The Karstedt's catalyst is more generally believed to be the more active catalyst, an example being its use during the synthesis of higher generation dendrimers when compared to the Speier's catalyst that was used in synthesising first generation dendrimers by Seyferth [2]. The difference in activity has been reported as the Karstedt's catalyst being 10 times more active than the Speier's catalyst. In the paper by Lewis and Lewis, this was attributed (using a catalyst of similar activity to Karstedt's catalyst) to the catalyst being more heterogeneous in nature than the Speier's catalyst [7]. The paper stated that both catalysts, Speier's and the Karstedt's-like catalyst, were heterogeneous and while the Karstedt-like catalyst had a honey-combed structure, the Speier's catalyst contained active nanoparticles. Although the paper gives a source that implies that heterogeneous catalysts are more active than homogeneous ones, several researchers have mentioned that homogenous catalysts are usually more active than heterogeneous ones.

One of the main arguments to support the heterogeneous claims of the catalysts was that since mercury inhibited the catalytic process that it must be heterogeneous. King states that there is no evidence that mercury would not block a homogenous catalyst. He also states that when you get to nanoparticles you can't really say whether or not they are acting homogeneous or heterogeneously unless it can be shown that if the particle is below a certain size its activity drops off [8]. Other evidence presented for the heterogeneous nature of the catalysts involved the activation time before the catalyst became effective and that the catalyst previously activated with silane was more active than the catalyst that hadn't been previously activated with silane [7].

A newer paper about Karstedt's catalyst now says that the Karstedt's catalyst and the Speier's catalyst are precursors to the actual catalyst that explains the induction time needed for these catalysts. The nanoparticles formed are end products and not the active species. The active species is believed to be a monomeric platinium species and the cycle is similar to the Chalk Harrod cycle [9] (see Scheme 2.1 and Scheme 2.2). During the induction period, the Pt(0) precatalyst undergoes dissociation of the bridging olefin to form mononuclear, two-coordinate complex. Oxidative addition of the silane leads to formation of a Pt(II) complex, which is followed by migratory insertion of the olefin into the Pt-H bonds. The steps in the catalytic cycle are similar to those occurring during the induction period.



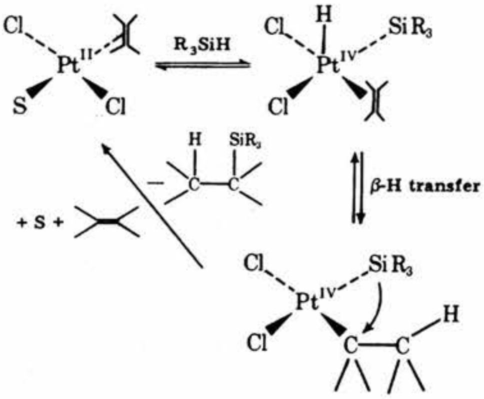
Scheme 2.1 Hydrosilation cycle using Karstedt's catalyst [9]



Scheme 2.2 Chalk-Harrold mechanism for hydrosilation

Shown in Scheme 2.2, is the Chalk-Harrold hydrosilation cycle based on their observations and on Speier's results [8]. The original mechanism involved: (1) coordination of the alkene to the metal; (2) reversible oxidative addition of Si-H to the metal-alkene bond; (3) rapid insertion of alkene into the M-H bond; and (4) irreversible reductive elimination of alkyl silane. Steps (1) to (3) are well established but there only exists one example of step (4) which involves an iron complex. This mechanism is shown on the left hand side of the loop. If the metal complex was a platinum complex then it could cycle between the oxidation states Pt^{II} and Pt^{IV} (for the Speier's catalyst) or Pt^{0} to Pt^{II} (for the Karstedt's catalyst). The right hand side of the loop explains results obtained from using $Fe(CO)_5$ as a catalyst for the hydrosilation of ethylene by triethylsilane [8].

Scheme 2.3 showes a simplified version of this cycle from Cotton and Wilkinson [10].

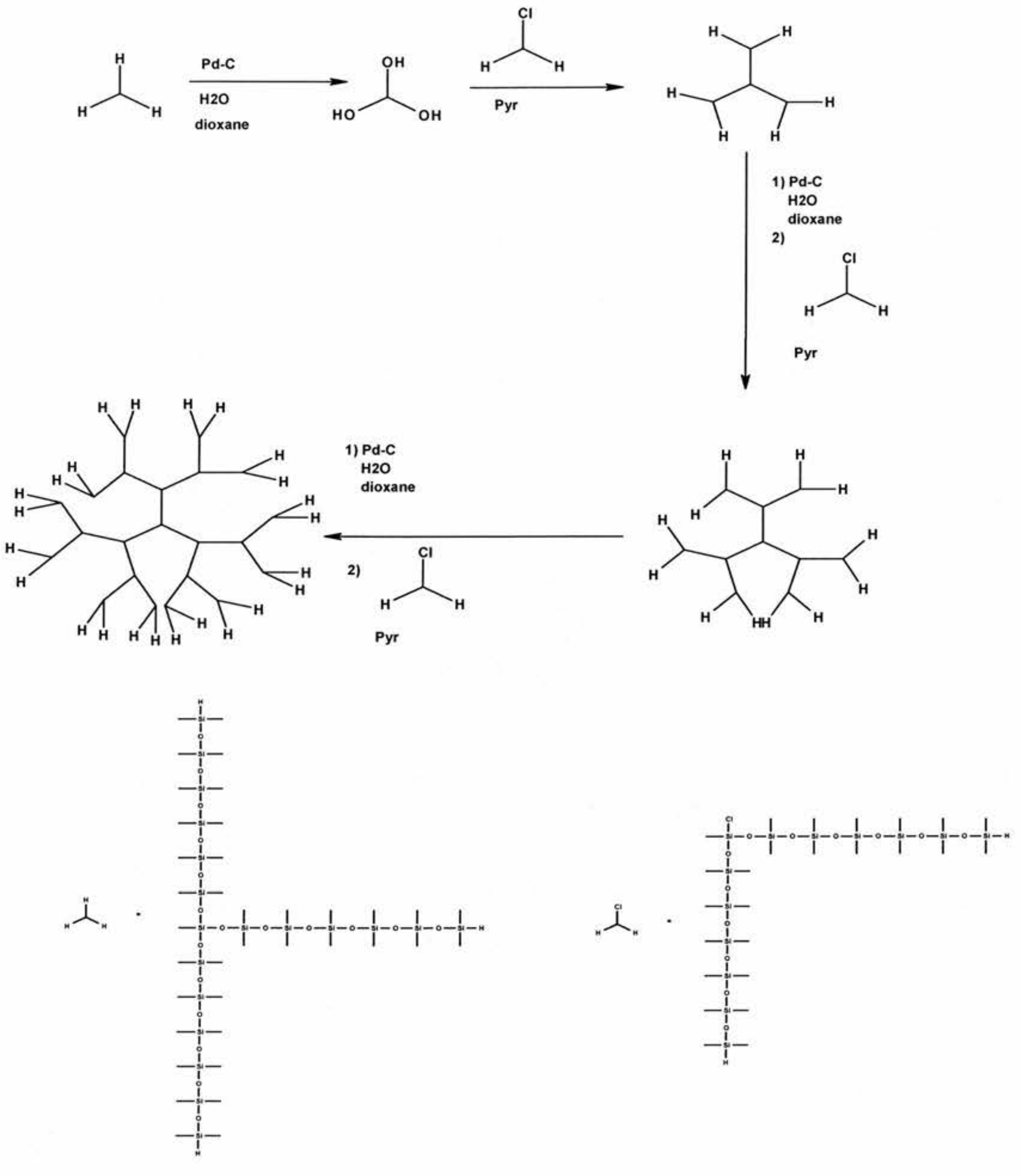


Scheme 2.3 Simplified cycle of hydrosilation of alkene by platinum complexes.

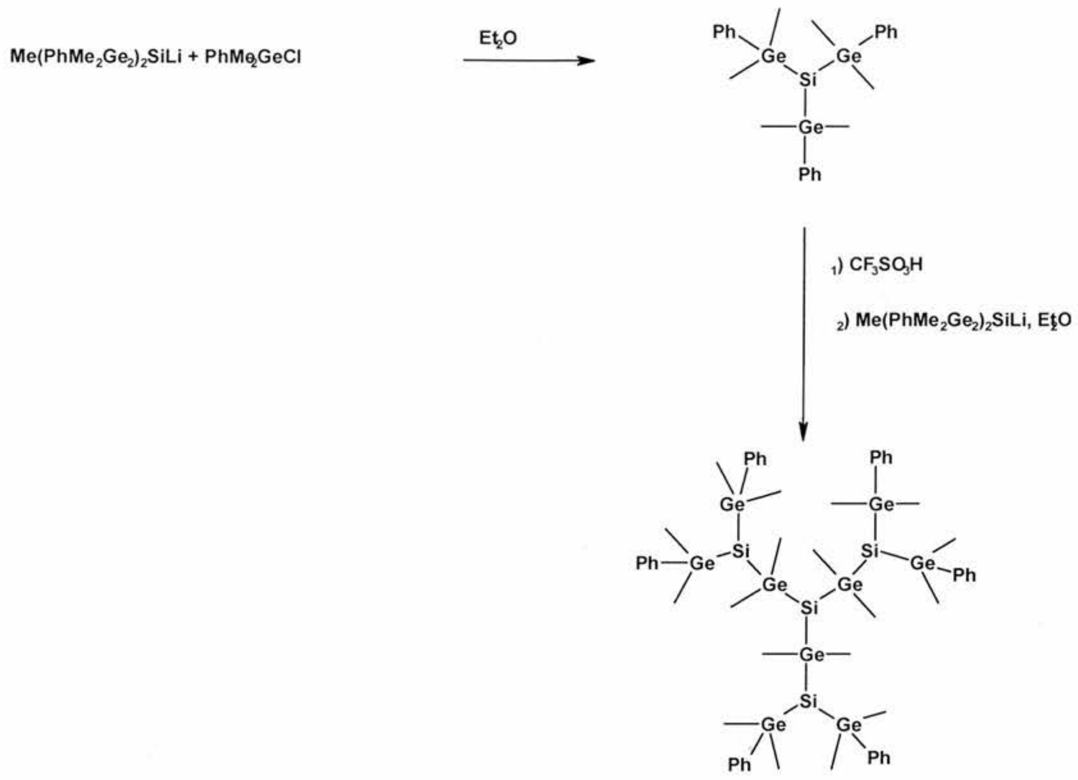
Other silicon containing dendrimers do exist in the literature, and are not built up from hydrosilation/Grignard reactions. One example is the synthesis of a high molecular-weight silicone dendrimer by Masamune [11] (Scheme 2.4). Feher at al [12], made a core for starburst dendrimers by hydrosilating $H_2C{=}CHCMe_2CH_2CO_2Me$ onto the silsesquioxane $H_8Si_8O_{12}$. Nanjo and Sekguchi synthesised a metallodendrimer possessing alternating Si-branching centres and Ge-branching chain connectors (see Scheme 2.5) [13].

An alternative reaction to hydrosilation of a silane onto a double bond would be to use the hydrobromination reaction on the double bond instead. Using a radical method, this would give a dendrimer that has bromine atoms at the ends of the branches. This approach was attempted and the results and conclusions to this reaction are presented later in this chapter.

Another alternative strategy to functionalising a double bond is hydroboration [14]. Hydroboration is similar to hydrobromination since they both produce the anti-Markownikoff product. The hydroboration product could then be further reacted to form amines, alcohols or aldehydes amongst other products depending on the chemist's desire. This strategy was not investigated.

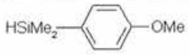


Scheme 2.4 Masamune's silicon based dendrimer synthesis



Scheme 2.5 Nanjo and Sekguichi's metallodendrimer containing silicon germanium

A variety of cores (see Figure 2.2) and branching units were used to synthesise a variety of dendrimers (see Table 2.1).

	$HSiCl_3$**	$HSiMe_2Cl$	$HSiMeCl_2$		$HSi(OEt)_3$
1	**(8)**	**(9)**	**(10)**	**(27)**	
2	**(20)**	**(21)**	**(22)**		
3	**(11)**	**(12)**	**(13)**		
4	**(14)**	**(15)**	**(16)**	**(28)**	**(30)**
5	**(17)**	**(18)**	**(19)**		
6	*	*	*		**(31)**
7	**(23)**	**(24)**	**(25)**		

* Reactions carried out by another member of the group [6]

** see Figure 2.3

Table 2.1 Hydrosilation reactions attempted. All the cores used are shown in figure 2.2.

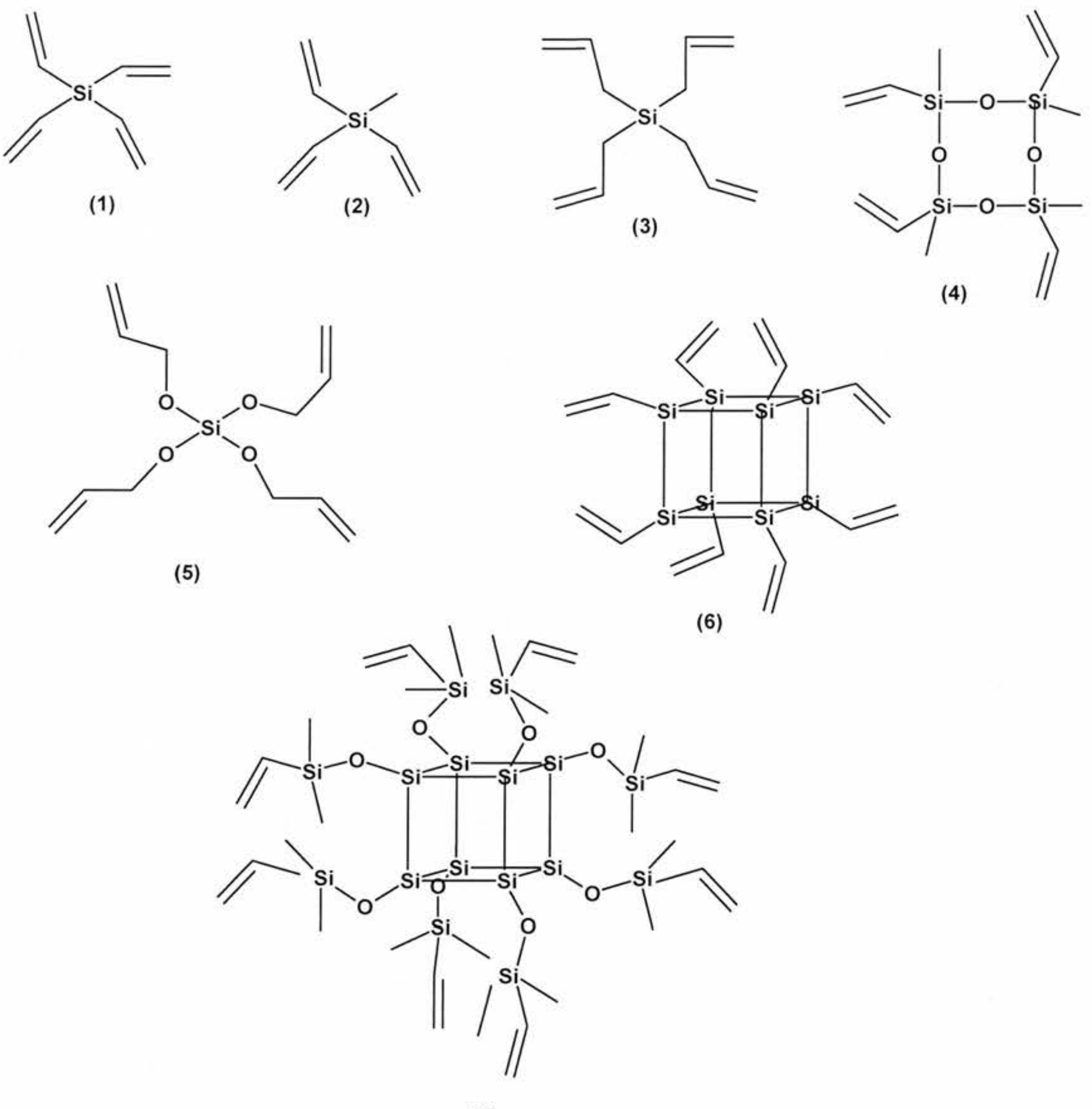


Figure 2.2 Cores used in the hydrosilation reactions:(1) tetravinylsilane (2) trivinylmethylsilane (3) tetraallylsilane (4) 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane (5) tetraallyloxysilane (6) 1,3,5,7,9,11,13,15-octavinylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (7) 1,3,5,7,9,11,13,15-octavinylsiloxypentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane. Cores (6) and (7) have oxygens missing in the cage for the purpose of clarity i.e. the Si-Si bonds of the cubes should be Si-O-Si bonds.

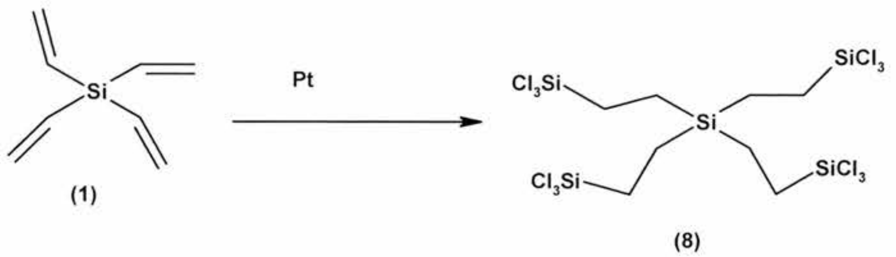


Figure 2.3 Hydrosilation reaction using tetravinylsilane as core and trichlorosilane as the branching unit.

The reactions utilising cores (1-5) with the branching units: trichlorosilane, dimethylchorosilane and dichloromethylsilane were all initially carried out in the same fashion. These reactions were carried out in air, using THF as the solvent and Speier's catalyst. The reaction mixtures were stirred for 30 minutes at room temperature before subsequently being refluxed for 8 hours [2]. The resulting products were then analysed by ^{13}C NMR to check that the reaction had gone to completion (this involved checking to see if there were any vinyl groups left in the product).

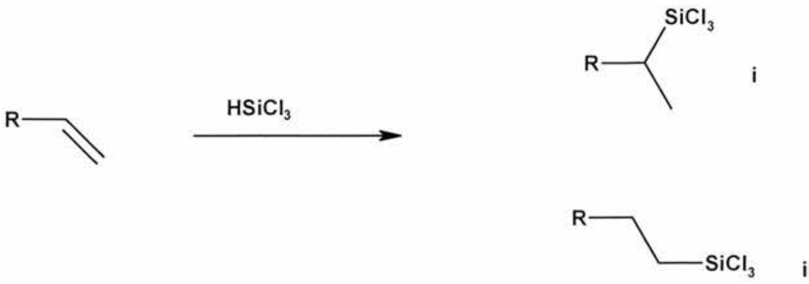
The compounds made with tetravinylsilane **(1)** as the core material, did lose all trace of vinyl groups in the ^{13}C NMR spectra whereas only compound **(13)** made from tetraallylsilane **(3)** and dichloromethylsilane produced a product with no trace of vinyl groups in its spectra. This would indicate that tetravinylsilane is more susceptible to the hydrosilation reaction than tetraallylsilane, under these conditions. This makes sense from the activating properties of Si. For instance compound **(11)** has been synthesised by van der Made et al by a reaction at room temperature for 1-2 days, using an excess of trichlorosilane and one of the platinum catalysts. This could be either Speier's or Karstedt's, the author does not specify which catalyst he used for the first generation product [4].

Of the other cores tried; core 4 (1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane) produced complete hydrosilation products with the branching units trichlorosilane and chlorodimethylsilane. Its reaction with dichloromethylsilane was complete but there were other products present. Core **(2)** (trivinylmethylsilane) produced one completely hydrosilated product with trichlorosilane, an impure product with chlorodimethylsilane and a product with a trace of vinyl peaks which was very impure with dichloromethylsilane. Core **(5)** (tetraallyloxysilane) produced a product with trichlorosilane that had appeared to have completely hydrosilated but did contain some impurities, the product with chlorodimethylsilane did not completely hydrosilate and the product with dichloromethylsilane had one peak in the vinyl region and contained other impurities. Even under these non-inert atmospheric conditions, which were those initially reported, it looked like the hydrosilation reaction was indeed a reaction that could be used in many instances for different cores. However, given that chlorosilane and the platinum catalysts used can go off when exposed to water or air, more stringent conditions were used for those reactions that had not worked to their full extent in the first instance. So attempts to make dendrimer **(11)** and **(12)** were repeated with dry solvents in an inert atmosphere using Speier's catalyst. The ^{13}C NMR spectra of the reactions still had alkenyl groups in them suggesting that the reaction had not gone to completion. From these preliminary reactions it was decided that tetravinylsilane and 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane were good cores to try different hydrosilation reactions on.

At the same time, another member of the group used compound 6 as a core to produce dendrimers using the branching materials: trichlorosilane, dimethylchlorosilane and chlorodimethylsilane. He carried out the reaction using trichlorosilane in diethyl ether using the Speier's catalyst by refluxing for 8 hours then stirring at 20°C for 15 hours [6].

Hydrosilylation reactions were also tried with octakis(vinyldimethylsiloxy)octasilsesquioxane **(7)** as a core using the branching materials: trichlorosilane, dimethylchlorosilane and chlorodimethylsilane. These reactions didn't always work possibly due to water being present in the core sample and thus causing havoc in the hydrosilation reactions by condensing the cores or destroying the catalyst or condensing the branching material, although reproducible results were eventually achieved. For the reactions that had not worked the NMR showed many peaks. Also octakis(vinyldimethylsiloxy)octasilsesquioxane is a chemically less reactive core than octakisoctavinylsilsesquioxane [15]. Problems were experienced using this core since water is used in the synthesis of this material (see Chapter 4). This could explain why the reactions sometimes worked and sometimes didn't, if in some cases the core material had less water in it than at other times. It might also account for the slight differences in solubility that occurred. Reproducible results were gathered. The reactions were carried out in THF or diethyl ether, sometimes the reactants were allowed to stir at room temperature before being refluxed overnight, but all reactions were carried out in dry solvents, under an inert atmosphere and using Speier's catalyst.

It was also generally believed that chlorodimethylsilane was a good directing group i.e. mostly α addition when added onto cores. As will be seen later this is not always the case i.e. Grignards made from chlorodimethylsilane did not always give pure α addition when hydrosilated onto a core molecule (see aromatic aldehydes section in Chapter 3). It is believed that if the catalyst is added to the solution in ice then this would slow down the reaction and hopefully promote α-addition over β-addition (see Scheme 2.6 for examples of these additions). α-Addition, in this thesis, is with respect to the end of the dendrimer therefore addition of the silane occurs at the carbon at the edge of the molecule and β-addition occurs at the carbon that is the next nearest carbon to the edge of the molecule.



Scheme 2.6i shows β addition 2.6ii shows α addition

It maybe that all these reactions should work but that it is a question of finding the optimum conditions in which they will work. Certainly if the products are to be used in further reactions they should be kept under inert atmosphere (also formed in inert atmosphere, with dry solvents, with the volatile compounds being removed under inert atmosphere and stored in the fridge when not in use).

The papers that feature hydrosilation for growing dendrimers controlled hydrosilation in different ways. Seyferth and Son [2] used the tetravinyl core and trichlorosilane as the branching material, changed the conditions of the hydrosilation reaction for the different generations. For the first generation they used Speier's catalyst in THF since THF has a directional effect on the addition of the silane to the core molecule i.e. THF produces α addition of the silane to the core molecule. In the production of the second generation they used Karstedt's catalyst in THF since using Speier's catalyst gave an impure material. When they made the third generation dendrimer, diethyl ether was used as a solvent since the reaction in THF produced an impure product.

Morris et al. [6] carried out all the hydrosilation reactions in the same fashion i.e. in diethyl ether, using Speier's catalyst, at reflux, using the core 1,3,5,7,9,11,13,15-octavinylpentacyclo[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]octasiloxane and various branching materials. They claimed that the steric effects of the core should force α addition.

Kim and An's [5] hydrosilation reactions used THF and Pt on activated carbon at reflux, using the core material 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane. Van der Made [4] used Speier's catalyst or Karstedt's catalyst at room temperature (tetraallyl core and trichlorosilane) and they don't say what solvent was used. This could mean that no solvent was used. Seyferth and Son [2] reported that hydrosilation without a solvent produced impure products.

Zhou and Roovers [3] (using tetravinyl core and dichoromethylsilane) used platinum divinyltetramethyldisiloxane complex in xylene, in THF and at 50°C for all four of their generations. They believed that it was important for the reaction to "go exothermic", otherwise the reaction would not be quantitative and since longer reaction times would be needed, more side reactions would occur.

Some of the groups, mentioned above, used quantitative amounts of reactants, others used excess silane to ensure complete reaction. One interesting method was employed by Feher et al [12], who decided that to decrease the amount of side reactions in the hydrosilation reaction would be to hydrosilate $H_2C{=}CHCMe_2CH_2CO_2Me$ onto the silsesquioxane $H_8Si_8O_{12}$. This produced a core for the starburst dendrimer and a pure product, which crystallised, was obtained.

Synthesis of Grignard Reagents

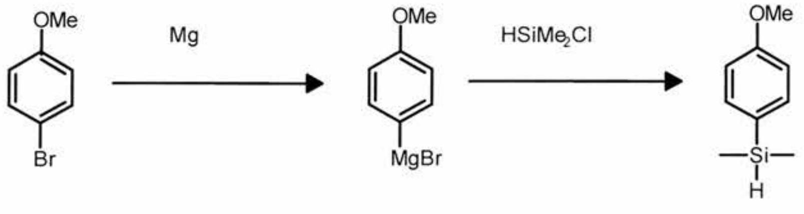
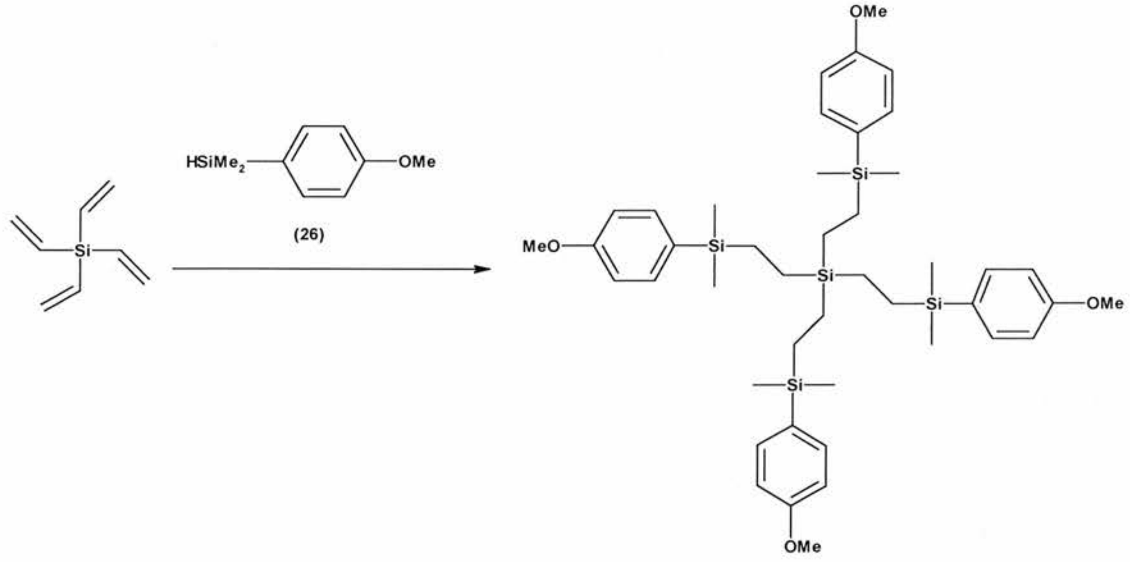


Figure 2.4 Making a silane using a Grignard intermediate

4-Bromoanisole was made into a silane (via a Grignard intermediate, see Figure 2.4) and this was reacted using a hydrosilation reaction with the Speier's catalyst in diethyl ether with the core materials tetravinylsilane, dendrimer **(27)**, (see Figure 2.5) and 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane dendrimer **(28)**. The reaction was carried out under an inert atmosphere and refluxed overnight, the excess silane was removed on a Kugelrohr. Other silanes were made by this route that had a protected aldehyde functionality (see Chapter 3).

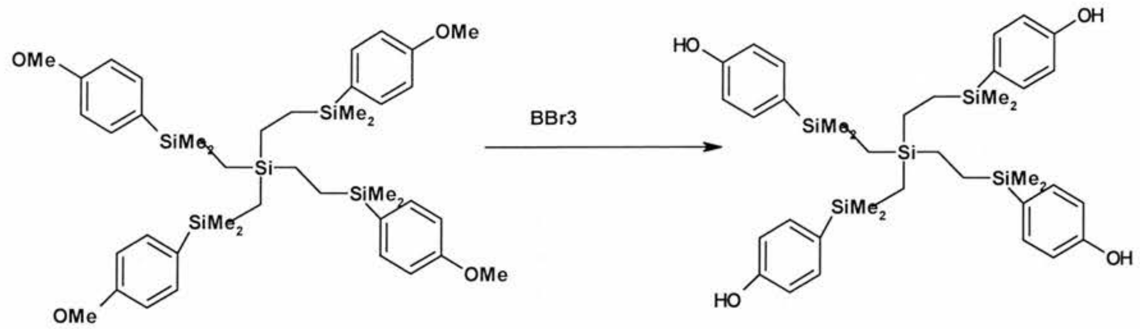


(27)

Figure 2.5 Hydrosilation reaction between tetravinylsilane and p-dimethylanisolesilane.

Dendrimer **(27)** was an off white solid on which the ether cleavage reaction was tried using boron tribromide (see Figure 2.6).

Dendrimer **(28)** did not precipitate like **(27)** did, and eventually the volatile compounds were removed to find out why this was the case. It appears from the spectra that there could be some non-reacted vinyl groups present but there is definitely some β addition product also present in the product, therefore the product wouldn't precipitate since it wasn't pure.



(27) (29)

Figure 2.6 Expected product from the reaction between dendrimer (27) and borontribromide.

The reaction between dendrimer **(27)** and boron tribromide was tried twice with no success, another member of the group also had no success with this reaction [16]. The first time the reaction was tried the ratio of boron tribromide to methoxy groups was 1:1 and the reaction was carried out at room temperature. There was very little product produced, if any. The second time this reaction was tried the ratio of boron tribromide to methoxy groups was 3:1 and the reaction was carried out at sub zero temperatures. On this occasion the heating of the product on an oil bath was not carried out, by mistake, so it is a possible reason why the product did not form. If this product had been formed it could possibly have been used as a catalytic support. The reaction was abandoned as another researcher had mentioned that the reaction was unreliable.

Another way to convert methoxy groups to alcohol groups is using hydrogen iodide and heat. Although a better strategy would be to use an easier protective group, to remove, on the phenol than methoxy, if this was possible. Another alternative strategy, if hydrosilation of the silane onto the core produced unwanted reactions, would be to react $SiCl_4$ with the protected bromophenol Grignard reagent.

Attempts were made to make dendrimers with triethoxy branch ends so that these could be hydrolysed into polymers. The cores 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane and octakisoctasilsesquioxane had triethoxysilane hydrosilated onto them. The reactions using 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane did not go to completion since there were still traces of vinyl groups present in their NMR spectra and the other reaction was inconclusive. These reactions, with a bit more work, could lead to the desired products, if the right conditions were found.

Conclusions drawn from the hydrosilation reactions

In general, hydrosilation was seen to be a good general reaction with which to pursue the divergent synthesis of dendrimers. Usually, with vinyl silane, vinyl silsesquioxane or vinyl siloxane materials, addition was stereospecific in the α position. However, this is dependent on the specific groups in question, and will be discussed further in the following chapters. For allyl containing molecules, hydrosilation was seen to be less successful, with less conversion to the desired product, and with less stereospecifity. This behaviour can be traced back to the effects of the silicon.

The reason why some of the reactions did not work could be due to the reaction being carried out at too high a temperature or the catalyst becoming old or letting the volatile compounds evaporate off in air. There are also added problems of core condensation and vinyl-Si, H-Si swapping which can occur. The dendrimers that had Si-Cl bonds are prone to hydrolysis by water vapour. Therefore dendrimers made with these branch ends are not stable in air, so they were not purified until the branch ends were changed. Therefore reactions to produce dendrimers and using these dendrimers as starting materials (where the branch ends of the dendrimers are Si-Cl groups) must be carried out in dry solvents, in inert atmospheres, and stored in the fridge when not in use.

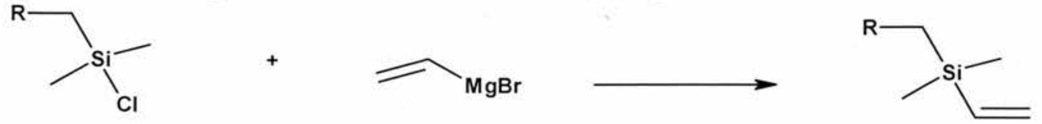
There could be additional problems from possible core condensation [17] by advantageous water and β-addition. β-Addition appeared to be a more significant problem with the 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane than with the tetravinylsilane. This could be due to there being more space around the square core's silicon atoms compared to tetravinylsilane. This could account for the extra peaks that appear in some of the NMR spectra.

2.2.2 Use of Grignard Reagents to produce vinyl functionalised dendrimers

The process of growing divergent carbosilane dendrimers involves hydrosilation followed by a functionalisation step which produces a vinyl group onto which hydrosilation can be performed. Grignard reagents have been used by several research groups to produce alkenyl ended dendrimers [2-6]. Another way to alkenyl-functionalised dendrimers is by reacting allyl alcohol with the Si-Cl functionalised dendrimers [18]. Other alternative strageties would be to use other organometallic compounds i.e. organolithium reagents (see later in the chapter) or organocopper (I) reagents [14].

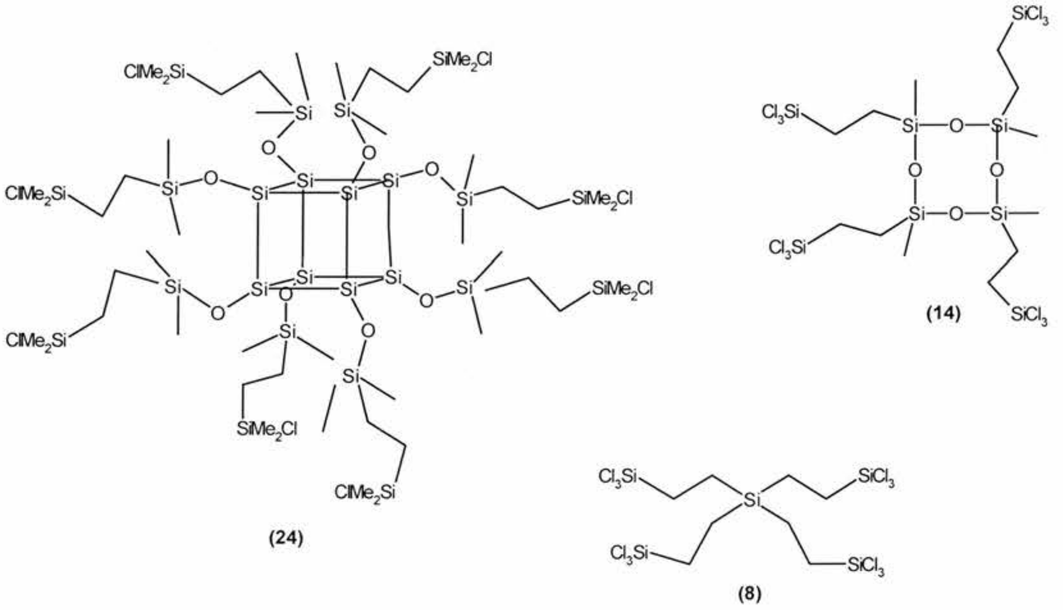
By following the work of Seyferth and Son [2], they carried out reactions using vinylmagnesiumbromide (ViMgBr) to make dendrimers with vinyl groups as branch ends (see Scheme 2.7). This meant that either the dendrimer could be grown further out, reacted with other dendrimers to produce polymers or a function group could be hydrosilated onto it.

The standard reaction was carried out under an inert atmosphere with dry solvents. The starting material was added drop-wise in THF to the vinylmagnesiumbromide also in THF. The resulting mixture was refluxed overnight. After the mixture had cooled, it was added to a saturated ice-cooled solution of NH_4Cl. This was separated with diethyl ether twice before being washed twice with K_2CO_3 solution and then twice with water. The organic layer was dried over $MgSO_4$ before being filtered and the volatile compounds removed on the rotary evaporator.



Scheme 2.7 Grignard reaction

The cores used are shown in Figure 2.7.



(24) (14) (8)

Figure 2.7 Cores used in the Grignard reactions

Dendrimer **(8)** was reacted with the Grignard reagent vinylmagnesiumbromide in an attempt to make dendrimer **(32)**. The dendrimer made was a dark brown oil rather than the expected yellow oil [2]. The dark brown oil was not dendrimer **(32)** since the ^{13}C NMR had no vinyl peaks. The following changes to the way in that the reaction was carried out gave the expected product: dendrimer **(8)** has to be made and stored under an inert atmosphere and transported into the reaction vessel (already in an inert atmosphere) by catheter tube, the vinylmagnesiumbromide also has to be transferred to the reaction vessel via catheter tubing and the solvent used must be dry. The product was put through a column (silica gel/petrol ether 40-60) to purify it.

1,3,5,7-tetramethyl-1,3,5,7-tetrakis{2-(trichlorosilyl)ethyl}tetracyclosiloxane (dendrimer **(14)**) core produced the desired product after one failed attempt caused by not enough Grignard being added.

Dendrimer **(34)** (the product of the reaction between dendrimer **(24)** and a Grignard reagent) was not produced possibly due to the quality of the Grignard reagent not being good enough therefore not enough decent reagent was added and the reaction did not go to completion. The questionable quality of commercially bought Grignard reagents was mentioned in the paper by Zhou and Roovers [3].

2.2.3 Repetitive divergent synthesis of higher generations

Most papers published in the area of divergent dendrimer synthesis have the common theme of trying to build the biggest dendrimer possible before surface congestion causes incomplete reaction [2-6,18]. This involves hydrosilation followed by alkenyl functionalisation ad infinitum. So not to be outdone, this was tried with not so successful results.

A second generation dendrimer was made by hydrosilylating dendrimer **(33)** with $HSiMe_2Cl$ to produce dendrimer **(35)** (see Figure 2.8). Since the yield of the Grignard reaction to produce dendrimer **(33)** was only 8% it was decided not to build out the dendrimer any further.

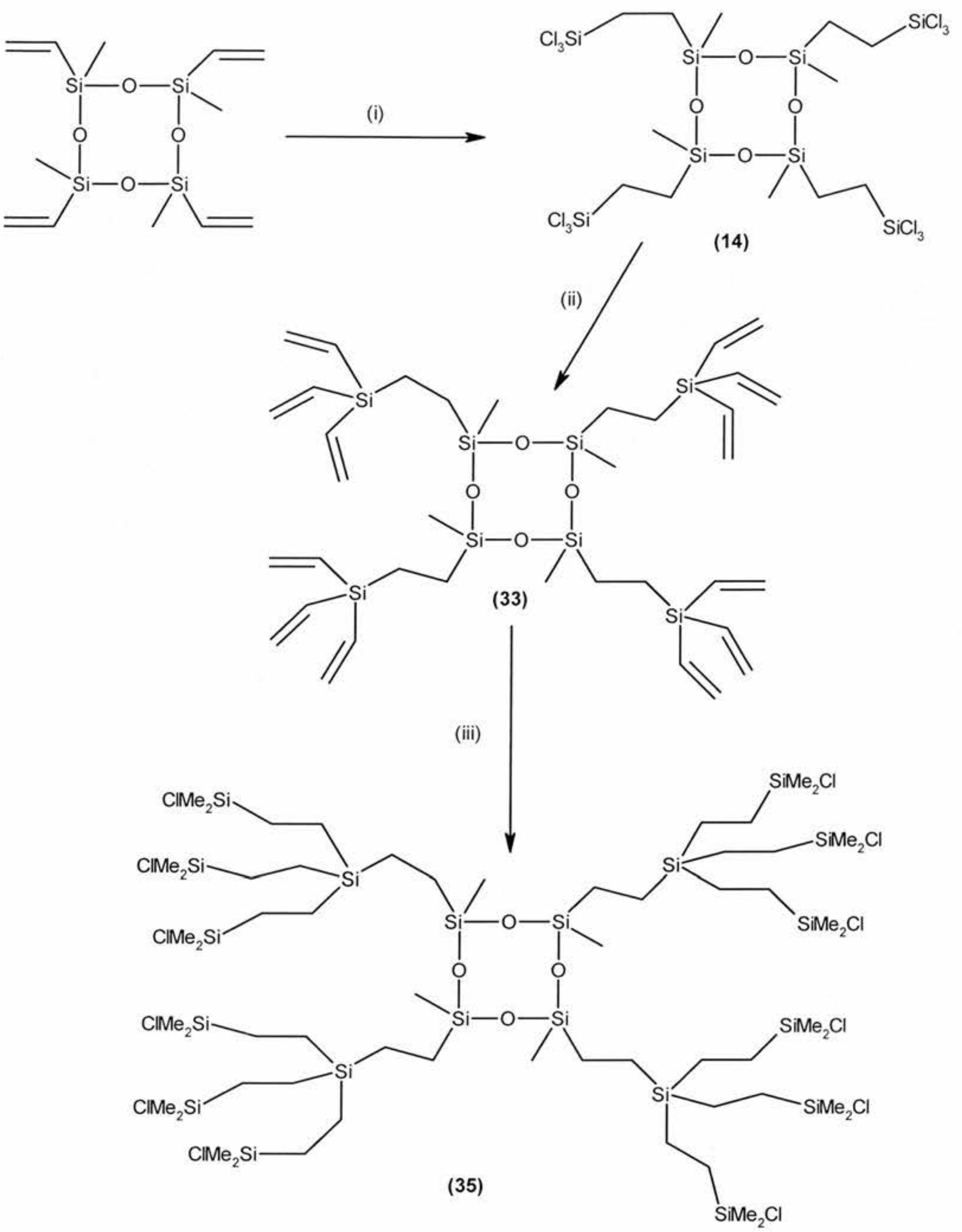


Figure 2.8 Diagram showing the formation of a second generation dendrimer from 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane. (i) $HSiCl_3$, Speier's catalyst, THF, reflux, 10 hours; (ii) $CH_2CHMgBr$, THF, reflux overnight; (iii) $HSiMe_2Cl$, Et_2O, reflux, 5 hours.

Another member of the group [6] built up dendrimers from the octavinylsilsesquioxane core to the second generation vinyl dendrimer using trichlorosilane as the branching unit and reactions with vinylmagnesiumbromide to produce the vinyl dendrimers (see Figure 2.9). He did not make dendrimers of generations higher than the second generation since the yield of making the second generation vinyl product from the chloro product was only 21%. He also made dendrimers from this core using chlorodimethylsilane and dichloromethylsilane as the branching units [6]. Dendrimers built from the octavinylsilsesquioxane core reach their De Gennes limit faster than dendrimers built from cores with less than eight branching units on the core molecule. This is the reason why the octavinylsilsesquioxane built dendrimer only reached 2 generations. He also claimed that by using the octavinylsilsesquioxane core that β addition would be minimised by steric hindrance.

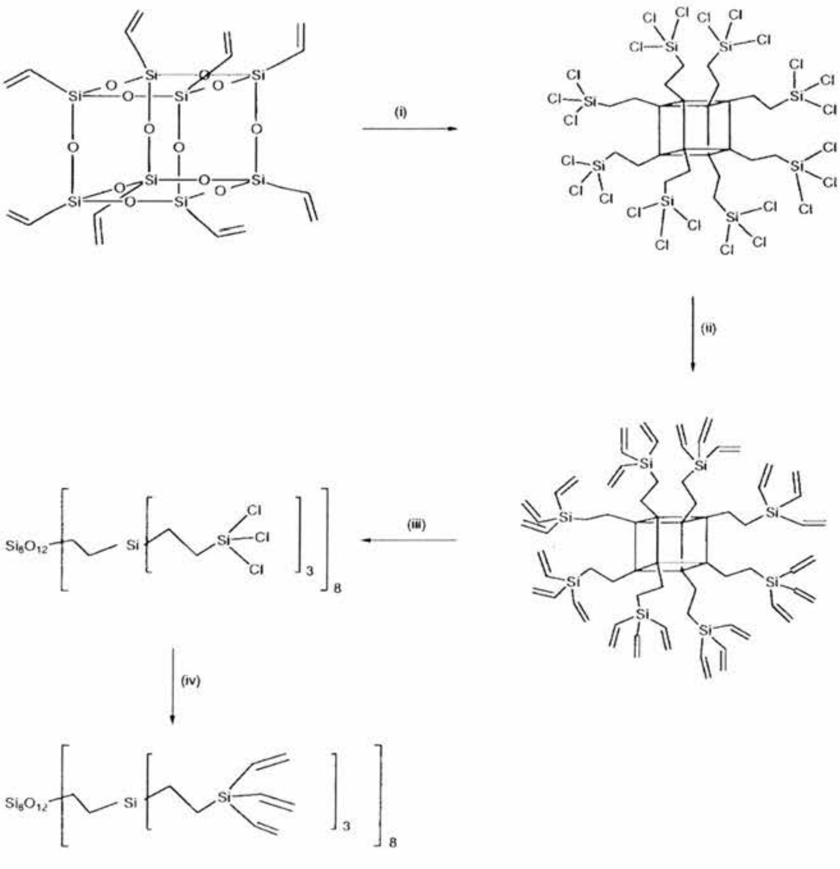


Figure 2.9 Dendrimers grown from the octavinylsilsesquioxane core [6]

2.2.4 Mono-vinyl functionalised POSS

Since reactions to make dendrimers with POSS molecules on the ends of their branches had not been accomplished by hydrosilating the Si-H functionalised core molecules onto the monovinylfunctionalised silsesquioxane, tests were carried out to see if there was a problem with the hydrosilation reaction. Table 2.2 shows which hydrosilation reactions were used as tests since the hydrosilation reactions that were being tested involved reacting a dendrimer with Si-H branch ends with mono-alkenyl functionalised POSS molecules.

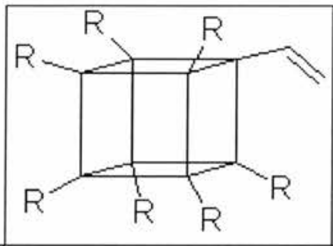
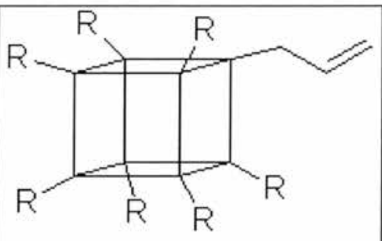
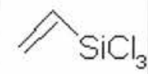
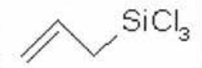
				
$HSiCl_3$	**(36)**	**(37)**	**(39)**	**(40)**
$HSiMe_2Cl$	**(38)**			

Table 2.2 Hydrosilation test reactions

Since it was possible to make POSS molecules with a corner atom missing and Feher was able to "corner cap" these molecules with silicon or a metal atom, we placed a vinyl group in the corner and tried to hydrosilate a silane onto this. Two corner capped molecules were produced, (one with vinyl and one with allyl functional groups in one corner (see Chapter 4 for full experimental details)) and reacted with trichlorosilane. Chlorodimethylsilane was also reacted with the vinyl corner capped POSS. A typical reaction involving either vinyl or allyl POSS and trichlorosilane involved a reaction in dry THF with Karstedt's catalyst and the other two reactants being stirred at room temperature for half an hour before being refluxed for 10 hours.

These reactions were also tried with Speier's catalyst but vinyl groups were present in the product of all the reactions tried. Alternatives to the hydrosilation reaction are mentioned in the hydrosilation section (see earlier in the Chapter).

The hydrosilation of allylheptacyclopentyl POSS and vinylheptacyclopentyl POSS with trichlorosilane reactions were tried as tests for the hydrosilation reaction but the reactions did not go to completion (see Figure 2.10).

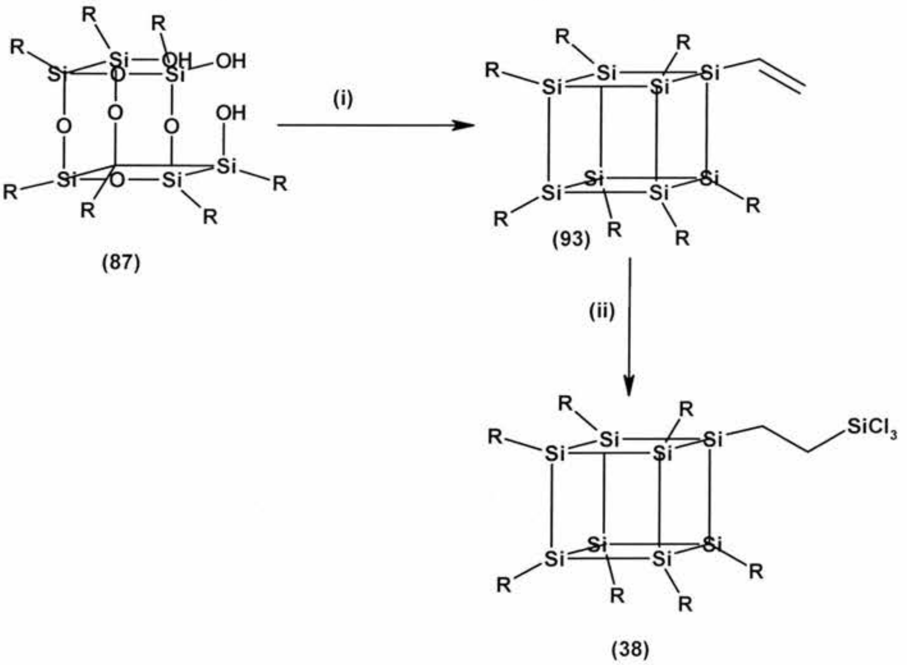


Figure 2.10 Diagram showing (i) the formation of vinylheptacyclopentyl POSS from T_7 cyclopentyl POSS and vinyltrichlorosilane, and (ii) hydrosilation of vinylheptacyclopentyl POSS with trichlorosilane's expected product (the diagrams of vinylheptacyclopentyl POSS and product have the oxygens missed out from the Si-Si bonds to make the diagram clearer).

Other hydrosilation tests tried were: the hydrosilation of allyltrichlorosilane and vinyltrichlorosilane with trichlorosilane. These were carried out using Speier's catalyst in dry THF, stirring overnight and under an inert atmosphere. These molecules, if formed could have been used in corner capping reactions with T_7-cyclopentyl POSS to produce viscosity modifiers (see Figure 2.11).

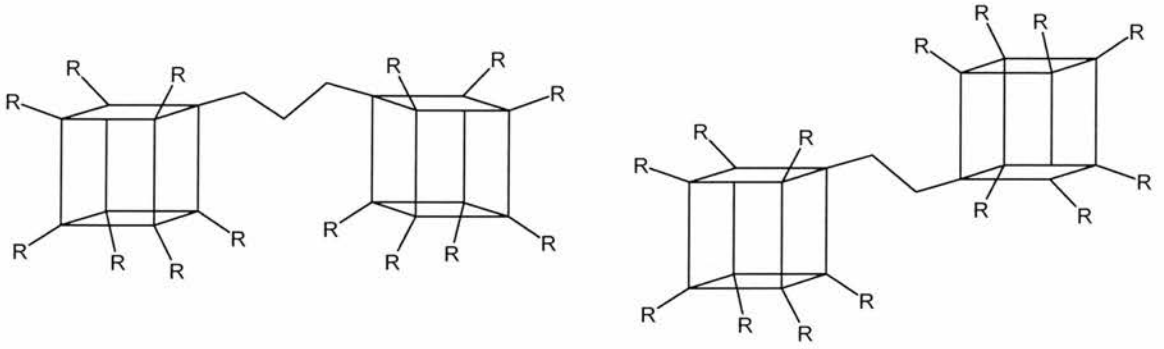


Figure 2.11 Possible viscosity modifiers

Another member of the group [16] also tried to make these viscosity modifiers by reacting hydridoheptacyclopentylPOSS with vinylheptacyclopentylPOSS but got more than one product. He was not able to separate these products.

The reactions of vinylheptacyclopentyl POSS and $HSiMe_2Cl$ were tried in dry diethyl ether, dry THF and dry diethyl ether/THF as solvents since the hydrosilation reaction seems to proceed better in diethyl ether whereas the vinylheptacyclopentyl POSS molecules dissolved better in THF.

The hydrosilation reaction of vinylheptacyclopentyl POSS molecules and chlorodimethylsilane does go to completion under the right conditions. It depends on how soluble the vinylheptacyclopentyl POSS molecules are, the more soluble they are the more likely the reaction will go to completion (see Figure 2.12 for the product of the reaction).

This molecule could then be used in a silicate forming reaction (see Chapter 4, formation of silicate with silsesquioxane arms), which if formed could have been used as a viscosity modifier.

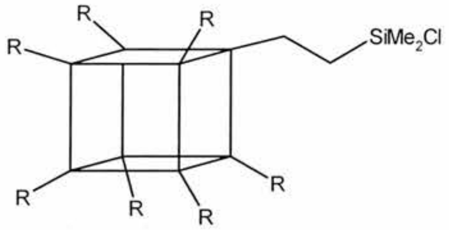
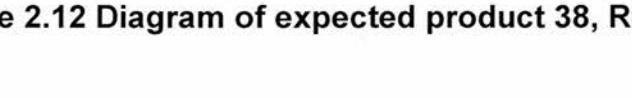


Figure 2.12 Diagram of expected product 38, R=C_5H_9.

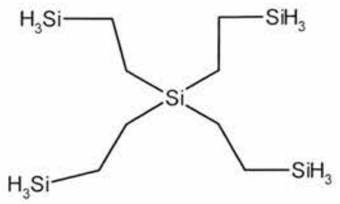
2.2.5 Reduction reactions

Seyferth and Son's paper [2] contained the production of Si-H functionalised dendrimers from Si-Cl functionalised dendrimers (see Scheme 2.8). It was believed that these could be used in hydrosilation reactions to produce second generation dendrimers (as an alternative to using the Grignard reaction), polymers or dendrimers with POSS on the branch ends or as a precursor to silanol dendrimers that could be used as silica mimics (see Chapter 3).



Scheme 2.8 Diagram showing the reduction of $SiCl_3$ by LAH

These reactions were carried out by pouring the chloro ended dendrimers (in diethyl ether) into a suspension of lithium aluminium hydride and diethyl ether. The reaction is stirred overnight, at room temperature, before being filtered through celite and added to a 2N HCl aqueous solution (ice-cooled). The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous NaCl solution. The organic layer is dried over $MgSO_4$ before being filtered and the volatile compounds are removed on the rotary evaporator (an example of the dendritic product formed is shown in Figure 2.13).



(41)

Figure 2.13 Diagram of a reduced dendrimer (41)

The reductions of Si-Cl groups with LAH worked well unless there was a problem with the starting material, i.e. water being present, not fully hydrosilated starting material. Usually they worked well using a large excess of LAH and also provided the starting materials with Si-Cl branch ends were kept dry, under inert atmosphere and in the fridge when not in use. See compounds **(41)** – **(54)** for details of the reductions tried.

Maldi-TOF mass spectra analysis was tried out on one of the reduced dendrimers but due to not finding the correct matrix in which to run the analysis, there were no peaks in the spectra. This has since been rectified.

2.2.6 Attempted reactions using reduced dendrimers as hydrosilating agents

Since the hydrosilylation and reduction reactions gave good yields and fairly pure products, it was decided to try to form a second generation dendrimer by the reaction of a core material functionalised with Si-H end groups and an alkenyltrichlorosilane. The results were less than encouraging. This method was used to try and attach POSS molecules onto Si-H functionalised dendrimer. This was also an unsuccessful venture (see later for details).

Attempted synthesis of second generation dendrimer using allyltrichlorosilane as the branching unit

There was an attempt to make a second generation dendrimer by hydrosilating dendrimer **(41)** (tetrakis(2-silyl)ethyl)silane) with allyltrichlorosilane (instead of doing a Grignard reaction, see Figure 2.14).

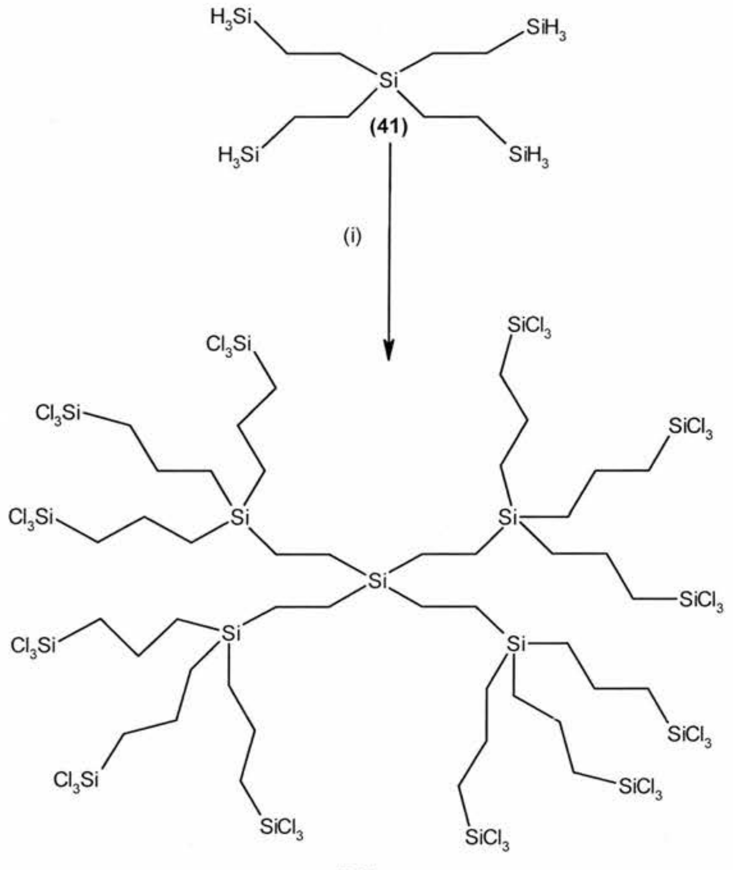


Figure 2.14 Diagram showing the expected reaction when dendrimer (41) is hydrosilated with allyltrichlorosilane.

Dendrimer **(41)** was reacted with allyltrichlorosilane in an attempt to synthesise a second generation dendrimer and to optimise the hydrosilation reaction. It did not work when refluxed for 10 hours, so it was repeated with the Speier's catalyst, and refluxed over the weekend. This reaction still did not produce the desired product. It is possible this reaction may never work since it is possible that having a molecule with more than one Si-H group on a silicon atom would make all the Si-H groups on that atom less reactive. There could also be a problem with water being present so that the Si-H would become Si-OH and hence no hydrosilation reaction would take place.

POSS-dendrimer synthesis using hydrosilation

One of the aims of this project so far has been to try and make dendrimers with POSS units on the ends of the arms. So far several possibilities have arisen to achieve this goal. These molecules, if made, could be used as viscosity modifiers or treated with acid and turned into catalysts [19]. The reactions tried are described in Table 2.3.

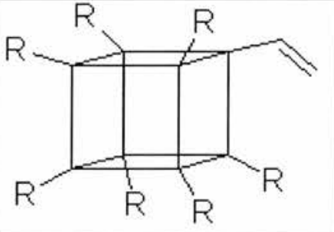
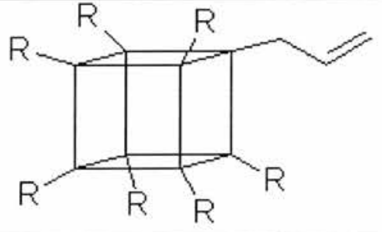
		
$Si(CH_2CH_2SiH_3)_4$	**(56)**	
$Si(CH_2CH_2SiMe_2H)_4$	**(58)**	**(57)**

Table 2.3 Hydrosilation reactions to produce viscosity modifiers.

*Hydrosilation of alkenyl functionalised POSS molecules with dendrimer **(41)***

One of the strategies used while trying to make a POSS dendrimer was to make a POSS molecule with one alkenyl substituent and hydrosilate it to dendrimer **(41)**. There are two ways of making POSS molecules with an alkenyl substituent: corner cap a T7 cyclopentyltrisilanol POSS molecule with an alkenyltrichlorosilane or build a POSS molecule with the alkenyl group on it.

The hydrosilation reaction of the vinyl corner capped T7 cyclopentyltrisilanol POSS molecule and dendrimer **(41)** did not occur. This could be due to the Karstedt's catalyst not being good (the Karstedt's catalyst used in this reaction was made in house) or the small quantities used in this experiment (the wrong amount of vinylheptacyclopentyl POSS molecule was used, although vinyl groups appeared in the carbon NMR). It also appears that this molecule would not be formed as it appears to be very sterically hindered (see diagram of molecule in experimental section). This reaction was also tried using dendrimer **(42)** and allylheptacyclopentyl POSS molecule with the Karstedt's catalyst and refluxing for thirty hours but this still did not work. It was also tried with dendrimer **(42)** with vinylheptacyclopentyl POSS. It seems that most reactions have to be carried out under nitrogen and using dry solvents to get a favourable result. Since this discovery, the hydrosilation reaction has been tested using allylheptacyclopentyl POSS molecule and trichlorosilane, vinylheptacyclopentyl POSS molecule and trichlorosilane, vinylheptacyclopentyl POSS molecule and chlorodimethylsilane, allyltrichlorosilane and trichlorosilane, and with vinyltrichlorosilane and trichlorosilane (see earlier in this Chapter). It has still to be mastered.

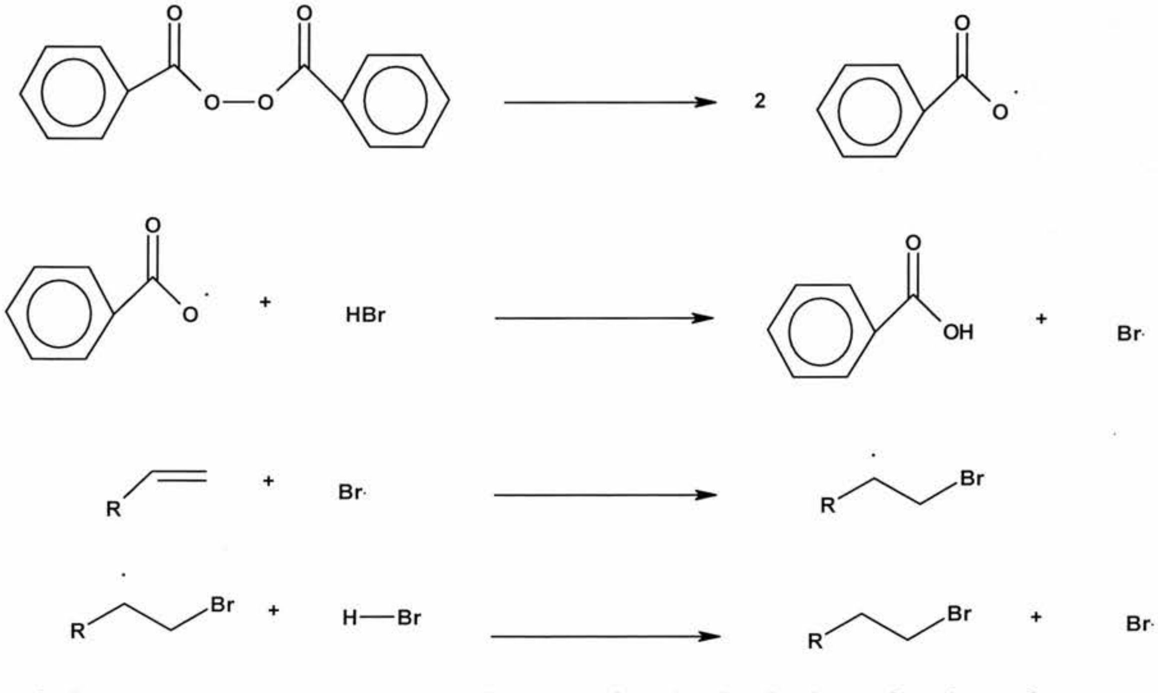
Hydrosilation of hydrogen capped T7-cyclopentyl POSS molecule with a vinyl terminated dendrimer

Another way of making the POSS dendrimer would be to hydrosilate a vinyl dendrimer with a T7-cyclopentyl POSS molecule corner capped with hydrogen. This type of reaction was tried by another member of the group and he did not get complete hydrosilation after 40 hours of reflux in diethyl ether with CPA solution [16].

2.2.7 Hydrobromination reactions

Hydrobromination reactions were looked at as an alternative to functionalisation with hydrosilation reactions. It was hoped that the hydrobrominated product could be reacted with an amine and further reacted with a metal e.g. rhodium to produce catalysts [20].

Hydrobromination occurs across a double bond by bubbling HBr gas through a solution of the core material and benzoyl peroxide (a producer of radicals) in the solvent hexane for half an hour (see Scheme 2.9). The resulting mixture is stirred overnight at room temperature before the mixture is purged with argon to remove excess HBr gas. The product is washed twice with a slightly basic aqueous solution and the volatile compounds are removed on the rotary evaporator [21].

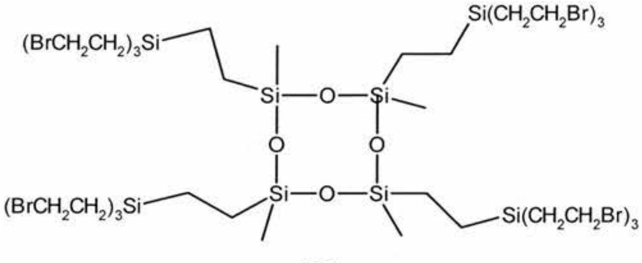


Scheme 2.9 Free radical mechanism for the hydrobromination of a vinyl group

It is important that the radical initiation method is used since it is the only method of hydrohalogenation where the Anti-Markovnikov addition product is produced (i.e. the primary alkylhalide is made (see Scheme 2.10)). Only hydrobromination occurs via this method. $Si_4O_4Me_4(CHCH_2)_4$ (dendrimer **(59)**) and $Si(CHCH_2)_4$ (dendrimer **(60)**) gave good results for the hydrobromination reaction across a double bond [21].

Scheme 2.10 Hydrobromination general reaction scheme.

Hydrobromination of two second generation cores was tried, the reaction using dendrimer **(32)** as the core material did not give the desired results (but had been successfully reacted by another member of the group [16]), but using dendrimer **(33)** as the core material worked once to produced dendrimer **(62)** (see Figure 2.15) .



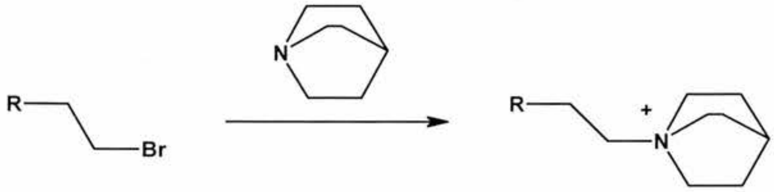
(62)

Figure 2.15 Diagram of dendrimer (62)

HBr gas was produced by adding bromine to tetrahydronaphthalene [16], as the bromine was being consumed in the reaction, the tetrahydronaphthalene/bromine mixture would become less brown in colour. From the first attempt at these reactions the HBr gas production was probably not constant while reacting with the vinylated dendrimer since the tetrahydronaphthalene became a paler colour as the bromine was being used. During the second attempt at these reactions, too much bromine was added to the tetrahydronaphthalene, so instead of reacting with it, it passed into whichever reaction vessel was being used at the time. This is the reason that the results were not always consistent or always made sense.

Attempted amination of alkylbromide dendrimers

Amination of the brominated products was tried using cyclohexylamine and quinuclidine. The reaction using cyclohexylamine didn't work possibly due to cyclohexylamine being a primary amine and therefore is not as reactive as other amines. The quinuclidine reaction had an excess of quinuclidine present after reaction so the product was washed with ethanol to remove this. Unfortunately there was not much product left after this purification (see Scheme 2.11).

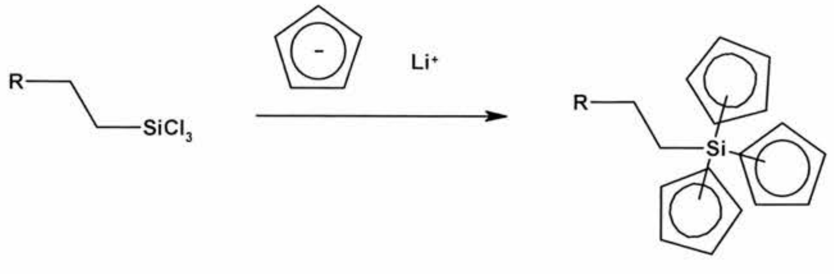


Scheme 2.11 General reaction for reaction of brominated product and quinuclidine

It was hoped that these aminated dendrimers could have been used as catalytic supports.

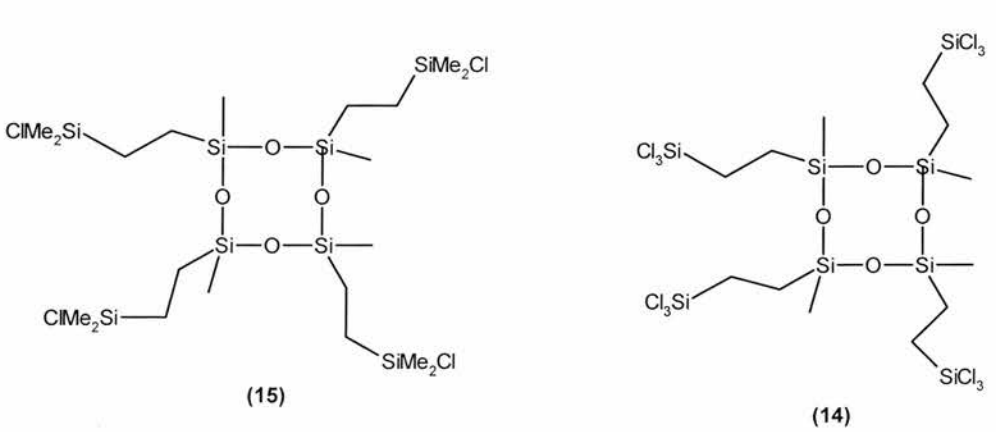
2.2.8 Substitutions of Cl using organolithium reagents

There are other nucleophilic substitutions that can be carried out on Si-Cl ended dendrimers than using Grignard reagents. Organolithium reagents have been used [5]. Attempts were made using lithium picoline and lithium cyclopentadienylide to functionalise some of the dendrimers. It was hoped that these compounds could be used as catalytic supports.



Scheme 2.12 Diagram of a lithium reagent reacting with $SiCl_3$

Reaction with lithium picoline was another possible route to amine functionalised dendrimers other than by reacting bromine functionalised dendrimers with amines (see Scheme 2.12 for the reaction scheme of the reaction of Si-Cl with an organolithium reagent). The amine functionalised dendrimer, if made, could have been reacted with a metal to give a possible catalyst whereas the dendrimers functionalised with cyclopentadienylide would have to have an electron removed from each cyclopentadienylide group before a metal could be attached, for instance titanium. Only two different cores were used in these reactions (see Figure 2.16). Organolithium reagents were reacted with dendrimers with SiCl branch ends [22]. When tried with branch ends with SiCl3 groups it appears that the organo groups which are being added are to big to fit round the silicon atom and only partial reaction can take place. The organolithium reagents tried were lithiumpicoline and lithiumcyclopentadienylide with dendrimer **(14)**.



(15)

(14)

Figure 2.16 Cores used in lithium reactions

Lithium picoline was also reacted with dendrimer **(15)** to see if only having one site at the silicon for the reagent to react at would give it enough space to add. This was not successful. It appeared that some of the Si-Cl bonds were not reacting with the lithium reagent and were quenched instead when ethanol was added to quench the excess BuLi. It could also be possible that the Si-C bonds are being attacked by ethanol to form Si-O bonds.

The addition of linear alkyne lithium reagents has been accomplished with a silicon dendrimer with 2 SiCl groups at the silicon atom, by C. Kim (see Figure 2.17) [5]. It would probably be productive to try their method to produce dendrimers by reaction of organolithium reagents (lithium picoline and lithium cyclopentadienyl) onto dendrimers functionalised with Si-Cl.

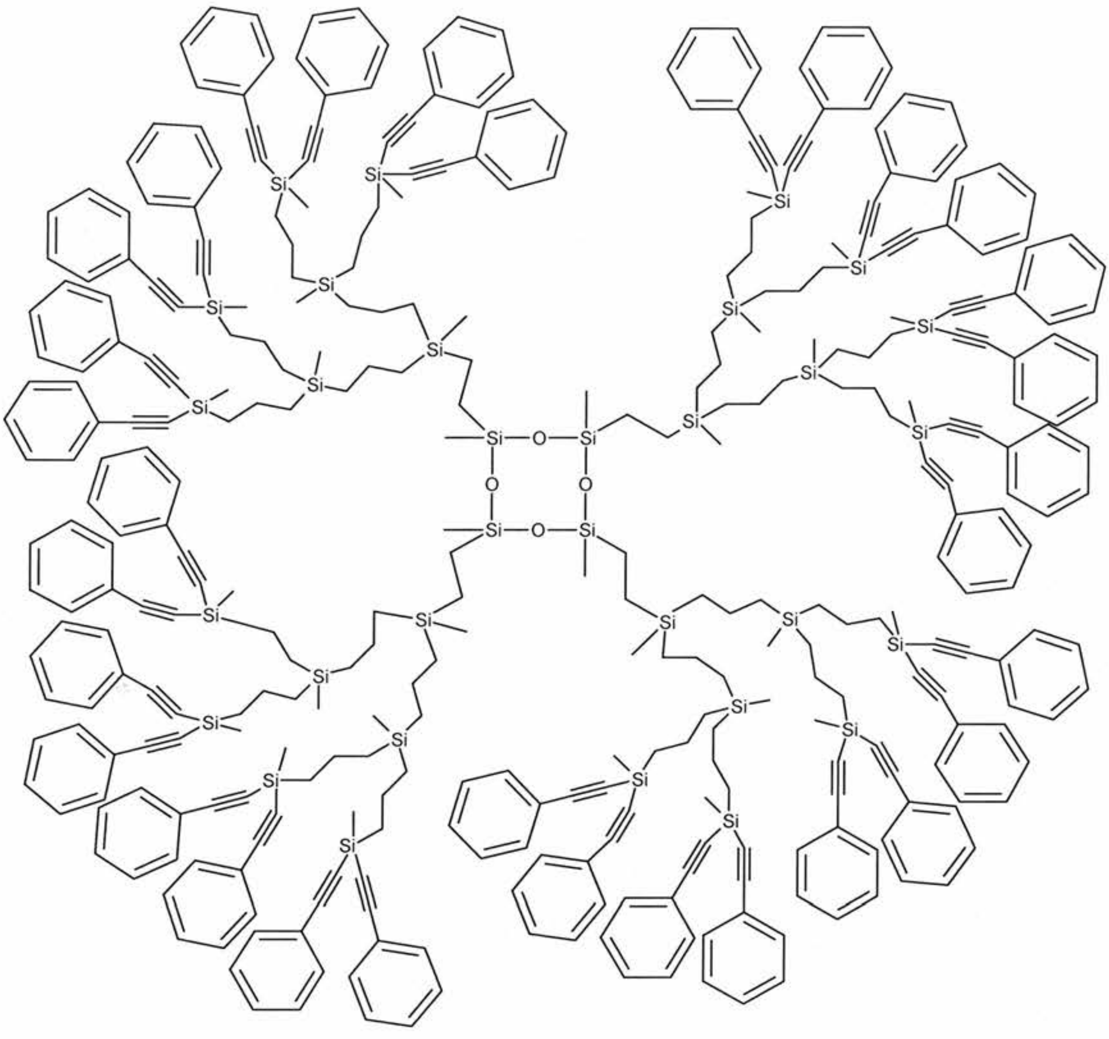


Figure 2.17 Diagram of the dendrimer made by C Kim [5].

2.2.9 Corner capping reactions

The corner capping reaction was described by Feher and involves placing a molecule into the corner of an incompletely condensed POSS molecule. It has been carried out with organotrichlorosilane compounds and also some metal trichloro compounds [23-27].

The first attempt at making dendrimers with POSS arms, was by reacting dendrimer **(8)** with SiCl branch ends with incompletely condensed POSS molecules using triethylamine as a base to remove the hydrogens from the hydroxide groups on the silsesquioxanes but this was not successful. Since it was possible that dendrimer **(8)** could be too small as a core for these molecules, dendrimer **(14)** was tried instead, still there was no success. It was hoped that these molecules could be used as viscosity modifiers or functionalised to produce catalysts.

Alternative attempts at making these molecules have centred around a corner capping reaction and a hydrosilation reaction, the only main difference in the approach is which one comes first (see previously in this Chapter). A slightly different approach (although it did feature hydrosilation and a condensation reaction) was the attempt to produce a silicate with silsesquioxane arms (see Chapter 4).

*Reaction of T7 cyclopentyl POSS molecule with dendrimer **(8)***

The reaction tried between T_7 cyclopentyltrisilanol POSS molecule and dendrimer **(8)** originally involved stirring with triethylamine in toluene but the product isolated at the end of this experiment was the T_7 cyclopentyltrisilanol POSS molecule. This experiment was tried again with heating and the product was different by NMR to the previous experiment, but after trying a control experiment, it was discovered that the POSS molecules were polymerising on heating. Cyclodehydration has been described elsewhere as being caused by triethylamine as well as high valent metal halides acting as bases [28]. The original experiment was also tried using BuLi as a base instead of triethylamine but this still did not give the desired product by NMR. The original reaction was repeated in dry THF, under nitrogen and the volatile compounds left to evaporate in air. This also produced the starting material. It may be the case that the reaction conditions need to be more stringent i.e. by using dry triethylamine. There seem to be only two ways left to try this reaction. One is to use dry pyridine as the base or as a cosolvent (to help dissolve the boxes) with dry triethylamine as base, (the reaction would be carried out in dry solvent, under nitrogen). Alternatively the boxes could have a protective group added to make the hydroxyl groups more reactive. The protective group has yet to be synthesised (see $(Me_3Sn)_3N$ in Chapter 5 for more details).

It is possible that the experiment between T_7 cyclopentyltrisilanol POSS molecules and dendrimer **(8)** may never work due to the dendrimer being too small to cram all four T_7 cyclopentyltrisilanol POSS molecules around it. So dendrimer **(14)** was tried since it is more spacious than dendrimer **(8)** and would hopefully reduce any steric factors that might be inhibiting the reaction. T_8vinyl POSS and T_8 vinyl silicate were hydrosilated into polymers with T_8 hydridosilicate and T_8 hydrido POSS by Laine et al [15]. They found that silicate was more reactive than the POSS molecules most likely because of the improvements that the Me_2SiO spacer groups provided in segmental mobility and in reactive group flexibility and accessibility [15]. Therefore there could be better results using a core with Me_2SiO spaces than the spacers that were used in this reaction.

2.3 Conclusions

Of the two ways that were tried to functionalise vinyl branched dendrimers (i.e. hydrosilation and hydrobromination) hydrosilation was the most used. This is in spite of the problems associated with hydrosilation of β addition and Si-H/SiVi swapping (can't get β addition in hydrobrominated products due to only anti-Markovnikov addition being allowed). This could be due to the hydrosilation reaction having more flexibility in what reactants can be hydrosilated onto a core (i.e. if a Grignard reagent can be made out of a reactant then it could be made into a silane and hydrosilated onto a dendrimer core). Whereas with the hydrobromination products, other than amine and alcohols, most reactions which can be carried out on these products produce products which do not seem to be synthetically useful or useful as catalytic supports.

Of the reactions involving organometallic reagents; the organolithium reactions did not work as planned. It could be they need a great excess of organolithium reagents present to work like the reduction reactions did with excess lithium aluminium hydride. It could also be advantageous to try the synthetic method of Kim et al [5]. The Grignard reactions worked but probably would have worked better if the Grignard was freshly made and the dendrimer was kept in inert conditions as much as possible.

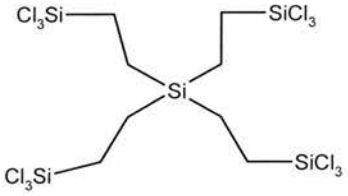
The reduced dendrimers didn't hydrosilate well with the POSS molecules or with allyltrichlorosilane (granted the allyltrichorosilane problem was possibly made worse by the dendrimer not being kept in an inert atmosphere and the allyltrichlorosilane not being totally removed from any product that might have been formed). The problem of not being able to remove non-reacted reagents was emphasised with the hydrosilations using triethylsilane (probably needed to use a stronger vacuum). The difficulty in hydrosilating POSS molecules to dendrimers could be caused by the cyclopentyl groups pushing electrons onto the silicon-oxygen core. This would make the single vinyl group on this molecule less reactive than its octavinylsilsesquioxane counterpart.

The corner capping reactions were possibly hampered by dendrimers with SiCl branch ends that had hydrolysed. It is feasible that they may have worked if a protecting group had been used on the incompletely condensed POSS molecule to make its hydroxyl groups more reactive but ultimately the problems could have been worsened by steric hindrance.

2.4 Experimental

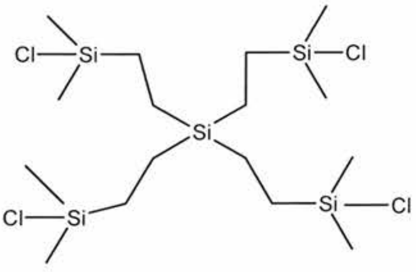
^{1}H (300MHz), ^{13}C (75MHz) and ^{29}Si (59.6MHz) NMR spectra were recorded on a Brucker AM 300. Some of the ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300. The ^{1}H and ^{13}C NMR solutions were placed in 5mm glass tubes whereas the ^{29}Si NMR solutions were placed in 10mm tubes. The spectra were recorded at room temperature in one of the following: d^{6} benzene, d^{4} methanol or $CDCl_3$ (Apollo Scientific/Aldrich) the ^{29}Si NMR samples were either in C_6D_6/C_6H_6 or $CDCl_3/CHCl_3$ solutions. The infra red spectra were recorded on a Perkin Elmer 1710. Liquid samples were placed between sodium chloride plates. Solid samples were made into potassium bromide (Aldrich) plates. Powder diffraction was carried out on a STOE Stadi/P that uses copper radiation of wavelength 1.54056 Å and has a motion sensitive detector. Single crystal diffraction was carried out on a Rigaku AFC7S diffractometer with graphite monochromated Mo-Kα radiation. All CHN measurements were made on a Carlo-Erba Modell 1106.

Tetrakis[2-(trichlorosilyl)ethyl]silane (8)



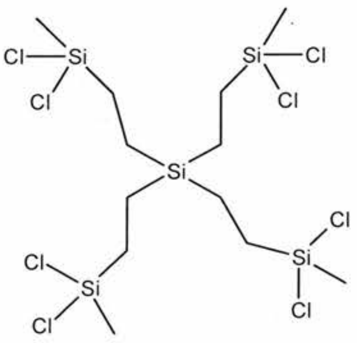
Tetravinylsilane (2g, 14.7mmoles) and THF (10ml) were placed into a 250-mL round-bottomed flask set up for a reflux experiment. To this solution trichlorosilane (12.1g, 89.3mmoles) and CPA solution (5 drops of 0.1M solution made up in propan-1-ol) were added. The resulting mixture was stirred for 30 minutes at room temperature and subsequently for 10 hours at 65°C. Volatile compounds were removed on a rotary evaporator and on standing a white solid came out of the solution, when the product is not left in air it is a clear colourless oil (10g, 14.7mmoles, 100%) [2]. ^{1}H NMR (300MHz, C_6D_6, 25°C): δ 1.03 (m, 8H), 0.61 (m, 8H). ^{13}C {^{1}H} NMR (75MHz, C_6D_6, 25°C): δ 17.46, 2.10. There are some impurities present and the multiplets are not first order. Literature values [1]^{1}H NMR ($CDCl_3$): δ 1.2 – 1.3 (m), 0.82 – 0.89 (m). ^{13}C {^1H} NMR ($CDCl_3$): δ 17.1, 2.00. ^{29}Si {^1H} NMR ($CDCl_3$): δ 12.4 (Si-Cl_3), 11.2 (Si-C).

Tetrakis[2-(chlorodimethylsilyl)ethyl]silane (9)



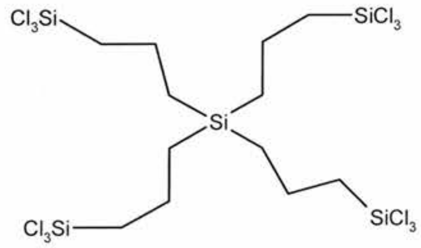
A 250ml round bottomed flask equipped with a reflux condenser and a stir bar had tetravinylsilane (2g, 14.7mmol), chlorodimethylsilane (7.17ml, 6.11g, 65.3mmol), THF (10ml) and CPA solution (5 drops) placed in it. The resulting mixture was stirred for 30 minutes at room temperature and subsequently for 10 hours at 65°C. Volatile compounds were removed on the rotary evaporator. This reaction was repeated using Karstedt's catalyst instead of Speier's catalyst and this gave products that were the same by ^{13}C NMR, the product was a clear, colourless oil unless it was left sitting in air whereby it became a white solid (7.63, 14.8mmoles, 100.8%). ^{13}C {^1H} NMR (75MHz, C_6D_6, 25°C): δ 12.18, 2.97, 1.59 [2].

Tetrakis[2-(dichloromethylsilyl)ethyl]silane (10)



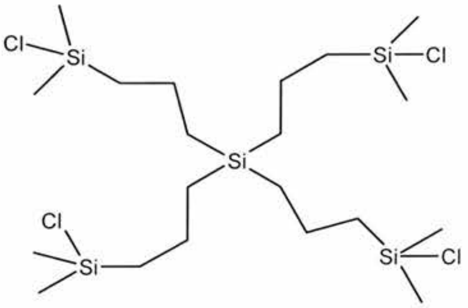
A 250ml round bottomed flask equipped with a reflux condenser and a stir bar had tetravinylsilane (2g, 14.7mmol), dichloromethylsilane (10.24g, 89.8mmol), THF (10ml) and CPA solution (5 drops) placed into it. The resulting mixture was stirred at room temperature for 30 minutes and subsequently at 65°C for 10 hours. Volatile compounds were removed on the rotary evaporator. The product was a clear, colourless oil. $^{13}C\ \{^1H\}$ NMR (75MHz, C_6D_6, 25°C): δ 14.77, 4.87, 2.35. Other peaks were present possibly due to isomers being formed [2]. This compound was made by Lin-Lin Zhou and Jacques Roovers but it was not analysed at this stage [3].

Tetrakis[2-(trichlorosilyl)propyl]silane (11)



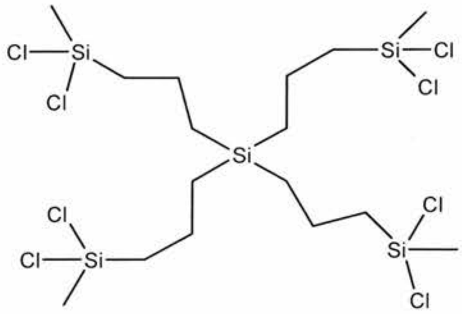
A 250ml round bottomed flask equipped with a stir bar and reflux condenser had tetraallylsilane (1.4g, 7.28mmoles), trichlorosilane (8ml, 10.7g, 79.3mmoles), THF (5ml) and CPA solution (3 drops) placed in it. The resulting mixture was stirred for 30 minutes at room temperature and subsequently for 10 hours at 65°C. Volatile compounds were removed on the rotary evaporator. Since the reaction had not worked the solid collected was placed back into the flask with Karstedt's catalyst (5 drops) and more THF and stirred at room temperature for 30 minutes and at 65°C for 10 hours. This reaction was repeated with Speier's catalyst (5 drops) and using dry solvents under nitrogen. There were peaks in the vinyl region of the ^{13}C NMR spectra that showed that the reaction had not gone to completion [2].

Tetrakis[2-(chlorodimethylsilyl)propyl]silane (12)



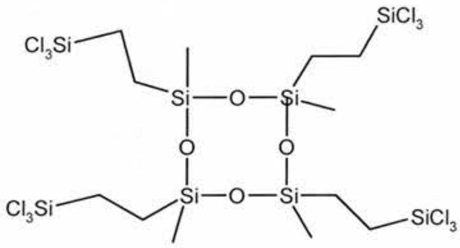
A 250ml round bottomed flask was equipped with a stir bar and a reflux condenser had tetraallylsilane (1.4g, 7.28mmoles), chlorodimethylsilane (4ml, 3.41g, 36.0mmoles), THF (5ml) and CPA solution (3 drops) placed into it. The resulting mixture was stirred for 30 minutes at room temperature and subsequently for 10 hours at 65°C. Volatile compounds were removed on the rotary evaporator. Since the reaction had not worked the solid collected was placed back into the flask with Karstedt's catalyst (5 drops) and more THF and stirred at room temperature for 30 minutes and at 65°C for 10 hours. This reaction was repeated using Karstedt's catalyst (5 drops) instead of Speier's catalyst. Vinyl peaks in ^{13}C NMR at δ 114 and 134 appeared again in the second reflux with Karstedt's catalyst. This reaction was also repeated using Speier's catalyst, dry solvent, under argon. These results are from the reaction using Karstedt's catalyst. $^{13}C\ \{^1H\}$ NMR (75MHz, C_6D_6, 25°C): δ 24.44, 19.00, 18.97, 17.67, 2.42, 1.68 plus several other peaks. There was a lot of THF present in the sample, so it could be that the sample was too dilute to show the vinyl peaks. Repeated reaction with only Speiers gave several peaks in the vinyl region.

Tetrakis[2-(dichloromethylsilyl)propyl]silane (13)



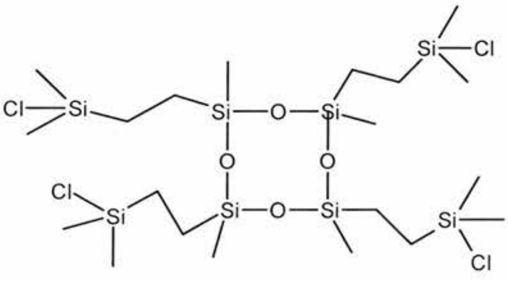
A 250ml round bottomed flask was equipped with a stir bar and a reflux condenser had tetraallylsilane (1.4g, 7.28mmoles), dichloromethylsilane (5.8g, 50.4mmoles), THF (5ml) and CPA solution placed in it. The resulting solution was stirred at room temperature for 30 minutes and subsequently at 65°C for 10 hours. Volatile compounds were removed on the rotary evaporator. Other peaks are present which could be due to other isomers. This reaction was repeated using dry solvents, under argon. The product was a clear, colourless oil. $^{13}C\ \{^1H\}$ NMR (75MHz, C_6D_6, 25^oC): δ 28.79, 27.48, 18.13, 15.67 [2].

1,3,5,7-tetramethyl-1,3,5,7-tetrakis{2-(trichlorosilyl)ethyl}tetracyclosiloxane (14)



$Si_4O_4Me_4(CHCH_2)_4$ (2.57g, 7.46mmoles), $HSiCl_3$ (10ml, 13.4g, 99.1mmoles), dry THF (20ml) and CPA solution (5 drops) were stirred for 30 minutes at room temperature and subsequently at reflux for 10 hours under an argon atmosphere. Volatile compounds were removed on the rotary evaporator. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25^oC): δ 16.64, 7.92, -1.50. The dendrimer core gave $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25^oC): δ 136, 133, 0 [2]. Literature values ^1H NMR ($CDCl_3$): δ 0.18 (s, 12H, CH_3), 0.17 – 0.79 (m, 8H, CH_2), 1.27 – 1.36 (m, 8H, CH_2). $^{13}C\ \{^1H\}$ NMR ($CDCl_3$): δ -1.42 (CH_3), 8.08 (CH_2), 16.78 (CH_2) [18].

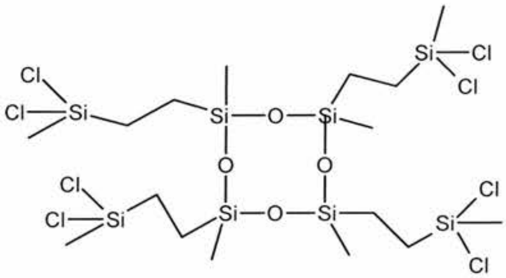
1,3,5,7-tetramethyl-1,3,5,7-tetrakis[2-(chlorodimethylsilyl)ethyl]tetracyclosiloxane (15)



$Si_4O_4Me_4(CHCH_2)_4$ (2.6g, 7.54mmoles), chlorodimethylsilane (4ml, 3.41g, 36.0mmoles), dry THF (20ml) and CPA solution (5 drops) were stirred at room temperature for 30 minutes and subsequently at reflux for 10 hours under argon.

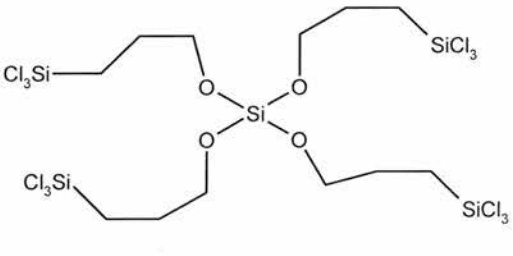
Volatile compounds were removed on the rotary evaporator. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 10.50, 8.33, 0.86, -1.56 plus other peaks. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 0.85 (m, 2H), 0.6 (m, 2H), 0.47 (s, 8H), 0.2 (s, 5H) [2]. The multiplets were not first order.

1,3,5,7-tetramethyl-1,3,5,7-tetrakis[2-dichloromethylsilyl)ethyl]tetracyclosiloxane (16)



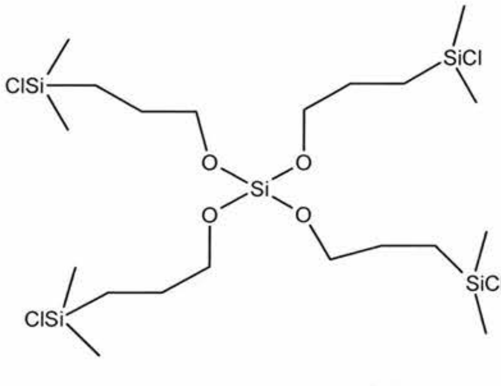
$Si_4O_4Me_4(CHCH_2)_4$ (2.6g, 7.54mmoles), dichloromethylsilane (8ml, 8.84g, 76.8mmoles), dry THF (20ml) and CPA solution (5 drops) were stirred at room temperature for 30 minutes and subsequently at reflux for 10 hours under argon. Volatile compounds were removed on the rotary evaporator. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ -1.58, 7.85, 13.5. This spectra had a lot of other lines which did not correspond to the dendrimer or its core molecule [2]. Literature values ^1H NMR (200.13MHz, $CDCl_3$): δ 0.15 (s, SiMe, 12H), 0.78 (s, $SiMeCl_2$, 12H), 0.69 (m, CH_2, 8H), 1.00 (m, 8H, CH_2). $^{13}C\ \{^1H\}$ NMR (50.32MHz, $CDCl_3$): δ -1.40 (MeSi), 8.04 ($MeSiCl_2$), 4.37 (CH_2), 13.68 (CH_2) [5].

Tetrakis[3-(trichlorosilyl)propoxy]silane (17)



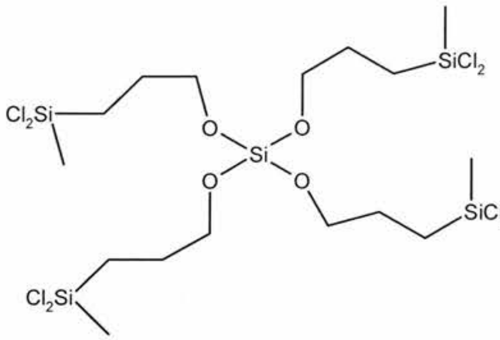
Tetraallyloxysilane (1.89g, 8.42mmoles), trichlorosilane (9ml, 12.1g, 89.2mmoles), dry THF (20ml) and CPA solution (5 drops) were stirred at room temperature for 30 minutes and subsequently at reflux for 10 hours under argon. Volatile compounds were removed on the rotary evaporator. The ^{13}C NMR spectra did not show any promise, it had many peaks between δ 10 - 100, so the reaction was repeated using the same materials but stirring at room temperature overnight, and with the Karstedt's catalyst with stirring at room temperature, overnight. These reactions gave cleaner spectra with no peaks in the vinyl region but too many peaks for the dendrimer. The dendrimer core gave $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 135.90, 114.58, 64.15. The repeat reaction using Speiers catalyst gave $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 70.51, 69.75, 44.91, 37.15, 29.47, 27.00, 26.40, 5.94. The reaction using Karstedts gave $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 70.72, 69.73, 62.61, 44.89, 29.44, 26.98, 26.83 [2].

Tetrakis[3-(chlorodimethylsilyl)propoxy]silane (18)



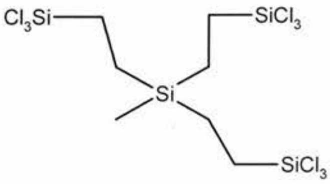
$Si(OCH_2CHCH_2)_4$ (1.92g, 8.56mmoles), chlorodimethylsilane (4ml, 3.41g, 36.0mmoles), dry THF (20ml) and CPA solution (5 drops) were added together and stirred at room temperature for 30 minutes and subsequently at reflux for 10 hours under argon. Volatile compounds were left to evaporate off. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 64.85, 25.90, 13.72, 0.02 plus lots of other peaks around these areas. There was some non-reacted core material present from the NMR at δ 104.08 [2].

Tetrakis[3-(dichloromethylsilyl)propoxy]silane (19)



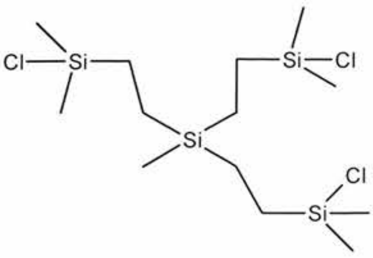
$Si(OCH_2CHCH_2)_4$ (1.89g, 8.42mmoles), $HSiMeCl_2$ (8ml, 8.84g, 76.8mmoles), dry THF (20ml) and CPA solution (5 drops) were added together and stirred at room temperature for 30 minutes and subsequently at reflux for 10 hours under nitrogen. Volatile compounds were left to evaporate off. ^{13}C NMR had many peaks, nothing that was obviously dendrimer peaks [2].

Tris[2-(trichlorosilyl)ethyl]methylsilane (20)



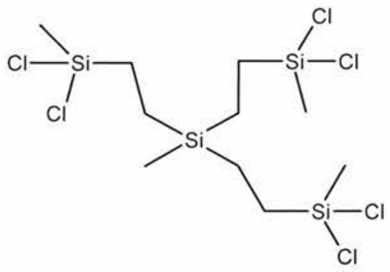
Trivinylmethylsilane (1.85g, 14.9mmoles), trichlorosilane (10ml, 13.4g, 99.1mmoles), dry THF (20ml) and CPA solution (5 drops) were stirred at room temperature for 30 minutes and subsequently at reflux for 10 hours under argon. Volatile compounds were removed on the rotary evaporator. ^{13}C $\{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 17.14, 3.63, -6.88 [2].

Tris[2-(chlorodimethylsilyl)ethyl]methylsilane (21)



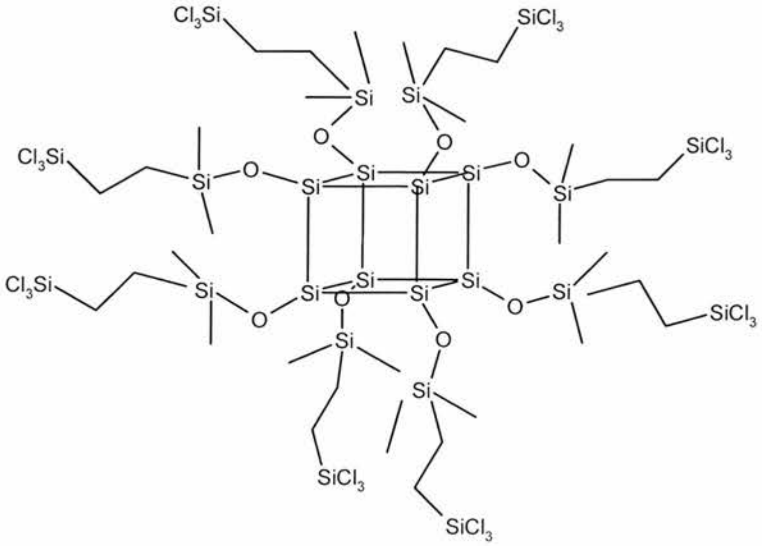
$SiMe(CHCH_2)_3$ (1.82g, 14.6mmoles), $HSiMe_2Cl$ (6ml, 5.1g, 54.0mmoles), dry THF (20ml) and CPA solution (5 drops) were stirred at room temperature for 30 minutes and subsequently at reflux for 10 hours, under argon. Volatile compounds were allowed to evaporate off in air. ^{13}C NMR had many peaks in the δ -5 - 13 region of the spectra [2].

Tris[2-(dichloromethylsilyl)ethyl]methylsilane (22)



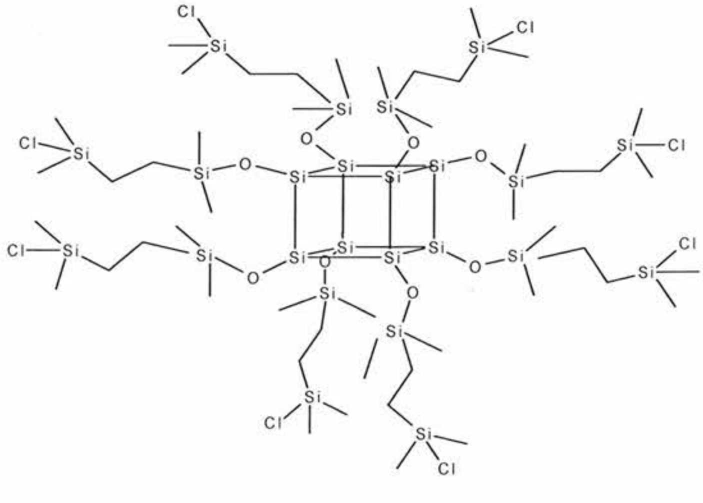
$SiMe(CHCH_2)_3$ (1.85g, 14.9mmoles), $HSiMeCl_2$ (8ml, 8.84g, 76.8mmoles), dry THF (20ml) and CPA solution (5 drops) were stirred at room temperature for 30 minutes and subsequently at reflux for 10 hours, under nitrogen. Volatile compounds were allowed to evaporate off in air. The ^{13}C NMR spectra had a lot of peaks [2].

1,3,5,7,9,11,13,15-octakis{2-(trichlorosilyl)ethyl)dimethylsiloxy}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (23)



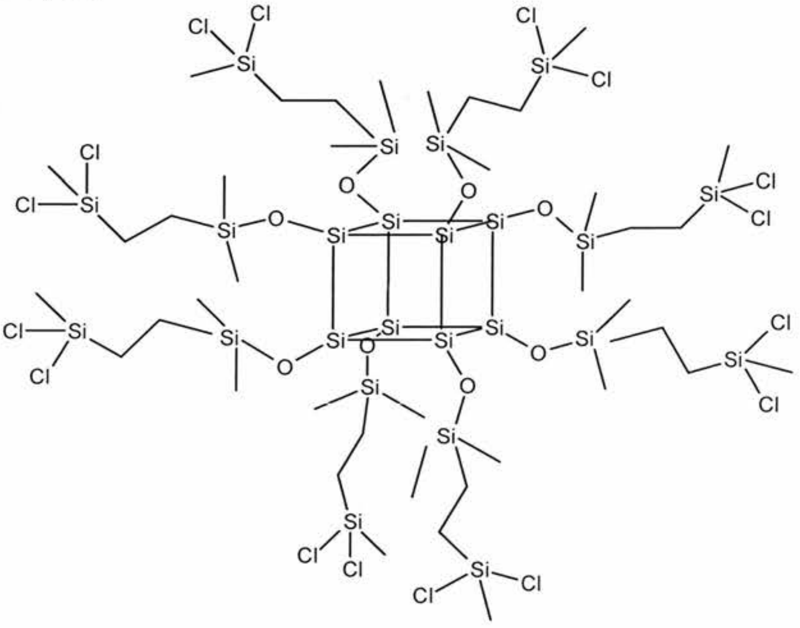
Dendrimer core (0.08g, 0.0812mmoles), trichlorosilane (0.5ml, 0.67g, 4.95mmoles), diethyl ether (5ml) and Speier's catalyst (5 drops) were refluxed together overnight, under argon. The volatile compounds were removed on the rotary evaporator. This reaction was also tried in THF to see if the core would dissolve any better in THF than in diethyl ether [2]. The original reaction, NMR was weak so the carbon NMR showed no definite peaks, the hydrogen NMR had peaks at δ 0.13 (s), 0.27 (s), 0.83 (m) and 1.27 (m) but the integration lines looked a bit strange. There were other smaller bumps present in the hydrogen NMR spectra. It is possible that the reaction worked and the spectra is too weak and ambiguous to tell but it is more likely that it didn't since the octakis box didn't dissolve very well into the solvent. In the repeat reaction there are lots of peaks present in the carbon and the hydrogen NMR spectra indicating that something has gone wrong. This was repeated again in THF (2ml), core (0.44g, 0.446mmoles) with trichlorosilane (0.5ml, 0.67g, 4.95mmoles) and Speiers catalyst (5drops) under argon. It was stirred for half an hour at room temperature (no fizzing) then refluxed overnight. The spectra had lots of peaks but when the reaction was repeated again using core (0.88g, 0.893mmoles), diethyl ether (10ml), trichlorosilane (1ml, 1.3g, 9.91mmoles), Speiers catalyst (5 drops) a cleaner spectra was obtained. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 1.38 (m, 2H), 0.84 (m, 2H), 0.22 – 0.26 (m, 6H) plus some impurities.

1,3,5,7,9,11,13,15-octakis{2-(chlorodimethylsilyl)ethyl)dimethylsiloxy}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}] octasiloxane (24)



Vinyl silicate (0.03g, 0.0305mmoles) was dissolved in diethyl ether (dry, 10ml) then chlorodimethylsilane (0.2ml, 0.17g, 1.80mmoles, excess) and CPA solution (5 drops) were added, under argon. The cube didn't dissolve in diethyl ether. The resulting solution was refluxed overnight. Volatile compounds were removed on the rotary evaporator. ^{1}H NMR in $CDCl_3$ had small peaks present in the CH_2 region of the spectra but nothing was conclusive. This reaction was repeated with more material in THF, before refluxing it was stirred for half an hour in which it fizzed. The results from the third attempt in THF were ^{1}H NMR (300MHz, $CDCl_3$, 25^{o}C): δ 0.86 (m, 2H), 0.66 (m, 2H), 0.5 (s, 6H), 0.26 (s, 8H).

1,3,5,7,9,11,13,15-octakis{2-(dichloromethylsilyl)ethyl)dimethylsiloxy}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}] octasiloxane (25)



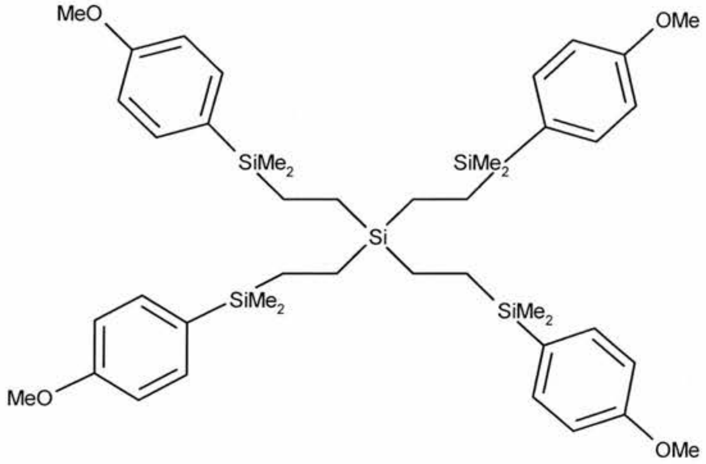
Vinyl silicate (0.99g, 1.00mmoles) was dissolved in diethyl ether (dry, 10ml) then dichloromethylsilane (1ml, 1.1g, 9.61mmoles) and CPA solution (5 drops) were added, under argon. The resulting solution was stirred for half an hour and refluxed overnight. Volatile compounds were removed on the rotary evaporator. ^{1}H NMR in $CDCl_3$ showed that there were still non-reacted vinyl groups present from the peaks at 5.8 – 6.2 so this reaction was repeated using cube (0.54g, 0.548mmoles), diethyl ether (10ml), dichloromethylsilane (2ml, 2.2g, 19.2mmoles) and CPA solution (10 drops) with the same reaction times. There are many peaks present in the ^{1}H NMR spectra but it was hoped that the reduction of this compound would clean up the product. This was repeated and gave a cleaner product. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 1.13 (m, 2H), 0.87 (s, 3H), 0.8 (m, 2H), 0.27 (s, 6H).

4-dimethylsilylanisole (26)

Magnesium turnings (1.32g, 54.3mmoles), iodine (some small crystals) and dry diethyl ether (30ml) were placed under argon. P-bromoanisole (9.5g, 50.8mmoles) in dry diethyl ether (20ml) were added drop-wise to the mixture with vigorous stirring to initiate reaction. Once the reaction had started (noted by the colour change of the solution) more solvent (20ml) was added to the bromo compound (it should have been added at a rate at which reflux could be attained but this did not occur). After the addition was complete it was refluxed for 40 minutes. The Grignard was added drop-wise to chlorodimethylsilane (3.9ml, 3.3g, 35.1mmoles) dissolved in THF (25ml), under argon and refluxed for 2 hours. The Grignard produced was biphasic, the bottom layer was brown and the top layer was yellow. Ammonium chloride solution (aqueous) was added to the resulting solution and the organic layer was extracted with diethyl ether, dried over sodium sulfate, filtered and the volatile compounds were removed on the rotary evaporator. The product was vacuum distilled at 52°C. This product was not the desired product since its IR spectrum lacked a Si-H peak over 2000cm^{-1}. This reaction was repeated in THF, and the product was vacuum-distilled at 90°C [29]. The product was a clear, colourless liquid (3.41g, 20.5mmoles, 40.4%). The IR spectrum of this compound had a peak at 2214.6 cm^{-1} that corresponded to a Si-H peak. IR (neat, cm^{-1}) 3062.4 (m), 3003.4 (m), 2958.2 (s), 2904.3 (m), 2836.1 (m), 2114.6 (s), 1595.2 (s), 1565.4 (m), 1501.3 (s), 1464.5 (m), 1441.7 (m), 1397 (m), 1336.2 (m), 1303.0 (m), 1279.8 (s), 1248.4

(vs), 1182.3 (s), 1152.8 (m), 1114.7 (s), 1077.8 (m), 1040.0 (s), 881.4 (vs), 826.3 (s), 795.1 (m), 784.0 (m), 755.5 (s), 692.4 (s), 666.9 (m), 626.0 (m), 606.7 (m). ^{13}C {^{1}H} NMR (75MHz, $CDCl_3$, 25°C): δ 160.7, 160.0, 146.0, 135.4, 129.4, 128.0, 120.6, 116.0, 113.7, 54.9, -3.7. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 7.53 (d, 2H), 7 (d, 4H), 4.48 (sept, 1H), 3.86 (s, 6H), 0.4 (d, 7H) plus other smaller peaks. There were no blow-ups available to measure the J values. It is possible that there is some non-reacted p-bromoanisole present in the sample accounting for the integration values for the protons.

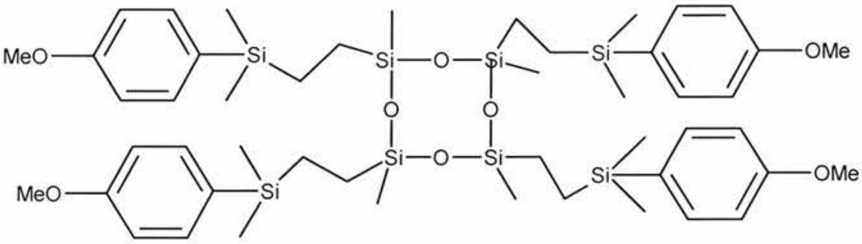
Tetrakis[2-(4-dimethylsilylanisole)ethyl]silane (27)



4-Dimethylsilylanisole (4.7g, 28.4mmoles), tetravinylsilane (0.9ml, 0.72g, 5.28mmoles), diethyl ether (10ml), and CPA solution (5 drops) were refluxed together, under argon, overnight. Volatile compounds were removed on the rotary evaporator. A tlc was run with the sample dissolved in diethyl ether and the plate run in hexane/diethyl ether 95/5. 4 spots including the baseline were observed. The sample was placed on the Kugelrohr at 130°C for 30 minutes under pressure from the water pump. The product was replaced onto the Kugelrohr using pressure from the vacuum line, some liquid distilled off and the product turned black at 130°C. This product was dissolved in ethanol and placed in the freezer to crystallise. After a night in the freezer there was a grey solid in the bottom of the flask so this was filtered off. ^{13}C {^{1}H} NMR (75MHz, $CDCl_3$, 25°C): δ 160.2, 146.0, 135.0, 130.8, 113.4, 54.8, 7.7, 2.4, -3.6. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 7.4 (d, 2H), 6.93

(d, 2H), 3.86 (s, 3H), 1.6 (s), 1.28 (t), 0.48 (m, 4H), 0.25 (s, 6H). There were no blow-ups of the ^{1}H NMR spectra, so J values could not be measured accurately. Since the product was not completely pure a small sample was dissolved in toluene and placed in the freezer to re-crystallise. The re-crystallisation was unsuccessful. CHN analysis gave %C 65.57 : %H 8.68 whereas the theoretical results were %C 65.94 : %H 8.55.

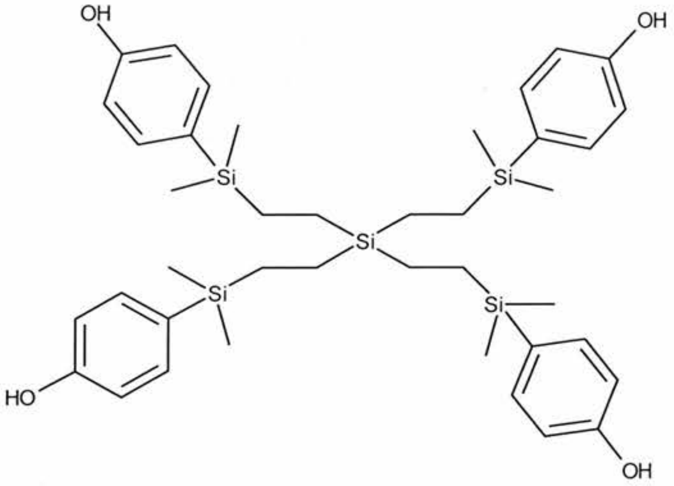
1,3,5,7-tetramethyl-1,3,5,7-tetrakis[2-(4-dimethylsilylanisole)ethyl]silane (28)



4-Dimethylsilylanisole (see above for synthesis) (2.67g, 16.2mmoles), dendrimer core (1.1ml, 1.1g, 3.18mmoles), diethyl ether (10ml) and CPA solution (5 drops) were refluxed together overnight, under argon. Volatile compounds were removed on the rotary evaporator. A tlc was run on the sample with the sample dissolved in diethyl ether and the plate run in hexane /diethyl ether 95/5. 4 spots excluding the baseline spot were observed. The product was placed on the Kugelrohr at 130°C for 30 minutes at the water pump. The product was replaced onto the Kugelrohr using pressure from the vacuum line, again not much liquid was distilled off at 130°C. The sample was dissolved in ethanol, filtered and placed in the freezer to crystallise. The crystallisation was unsuccessful. Volatile compounds were removed on the rotary evaporator to analyse the product. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 7.48 (m, 2H), 7.0 (m, 2H), 3.86 (m, 3H), 0.73 (m, 2H), 0.53 (m, 2H), 0.27 (m, 11H), 0.13 (m, 2H). $^{13}C\{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 135.01, 113.47, 54.74, 9.08, 6.90, -1.75, -3.58 plus several impurities. There appeared to be impurities in the hydrogen NMR that could have been not fully hydrosilated starting material. A tlc was run with the product dissolved in diethyl ether and eluted in hexane/diethyl ether

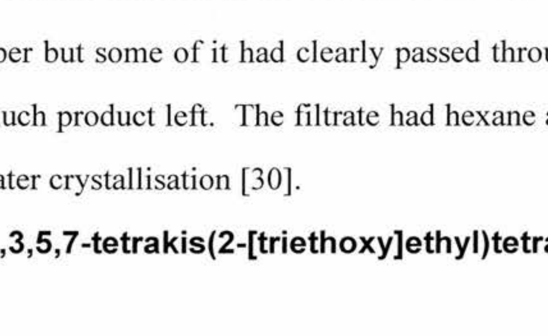
95/5. Four spots were apparent, three of the same intensity not far from the baseline, the fourth was fainter and nearer the solvent front.

Tetrakis[2-(4-dimethylsilylphenol)ethyl]silane (29)



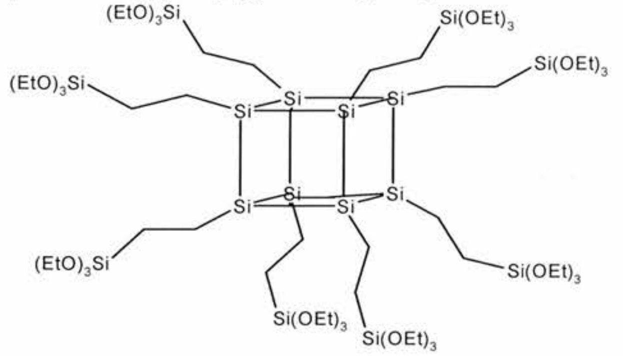
Tetrakis[2-(4-dimethylsilylanisole)ethyl]silane (0.52g, 2.20mmoles) in dry dichloromethane (10ml) under argon had borontribromide (0.8ml, 4.68mmoles) in dry dichloromethane added drop-wise whilst being cooled in ice. The mixture (a black solution prior to the addition of the borontribromide when it became a clear solution with a black precipitate) was then gently heated in an oil bath for 50 minutes and left stirring for several days at room temperature. The alkyl bromide was distilled off and 10% sodium hydroxide solution (1.46g) was added to hydrolyse the residue. The resulting mixture was acidified with hydrochloric acid and extracted with ether and then dried over $MgSO_4$. This was filtered and the volatile compounds were allowed to evaporate in air [9]. ^1H NMR was run in $CDCl_3$ that lacked aromatic groups and therefore was not the desired product. It is believed that the desired product would not dissolve in $CDCl_3$ and therefore it is not surprising that the product was not present in the ^1H spectra. The pink solid was removed from the flask and washed with dichloromethane, a re-crystallisation using hot methanol was attempted but the solid was insoluble in methanol. There appeared to be crystals stuck in the flask that turned out to be insoluble in dichloromethane, acetone, diethyl ether and methanol. Attempts to scratch the crystals off the flask and wash them onto filter paper using diethyl ether, did not yield that much product. So this reaction was retried using the other method with borontribromide i.e. 3 moles of borontribromide to 1 mole of methoxy with the addition of borontribromide to the ether at sub zero temperatures. This time it appeared that the reaction hadn't worked fully since borontribromide appeared to be present after the reaction time had finished, this could be due to not heating the reaction mixture in an oil bath before distilling off the alkylbromide. Once the volatile compounds had mostly evaporated in air there appeared to be some crystalline material in the bottom of the conical flask. This was scraped onto a filter paper but some of it had clearly passed through the filter paper and there was not too much product left. The filtrate had hexane added to it to see if this would facilitate greater crystallisation [30].

1,3,5,7-tetramethyl-1,3,5,7-tetrakis(2-[triethoxy]ethyl)tetracyclosiloxane (30)



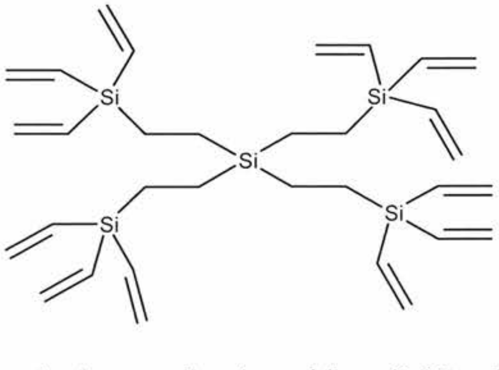
Core material (1.8ml, 1.8g, 5.21mmoles) in diethyl ether (10ml) and Karstedt's catalyst (6 drops) were stirred, under argon in ice before triethoxysilane (5.8ml, 5.2g, 31.4mmoles) was added. The resulting solution was stirred overnight. Volatile compounds were removed on the rotary evaporator. ^{1}H NMR shows that there has not been full reaction since there are peaks between 5.8 - 6 ppm. There is a significant Si-H and CH_2 peaks from the triethoxysilane but no obvious Me peak for this molecule. There also exists two methyl type peaks probably one due to reacted species and one due to the non-reacted species. There are also peaks between 0.9 - 1 and a peak at 0.4 - 0.6 possibly due to CH_2 of reacted species [31]. This was repeated using core (0.9ml, 0.9g, 2.60mmoles), ether (10ml), Karstedt's catalyst (6 drops) and triethoxysilane (2ml, 1.8g, 10.8mmoles), stirred at room temperature for half an hour then at reflux overnight. This produced a clear, colourless oil.

1,3,5,7,9,11,13,15-octakis{2-[triethoxy]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (31)



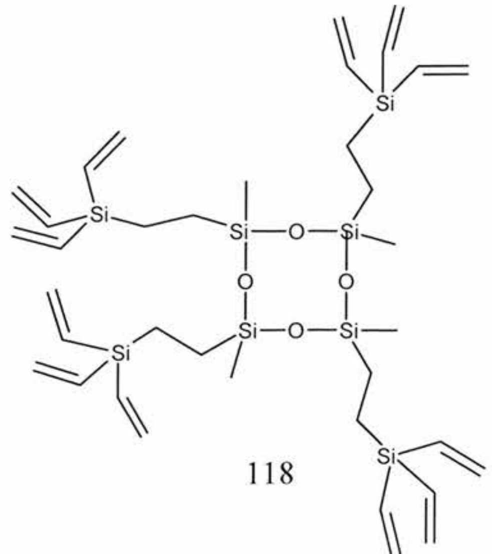
Core material (1.518g, 2.40mmoles) in diethyl ether (10ml) and Karstedt's catalyst (6 drops) were stirred, under argon, in ice before triethoxysilane (4.5ml, 4.0g, 24.4mmoles) was added. The resulting solution was stirred overnight, the core material did not dissolve well in diethyl ether. Volatile compounds were removed on the rotary evaporator. ^{1}H NMR showed peaks for triethoxysilane and not much else. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 3.8 – 4 , 1.2 - 1.4 , 0.6 - 0.8 of triethoxysilane, there were also some very small peaks over 1 ppm and some around the Si-H peak [31]. This was repeated using core (0.991g, 1.56mmoles), toluene (10ml), Karstedt's catalyst (6 drops) and triethoxysilane (2.4ml, 2.1g, 13.0mmoles), stirred at room temperature for half an hour then at reflux overnight. The produced a clear, black oil.

Tetrakis{2-tris(2-(vinyl)silyl)ethyl}silane (32)



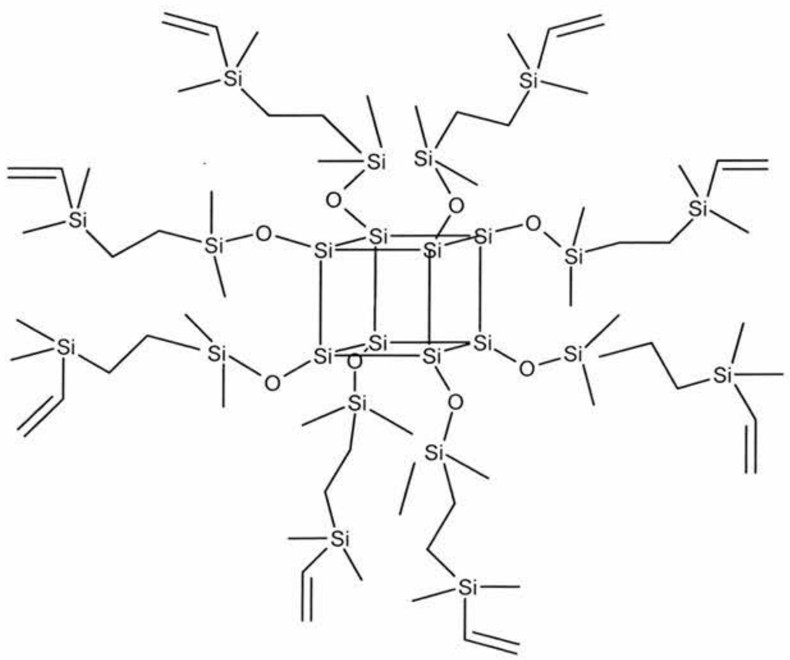
To a solution of vinylmagnesiumbromide (0.25mol) in THF (60ml), $Si(CH_2CH_2SiCl_3)_4$ (9.09g, 13.4mmoles) in THF (50ml) was added drop-wise. The reaction mixture was refluxed for 14 hours. The mixture was poured into ice-cold saturated aqueous NH_4Cl. The aqueous layer was extracted twice with Et_2O, and the combined organic layers were washed twice with water and once with saturated aqueous NaCl and dried over anhydrous $MgSO_4$. The mixture was filtered to remove the $MgSO_4$ and reduced on the rotary evaporator [2]. A dark brown oil was produced. ^{13}C NMR (75MHz, C_6D_6, 25°C): plenty of peaks, not one corresponding to the literature value for $Si(CH_2CH_2Si(CHCH_2)_3)_4$. This reaction has been repeated several times and has still not been successful. In two attempts, a small peak appeared in the ^{13}C NMR where the peak for the vinyl groups is meant to appear but this was a very small peak compared to the other peaks. This reaction was repeated with more stringent conditions; the dendrimer prior to reaction had been stored under argon, in the fridge and the reaction was carried out under argon in dry solvent. The organic layer was washed twice with saturated aqueous K_2CO_3 solution and then washed twice with water. The product was a yellow oil which was chromatographed on a silica gel/petroleum ether column and tested using tlc eluted in hexane. The final product was a colourless oil (1.06g, 1.84mmoles, 13.7%). ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 6.1 (m, 6H), 5.78 (dd, J = 8.6 Hz, J = 17.2 Hz, 3H), 0.58 (m, 4H). ^{13}C {^{1}H} NMR (75MHz, $CDCl_3$, 25°C): δ 134.36, 4.69, 2.45. Literature values^{1}H NMR ($CDCl_3$): δ 0.47 – 0.55 (m, CH_2, 16H), 5.69 - 5.77 (m, CH, 12H), 6.03 – 6.17 (m, CH_2, 24H). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 2.60 (CH & CH_2), 4.85 (CH_2), 134.5 and 134.6 (CH_2). ^{29}Si {^{1}H} NMR (75MHz, $CDCl_3$, 25°C): δ -18.3 (SiVi), 10.5 ($SiCH_2$).

1,3,5,7-Tetramethyl-1,3,5,7-tetrakis{2-(tris[2-vinyl)silyl)ethyl}tetracyclosiloxane (33)



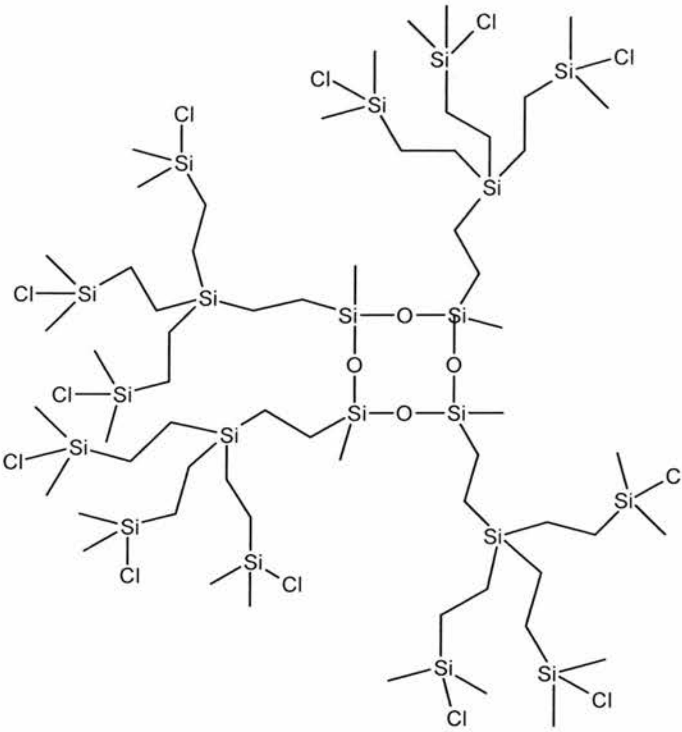
To a 1M solution of vinylmagnesiumbromide (200ml) in THF, the dendrimer (which had been prepared and stored in the fridge under nitrogen) was diluted with dry THF (30ml) and added drop-wise at a rate sufficient to make the reaction exothermic. The reaction mixture was refluxed over a day. Once the reaction mixture had cooled, it was poured into an ice-cooled saturated aqueous NH_4Cl solution. This was filtered and then the aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with K_2CO_3 saturated aqueous solution and then twice with water. The organic layer was dried over $MgSO_4$ or $NaSO_4$ until it was completely dried. The mixture was filtered and the volatile compounds were removed on the rotary evaporator. A pale yellow oil was obtained which was separated on a silica gel/petroleum ether column, the aliquots were tested using tlc eluted with hexane. The final product was a colourless oil (0.46g, 0.586mmoles, 8.1%). $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 134.38, 8.90, 3.79, -1.57. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 6.15 (m, 6H), 5.08 (dd, J = 5.3 Hz, J = 10.7 Hz, 3H), 0.75 (m, 2H), 0.50 (m, 2H), 0.13 (s, 3H) [2].

1,3,5,7,9,11,13,15-Octakis{2-(vinyldimethylsilyl)ethyldimethylsiloxy}-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (34)



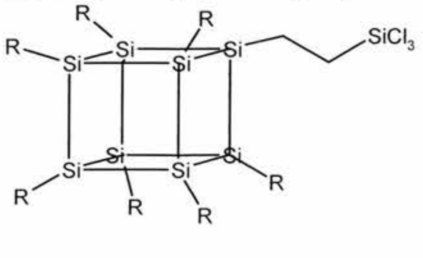
Octakis(chlorodimethylsilyl)silicate (0.221g, 0.111mmoles) in THF (15ml) was added drop-wise, under argon, to vinylmagnesium bromide (7ml of a 1M solution in THF). The resulting mixture was refluxed overnight. The reaction mixture was allowed to cool before being added to a saturated ice-cooled solution of NH_4Cl. This was separated with diethyl ether twice before being washed with K_2CO_3 solution and twice with water. The organic layer was dried over $MgSO_4$. This was filtered and the volatile compounds were removed on the rotary evaporator. From the peaks in the ^1H and ^{13}C NMR spectra it was deduced that a polymer had been formed probably due to the vinylmagnesium bromide being old and therefore not enough vinylmagnesium bromide had been added, leaving non-reacted Si-Cl groups which would polymerise when exposed to water. This was reacted using more core material and new vinylmagnesium bromide. A sample in $CDCl_3$ was spotted unto a tlc plate and placed in hexane, developed in iodine, viewed under UV but only the baseline spot was visible. A short column of silica 60 in hexane was run on the product in CH_2Cl_2 of 10cm. 25ml aliquots were taken of which aliquots 1 and 2 were blank and either 3 or 4 had two spots.

1,3,5,7-Tetramethyl-1,3,5,7-tetrakis{2-(tris[2-(chlorodimethylsilyl)ethyl]silyl)ethyl)tetracyclosiloxane (35)



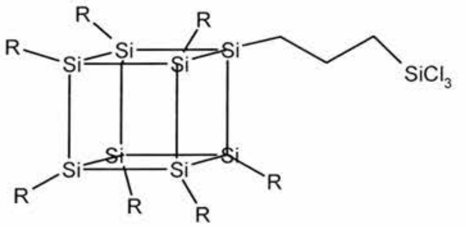
Crude dendrimer (2g, 2.55mmoles), $HSiMe_2Cl$ (6ml, 5.1g, 54.0mmoles), dry diethyl ether (50ml) and CPA solution (5 drops) were refluxed together for 5 hours, under argon. Volatile compounds were removed on the rotary evaporator. There was some difficulty in repeating this reaction so for best results it is best to use only 15 ml diethyl ether and reflux overnight to get a complete reaction. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 11.2, 1.9, 0.8, -1. ^1H NMR (300MHz, $CDCl_3$, 25°C): the hydrogen NMR had overlapping multiplites so it was hard to tell which peaks were which and the relative intensities of the peaks [2].

2-TrichlorosilylethylheptacyclopentylPOSS (36)



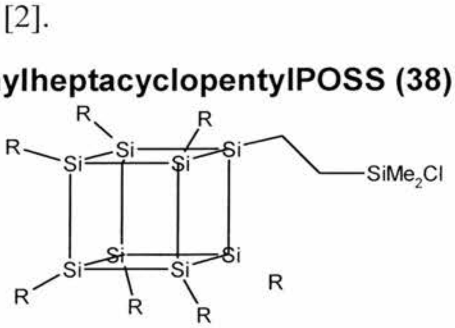
Vinylheptacyclopentyl POSS (0.45g, 0.485mmoles), trichorosilane (2ml, 2.7g, 19.8mmoles), dry THF (30ml) and Karstedt's catalyst (2 drops) were stirred for 30 minutes at room temperature and then refluxed for 10 hours. Volatile compounds were removed on the rotary evaporator. The sample obtained was placed back into the flask with Speier's catalyst (5 drops), dry THF (30ml) and trichlorosilane (2ml, 2.7g, 19.8mmoles) under nitrogen and stirred for 30 minutes at room temperature and subsequently refluxed for 10 hours. This reaction has been repeated with Speier's catalyst and stirring at room temperature over the weekend. ^{13}C NMR showed vinyl peaks that suggests that the reaction did not go to completion i.e. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 136, 130 [2].

2-TrichlorosilylpropylheptacyclopentylPOSS (37)



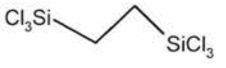
Allylheptacyclopentyl POSS (0.46g, 0.488mmoles), trichlorosilane (2ml, 2.7g, 19.8mmoles), Karstedt's catalyst (2 drops) and dry THF (30ml) were stirred for 30 minutes at room temperature and subsequently at reflux for 10 hours. Volatile compounds were removed on the rotary evaporator. This reaction has been repeated with Speier's catalyst and stirring at room temperature over the weekend. ^{13}C NMR showed vinyl peaks that suggests that the reaction did not go to completion and there was also an impurity present [2].

2-ChlorodimethylsilylethylheptacyclopentylPOSS (38)



Vinylheptacyclopentyl POSS (0.55g, 0.593mmoles), $HSiMe_2Cl$ (0.1ml, 0.08g, 0.9mmoles), diethyl ether (15ml) and CPA solution were refluxed together overnight, under argon. Volatile compounds were removed on the rotary evaporator. The reaction was repeated using THF since it was believed that the POSS molecule would be easily dissolved in THF (which was true). The reaction partially worked after being refluxed for a few days. This reaction was repeated in a mixture of diethyl ether and THF since the vinylheptacyclopentyl POSS dissolves better in THF and the hydrosilation reaction appears to work better in diethyl ether [2]. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 138, 136, 130, 128, 27.2, 27.1, 26.9, 26.8, 22.1, 23, 1. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 6.0 (m), 1.75 (s), 1.55 (s), 1.25 (d), 0.95 (m), 0.05 (m). Integration of the hydrogen spectra was difficult due to the strength of the NMR solution. Vinylheptacyclopentyl POSS (0.5g, 0.539mmoles) dissolved in diethyl ether (36.7ml) had chlorodimethylsilane (1ml, 0.8g, 9.00mmoles excess) and CPA solution (10 drops) added to it. The resulting solution was stirred for half an hour at room temperature and subsequently refluxed for 15.5 hours. Volatile compounds were removed on the rotary evaporator. ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ 1.75 (m, 19H), 1.525 (m, 64H), 0.85 (m, 2H), 0.65 (m, 2H), 0 (m, 18H) plus some impurities. This was repeated several times without success. This is possibly due to the fact that the vinylheptacyclopentyl POSS did not seem to be as soluble as the time when it worked well, so the reaction was repeated in an ice/brine bath, using the Karstedt's catalyst, and when it didn't work it was refluxed. The ^1H NMR showed no peaks in the vinyl region but there was not enough cyclopenyl groups present compared to CH_2 groups. This could be due to the T_7cyclopentyl POSS having sat around before being corner capped i.e. maybe it further hydrolyses in air.

1,2-Bis(trichlorosilyl)ethane (39)

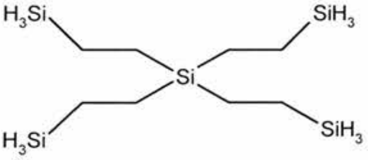


Vinyltrichlorosilane (2ml, 2.5g, 15.7mmoles), trichlorosilane (2ml, 2.7g, 19.8mmoles), dry THF (10ml) and CPA solution (5 drops) were stirred overnight, under argon. The volatile compounds were removed on the rotary evaporator and the product was stored under nitrogen in the fridge. The carbon NMR spectra did give a lot of peaks. $^{13}C\{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 11, 14, 16, 19, 25, 27, 28, 29, 32, 45, 64, 66, 68, 70 [2].

1,3-Bis(trichlorosilyl)propane (40)

Allyltrichlorosilane (2ml, 2.4g, 13.8mmoles), trichlorosilane (2ml, 2.7g, 19.8mmoles), dry THF (10ml) and CPA solution (5 drops) were stirred overnight, under argon. Volatile compounds were allowed to evaporate in air. The carbon NMR only showed solvent peaks. The hydrogen NMR did not show a peak for trichlorosilane [2]. The carbon spectra was too weak, it didn't show any peaks other than solvent. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 1.575 (s) there are other peaks at 1.15 - 1.25 that could be due to the α isomer and there are some other peaks as well.

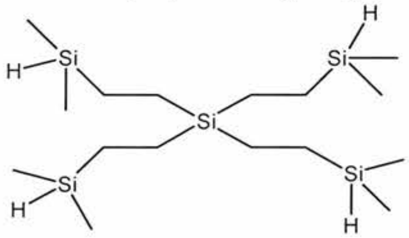
Tetrakis(2-(silyl)ethyl)silane (41)



A suspension of $Si(CH_2CH_2SiCl_3)_4$ (10g, 14.7mmoles) in diethyl ether (37.5ml) was cannulated slowly into an ice-cooled suspension of LAH (3.35g, 88.3mmoles) in diethyl ether (250ml). The mixture was stirred overnight at room temperature. The mixture was filtered through celite on a medium sintered glass funnel. The filtrate was added cautiously to 2N HCl (400ml). The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous NaCl solution. The organic layers were dried over anhydrous $MgSO_4$. The mixture was filtered and the volatile compounds were removed on the rotary evaporator [2]. The IR spectra had a peak at 2261 cm^{-1} that will be due to the Si-H stretch. IR (neat, cm^{-1}) 3000 (m), 2932 (s), 2909 (s), 2886 (s), 2807 (m), 2261 (vs), 1417 (s), 1246 (m), 1143 (s), 1080 (s), 1068 (s), 1000 (m), 920 (vs), 846 (m), 777 (m), 720 (vs), 657 (m), 600 (s), 513 (s), 462 (brvs). ^1H NMR (300MHz, C_6D_6, 25°C): δ 3.89 (t, J = 3.4 Hz, 12H), 0.59 (m, 16H). $^{13}C\{^1H\}$

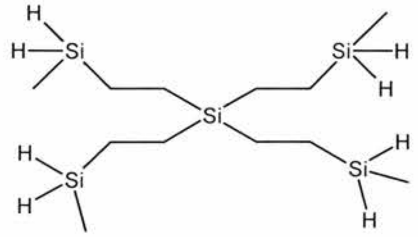
NMR (75MHz, C_6D_6, 25°C): δ 7.74, -0.20. ^{29}Si NMR (59.6MHz, 50% v/v $CDCl_3/CHCl_3$, 25°C): δ 8.31, -53.68. Literature values IR spectra (cm^{-1}, neat) 2918 (s), 2892 (s), 2145 (vs, Si-H), 1408 (m), 1137 (s), 1068 (m), 920 (br s), 716 (br s). ^{1}H NMR ($CDCl_3$): δ 0.63 (s, CH, 16H), 3.53 (s with weak satellites due to $J_{Si\text{-}H}$ = 192Hz, 12H). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 1.0 (CH), 7.0 (CH_2). ^{29}Si NMR ($CDCl_3$): δ 8.4 (Si-CH_2), -53.6 (q, Si-CH, $J_{Si\text{-}H}$ = 192Hz).

Tetrakis(2-(dimethylsilyl)ethyl)silane (42)



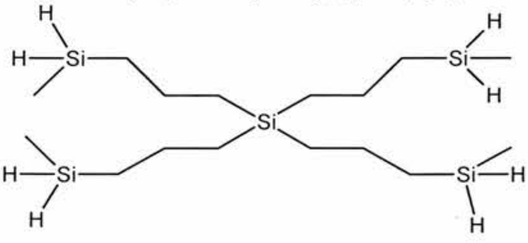
A solution of $Si(CH_2CH_2SiClMe_2)_4$ (7.63g, 14.75mmol) in diethyl ether (37.5ml) was cannulated slowly into an ice cooled suspension of lithium aluminium hydride (1.11g, 29.2mmoles) in diethyl ether (250ml). The mixture was stirred overnight. The mixture was filtered through celite and the filtrate was added to ice cooled 2N HCl (400ml). The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and then filtered. Most of the volatile compounds were removed using the rotary evaporator, the product was a clear, colourless liquid. The IR spectra had a peak at 2102 cm^{-1} that will be due to the Si-H stretch. ^{1}H NMR (300MHz, C_6D_6, 25°C): δ 4.34 (sept, J = 3.3 Hz, 4H), 0.8 (m, 17H), 0.3 (d, J = 5 Hz, 28H). ^{13}C {^{1}H} NMR (75MHz, C_6D_6, 25°C): δ 7.50, 4.76, -3.98 [2]. The repeat reaction didn't work since no Si-H peak was seen in the IR spectra. This reaction has since been repeated successfully CHN analysis yielded %C 49.44 : %H 11.41 whereas the theoretical values were calculated as being %C 50.98 : %H 11.76.

Tetrakis(2-methylsilyl)ethyl)silane (43)



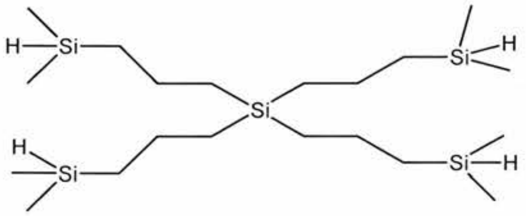
A suspension of Si($CH_2CH_2SiCl_2Me$)$_4$ (4.39g, 7.36mmoles) in diethyl ether (19ml) was cannulated into an ice cooled suspension of lithium aluminium hydride (1.11g, 29.2mmoles) in diethyl ether (125ml). The mixture was stirred overnight. The mixture was filtered through celite and the filtrate was added to 2N HCl (400ml, ice cooled). The aqueous layer was extracted twice with diethyl ether. The combined organic layers were washed twice with water and once with saturated aqueous NaCl solution. The organic layer was dried over $MgSO_4$ and filtered. Volatile compounds were removed on the rotary evaporator. The IR spectra had a peak at 2114 cm^{-1} that will be due to the Si-H stretch. IR (neat, cm^{-1}) 2977 (m), 2920 (m), 2886 (m), 2318 (m), 2284 (m), 2114 (vs), 1406 (m), 1251 (s), 1137 (s), 1097 (m), 1063 (s), 1000 (m), 943 (s), 897 (s), 868 (s), 766 (s), 731 (s), 691 (m). ^{1}H NMR (300MHz, C_6D_6, 25^{o}C): δ 4.10 (sept, 8H), 0.70 (m, 16H), 0.275 (m, 12H). ^{13}C {^{1}H} NMR (75MHz, C_6D_6, 25^{o}C): δ 6.06, 4.12, -7.86 [2].

Tetrakis(2-(methylsilyl)propyl)silane (44)



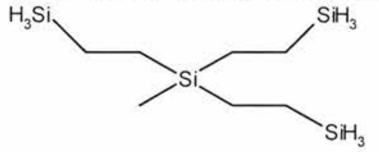
A suspension of Si($CH_2CH_2CH_2SiCl_2Me$)$_4$ (2.51g, 3.85mmoles) in diethyl ether (10ml) was cannulated into an ice cooled suspension of lithium aluminium hydride (0.56g, 14.8mmoles) in diethyl ether (62.5ml). The mixture was stirred over the weekend. The reaction mixture was filtered through celite and the filtrate was added to ice cooled 2N HCl (50ml). The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and filtered. The volatile compounds were removed on the rotary evaporator. The IR spectra had a peak at 2159 cm^{-1} that will be due to the Si-H stretch. There was a considerable OH stretch in the IR spectra. IR (neat, cm^{-1}), 3432 (brs), 3080 (s), 2966 (s), 2932 (s), 2886 (s), 2864 (m), 2159 (s), 1640 (s), 1440 (m), 1400 (m), 1308 (m), 1240 (m), 1200 (m), 1137 (m), 1097 (m), 1023 (m), 977 (s), 943 (s), 886 (s), 863 (s), 811 (s), 783 (s), 714 (s), 450 (brvs). ^1H NMR (300MHz, C_6D_6, 25°C): δ 4.10 (sept, 8H), 1.625 (m), 0.825 (m, 18H), 0.20 (m, 12H). The number of CH_2 groups is too low i.e. should be 24 not 18. The δ 1.625 (m) peak is 15H, there are some more peaks present in the spectra including some in the aromatic region. $^{13}C\ \{^1H\}$ NMR (75MHz, C_6D_6, 25°C): δ 20, 17, 15, 8 plus lots of extra peaks [2].

Tetrakis(2-dimethylsilyl)propyl)silane (45)



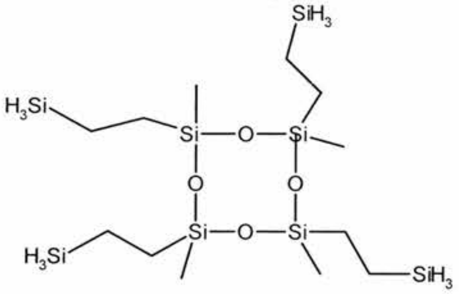
A suspension of $Si(CH_2CH_2CH_2SiClMe_2)_4$ (1.93g, 3.38mmoles) in diethyl ether (40ml) was cannulated into a suspension of lithium aluminium hydride (2.28g, 60.1mmoles) in diethyl ether (50ml). The mixture was stirred overnight at room temperature. The reaction mixture was filtered through celite and the filtrate was added cautiously to 2N HCl (40ml) mixed with ice. The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous NaCl solution. The organic layer was dried over $MgSO_4$ and filtered. Volatile compounds were removed on the rotary evaporator [2]. From the NMR spectra (^{13}C and ^1H) the expected product had not been formed.

Tris(2-(silyl)ethyl)methylsilane (46)



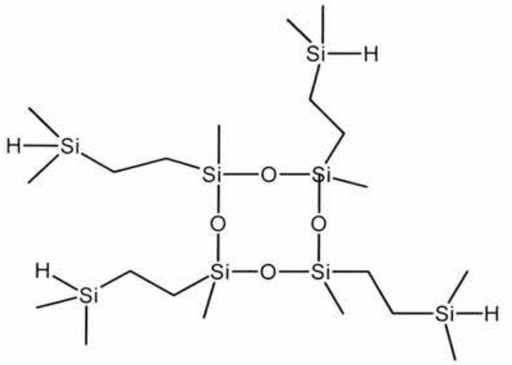
$SiMe(CH_2CH_2SiCl_3)_3$ (7.1g, 13.4mmoles) was added to LAH (2.28g, 60.1mmoles) in diethyl ether (200ml), the resulting mixture was allowed to stir over the weekend. The mixture was filtered through celite and poured into 2N HCl (ice cooled, 133ml). The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and filtered through a medium glass sintered funnel. Volatile compounds were removed on the rotary evaporator. The IR spectra had a peak at 2148 cm^{-1} that will be due to the Si-H stretch. IR (neat, cm^{-1}) 2954 (m), 2909 (s), 2886 (s), 2795 (m), 2148 (vs), 1417 (m), 1251 (m), 1143 (s), 988 (vs), 1063 (m), 931 (m), 851 (m), 806 (s), 766 (s), 726 (s), 697 (s), 651 (m), 628 (m), 588 (s).$^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ -6.48, -1.14, 8.61. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 0.04 (s, 3H), 0.7 (m, 12H), 3.6 (t, J = 3.3 Hz, 9H) [2].

1,3,5,7-Tetramethyl-1,3,5,7-tetrakis(2-(silyl)ethyl)tetracyclosiloxane (47)



$Si_4O_4Me_4(CH_2CH_2SiCl_3)_4$ (4.025g, 4.54mmoles) was added slowly to a stirred suspension of LAH (1.03g, 27.1mmoles) in diethyl ether (100ml). The mixture was left stirring over the weekend. The mixture was filtered through celite and the filtrate was added cautiously to 2N HCl (64ml, ice cooled). The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous NaCl solution. The organic layer was dried over $MgSO_4$. This was filtered and the volatile compounds were removed on the rotary evaporator. IR spectra had a strong peak at 2148 cm^{-1} that will be due to the Si-H stretch. IR (neat, cm^{-1}) 2977 (m), 2932 (m), 2148 (vs), 1411 (m), 1263 (s), 1143 (s), 1074 (vs), 988 (m), 920 (vs), 788 (s), 760 (s), 731 (s), 663 (m) and 600 (m). $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ -2.04, -1.38, 12.53. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 0.1 (s, 12H), 0.60 (m, 6H), 0.70 (m, 6H), 1.6 (s), 3.55 (t, J = 4.3 Hz, 12H) [2].

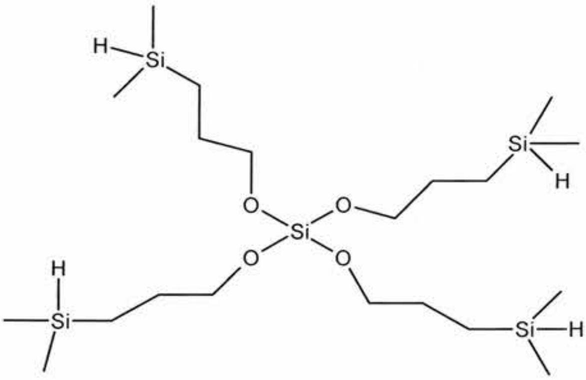
1,3,5,7-Tetramethyl-1,3,5,7-tetrakis(2-(dimethylsilyl)ethyl)tetracyclosiloxane (48)



$Si_4O_4Me_4(CH_2CH_2SiMe_2Cl)_4$ (3.23g, 4.47mmoles) was added to a stirred suspension of LAH (0.34g, 8.96mmoles) and diethyl ether (100ml) and left to stir overnight. The mixture was filtered through celite and the filtrate was added carefully to 2N HCl (61ml, ice cooled). The aqueous layer was washed twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous NaCl solution. The organic layer was dried over $MgSO_4$ and then filtered through celite. The volatile compounds were removed on the rotary evaporator. The IR spectra had a small and broad peak at 2159 cm^{-1} due to Si-H stretch there was a very large and broad OH stretch in this spectra. This experiment was repeated and a better IR spectra was obtained. The product was a clear, colourless oil (1.78g, 3.28mmoles, 73.3%). IR (neat, cm^{-1}) 2966 (s), 2920 (s), 2864 (s), 2818 (m), 2102 (s), 1411 (m), 1366 (m), 1263 (s), 1143 (s), 1091 (brs), 897 (brs), 840 (s), 806 (brs), 760 (s), 714 (m), 617 (m), 583 (m). $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 9.76, 5.47, -1.56, -4.97 plus extra peaks. ^1H NMR

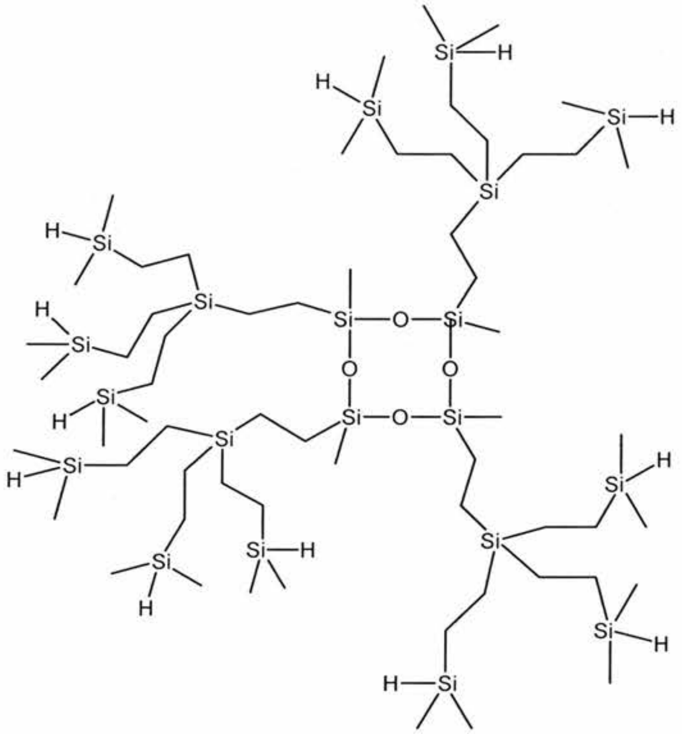
(300MHz, $CDCl_3$, 25°C): δ 4.88 (m, 1H), 0.54 (m, 4H), 0.11 (m, 9H) ^{29}Si NMR (59.6MHz, 50% v/v $CDCl_3/CHCl_3$, 25°C): δ -10.04, -20.19 plus some other little peaks [2]. CHN analysis gave %C 40.96 : %H 9.70 whereas the theoretical values were calculated as being %C 41.03 : %H 9.64.

Tetrakis(2-(dimethylsilyl)propoxy)silane (49)



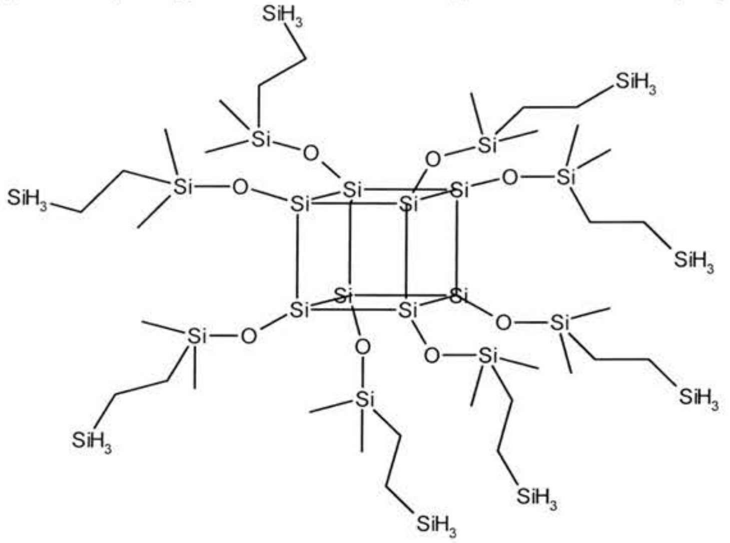
$Si(OCH_2CH_2CH_2SiClMe_2)_4$ (2.5042g, 3.94mmoles) was added to a stirred suspension of LAH (0.2996g, 7.89mmoles) in diethyl ether (120ml). The resulting mixture was stirred overnight. The mixture was filtered through celite and the filtrate was added carefully to 2N HCl (55ml, ice cooled). The aqueous layer was washed twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous NaCl solution. The organic layer was dried over $MgSO_4$ and then filtered through celite. The volatile compounds were removed on the rotary evaporator. The IR spectra had a small and broad peak at 2114 cm^{-1} that will be due to the Si-H stretch and there was a very large and broad OH stretch in this spectra. IR (neat, cm^{-1}) 3432 (vbrvs), 2125 (brm), 1651 (brs), 1263 (m), 1183 (m). ^{13}C NMR had more peaks than were necessary for the dendrimer. This reaction was repeated by carrying out the initial formation of the starting material under argon and storing this in the fridge prior to its use. The actual reaction was also carried out under argon and gave a strong peak in the IR spectra at 2045 cm^{-1} that corresponds to a Si-H stretch [2]. There was no septet around δ 3.8 in the ^{1}H NMR spectra that indicated that the expected product had not been formed.

1,3,5,7-Tetramethyl-1,3,5,7-tetrakis[2-(tris[2-dimethylsilylethyl)silyl)ethyl]tetracyclosiloxane (50)



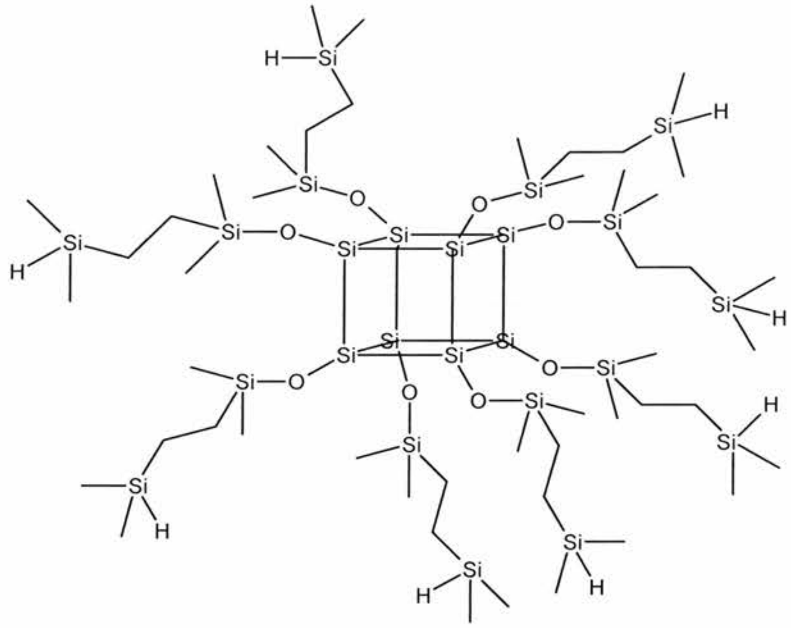
Dendrimer was dissolved in dry diethyl ether (50ml) and added drop-wise to a suspension of LAH (0.58g, 15.3mmoles) in dry diethyl ether (50ml), under argon. The reaction mixture was allowed to stir over the weekend. The resulting mixture was filtered through celite and poured carefully into ice-cooled 2N aqueous HCl solution (10ml). The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous NaCl solution. The organic layers were then dried over $MgSO_4$. This was filtered and the volatile compounds were removed on the rotary evaporator. The product was a clear, colourless oil (0.33g, 0.219mmoles, 8.6%). The IR gave a strong Si-H peak at 2125 cm^{-1}. IR (neat, cm^{-1}) 3375 (brm), 2954 (s), 2909 (s), 2875 (s), 2761 (m), 2386 (m), 2352 (m), 2125 (s), 1434 (m), 1411 (m), 1257 (s), 1137 (s), 1063 (brs), 886 (brs), 840 (s), 760 (brs), 663 (m), 640 (m). $^{13}C\{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 6.3, 3.4, 0.9, -5. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 0.05 (m), 0.25 (m), 3.88 (s) [2]. There was no visible splitting on the suspected Si-H peak at 3.88.

1,3,5,7,9,11,13,15-Octakis{2-[(silyl)ethyl]dimethylsiloxy}-pentacyclo[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]octasiloxane (51)



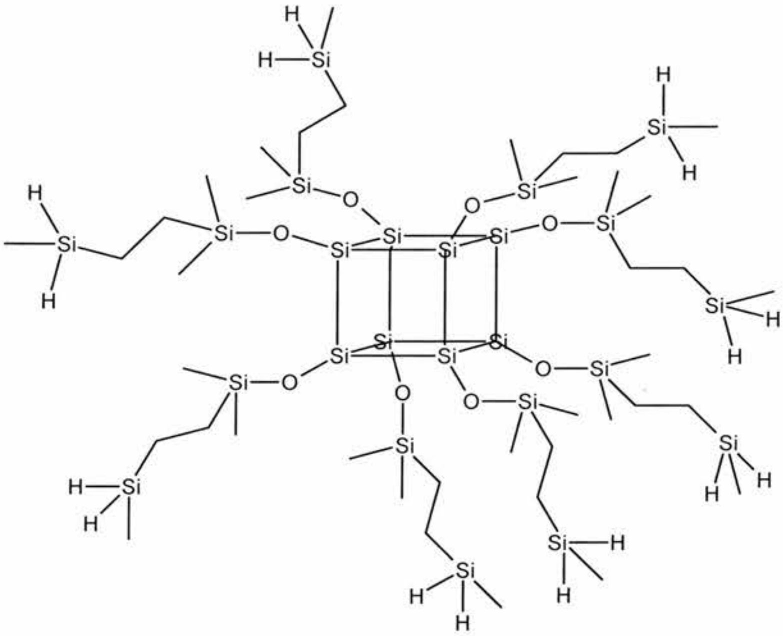
Octakis(trichlorosilyl)silicate dissolved in diethyl ether (5ml) was cannulated slowly into a stirring solution of LAH (0.36g, 9.48mmoles) in diethyl ether (20ml) under argon. The resulting mixture was stirred overnight. This was filtered through celite and added cautiously to ice cooled 2N HCl (21ml). The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous brine solution before being dried over magnesium sulfate. This was filtered through a sintered glass funnel and celite before the volatile compounds were removed on the rotary evaporator. ^{13}C {^{1}H} NMR (75MHz, CDCl$_3$, 25^{o}C): δ 13.06, -1.06, -2.23. ^{1}H NMR (300MHz, CDCl$_3$, 25^{o}C): δ 3.60 (t, J = 2.3 Hz, 3H), 0.77 (m, 5H), 0.03 (s, 8H) plus some impurities. ^{29}Si NMR (59.6MHz, 50% v/v CDCl$_3$/CHCl$_3$, 25^{o}C): δ 12.53, -21.92, -53.71, -108.99. CHN analysis yielded %C 30.91 : %H 7.59 whereas the theoretical results were %C 25.91 : %H 7.07. This was dissolved in pentane and placed in the freezer to re-crystallise. More ^{1}H NMR results yielded (300MHz, CDCl$_3$, 25^{o}C): δ 3.5 – 3.7 (m, 3H), 0.6 – 0.8 (m, 5H), 0.2 – 0.3 (s, 8H). Usually CH$_2$'s in these types of molecules have similar shifts so appear as one multiplet instead of two. The proton ratios are slightly out, this could be due to condensation of the cores by advantageous water.

1,3,5,7,9,11,13,15-Octakis{2-[dimethylsilyl)ethyl]dimethylsiloxy}-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (52)



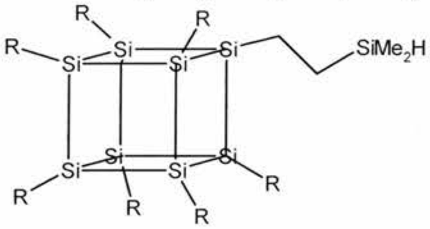
Octakis(dimethylchlorosilyl)silicate dissolved in diethyl ether (5ml) was cannulated slowly into a stirring solution of LAH (0.37g, 9.75mmoles) in diethyl ether (20ml) under argon. The resulting mixture was stirred overnight. This was filtered through celite and added cautiously to ice cooled 2N HCl (21ml). The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous brine solution before being dried over magnesium sulfate. This was filtered through a sintered glass funnel and celite before the volatile compounds were removed on the rotary evaporator. IR (neat, cm^{-1}) 2966 (vs), 2909 (s), 2886 (s), 2739 (m), 2114 (vs), 1400 (m), 1257 (vs), 1177 (vs), 1097 (brvs), 954 (m), 897 (vs), 840 (brvs), 731 (s), 708 (s), 657 (m), 606 (m), 560 (vs). $^{13}C\ \{^{1}H\}$ NMR (75MHz, $CDCl_3$, 25^{o}C): δ 10.12, 5.21, -1.12, -5.02. ^{1}H NMR (300MHz, $CDCl_3$, 25^{o}C): δ 3.89 (m, 1H), 0.58 (s, 4H), 0.18 (s, 7.5H), 0.10 (d, J = 2 Hz, 7.25H). CHN analysis yielded %C 34.35 : %H 8.14 whereas the theoretical results were %C 33.76 : %H 8.03. An IR was run on the sample that showed a peak at 2114cm^{-1} which corresponds to a silicon hydrogen bond stretch. This was dissolved in pentane and placed in the freezer to re-crystallise. The re-crystallisation was unsuccessful.

1,3,5,7,9,11,13,15-Octakis{2-[methylsilyl)ethyl]dimethylsiloxy}-pentacyclo[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]octasiloxane (53)



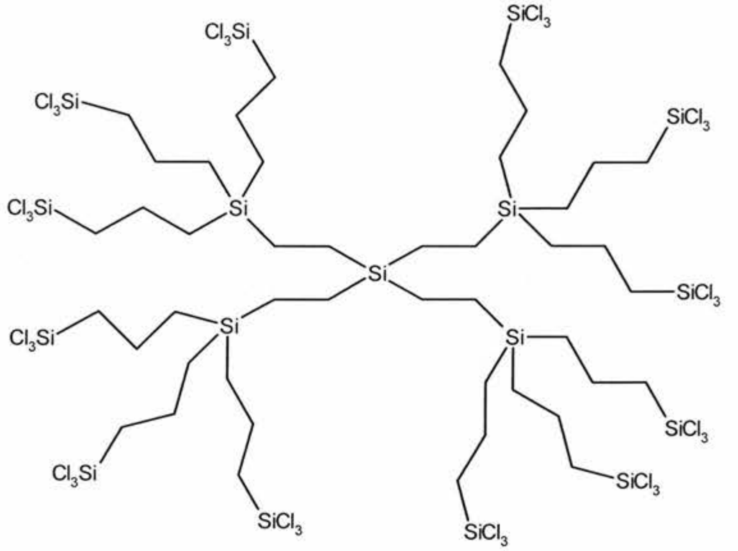
Octakis(dichloromethylsilyl)silicate dissolved in diethyl ether (15ml) was cannulated slowly into a stirring solution of LAH (0.31g, 8.17mmoles) in diethyl ether (20ml) under argon. The resulting mixture was stirred overnight. This was filtered through talc and added cautiously to ice cooled 2N HCl (21ml). The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed twice with water and once with saturated aqueous brine solution before being dried over magnesium sulfate. This was filtered through a sintered glass funnel and celite before the volatile compounds were removed on the rotary evaporator. IR (neat, cm^{-1}) 2961.5 (vs), 2913.8 (vs), 2129.5 (vs), 1407.1 (s), 1256.8 (vs), 1091.5 (brvs), 946.8 (vs), 838.2 (brvs), 722.2 (vs). ^{1}H NMR (300MHz, $CDCl_3$, 25^oC): δ 3.75 (m, 2H), 0.65 (m, 5H), 0.15 (m, 11.5H), 0.75 (m, 5.5H). The ratios of Si-H to the other groups is on the low side, could be due to the condensation of the cores by advantageous water. CHN analysis yielded %C 29.90 : %H 7.69 whereas the theoretical results were %C 30.11 : %H 7.58. An IR was run between NaCl plates that produced a strong peak at 2129.5 cm^{-1} corresponding to a Si-H stretch.

2-DimethylsilylethylheptacyclopentylPOSS (54)



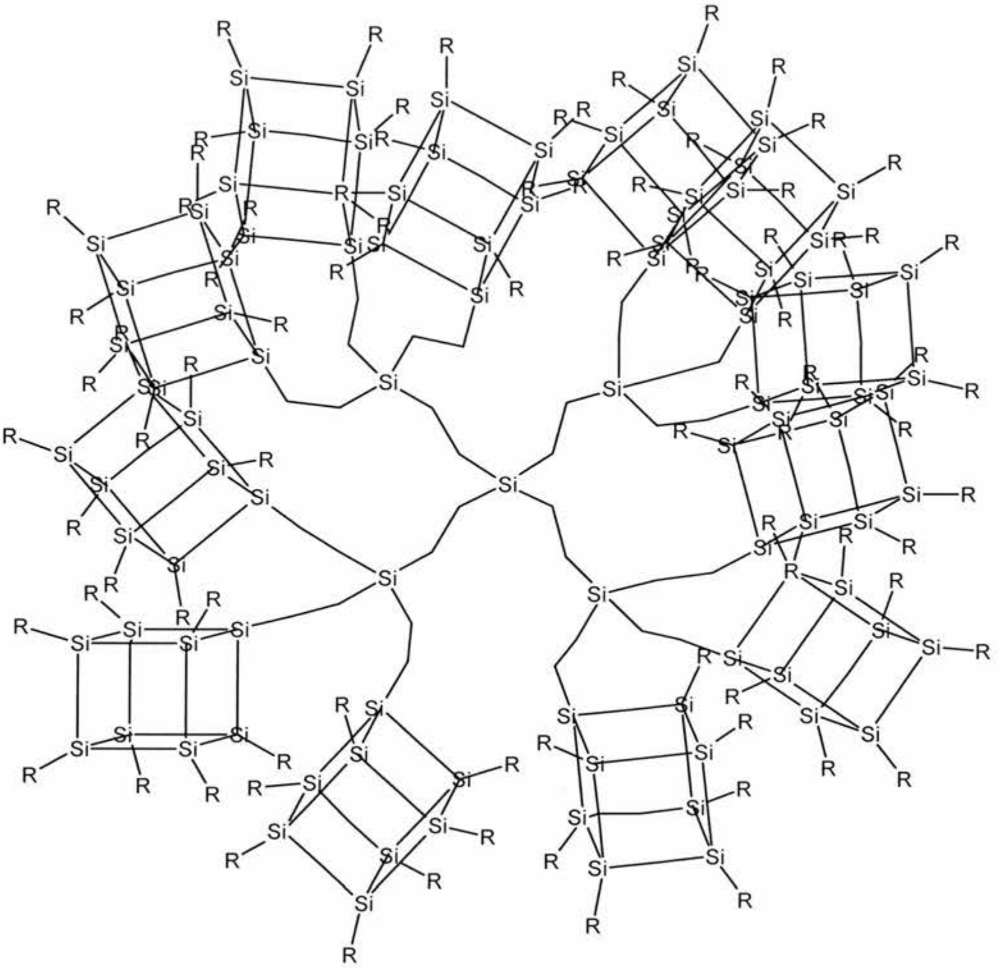
Chlorodimethylsilylethyl(cyclopentyl)$_7$POSS in diethyl ether (60ml, it didn't dissolve convincingly) was added to a stirring suspension of LAH (2.1g, 55.3mmoles) in diethyl ether (150ml). The resulting solution was stirred overnight. This was filtered through talc on a sintered glass funnel. The resulting solution was added cautiously to ice cooled 2N HCl (120ml). This was extracted twice with water and once with brine aqueous solution before being dried over magnesium sulfate. This was filtered and the volatile compounds were removed on the rotary evaporator. The IR spectra had peaks above 2000 cm^{-1} that could be due to SiH stretch. IR (KBr, cm^{-1}) 2954 (s), 2864 (s), 2818 (m), 2250 (m), 1863 (brm), 1743 (brm), 1446 (m), 1400 (m), 1320 (m), 1251 (s), 1120 (brvs), 948 (m), 914 (m), 886 (s), 851 (m), 817 (m), 766 (m), 743 (m), 708 (m), 686 (m), 617 (m), 565 (m), 508 (s). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ 3.85 (m, 1H), 1.60 (m, 79H), 0.60 (m, 4.6H), 0.05 (m, 7.3H) plus a substantial impurity at 0.9 – 1.1. ^{29}Si NMR (59.6MHz, 50% v/v $CDCl_3$/$CHCl_3$, 25°C): δ -10.19, -66.58 plus other smaller peaks. CHN analysis yielded %C 47.30 : %H 7.55 compared to the theoretical values of %C 47.42 : %H 7.55. This reaction was part of the hydrosilation test, it was hoped that by reducing the Si-Cl to Si-H better analysis could be carried out on the product. This molecule could have been hydrosilated to the octakisvinylsilicate to make a viscosity modifier but the integration values of the cyclopentyl groups compared to the CH_2 groups in subsequent reactions were very wrong.

Tetrakis[2-(tris(trichlorosilyl)propyl]silyl)ethyl]silane (55)



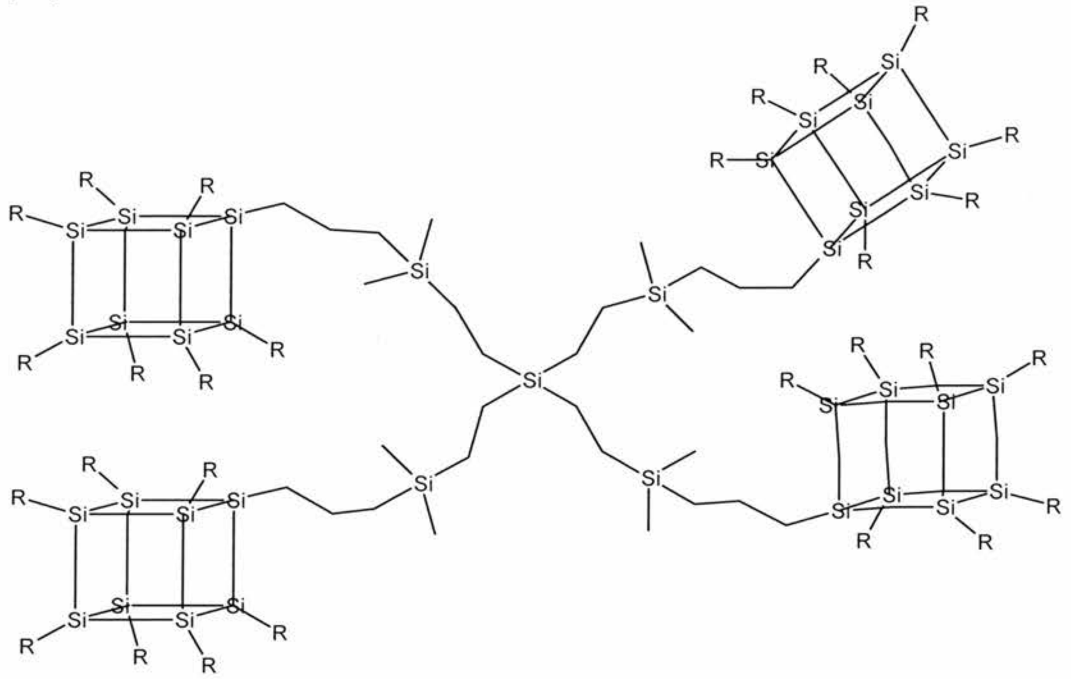
$Si(CH_2CH_2SiH_3)_4$ (0.64g, 2.42mmoles), allyltrichlorosilane (7.75g, 44.2mmoles), THF (20ml) and Karstedt's catalyst were placed in a 250ml round bottomed flask. The resulting mixture was stirred at room temperature for 30 minutes, and subsequently at 65°C for 10 hours. This reaction was repeated using the Speier's catalyst (5 drops) under nitrogen. In the ^{13}C NMR there were peaks in the vinyl region suggesting that the reaction had not gone to completion. ^{13}C NMR gave vinyl peaks at δ 114-118, 127-132 and so did the repeat reaction and there were too many peaks in the rest of the spectra [2].

Tetrakis{2-(tris(2-heptacyclopentylPOSS)ethyl)silyl)ethyl}silane (56)



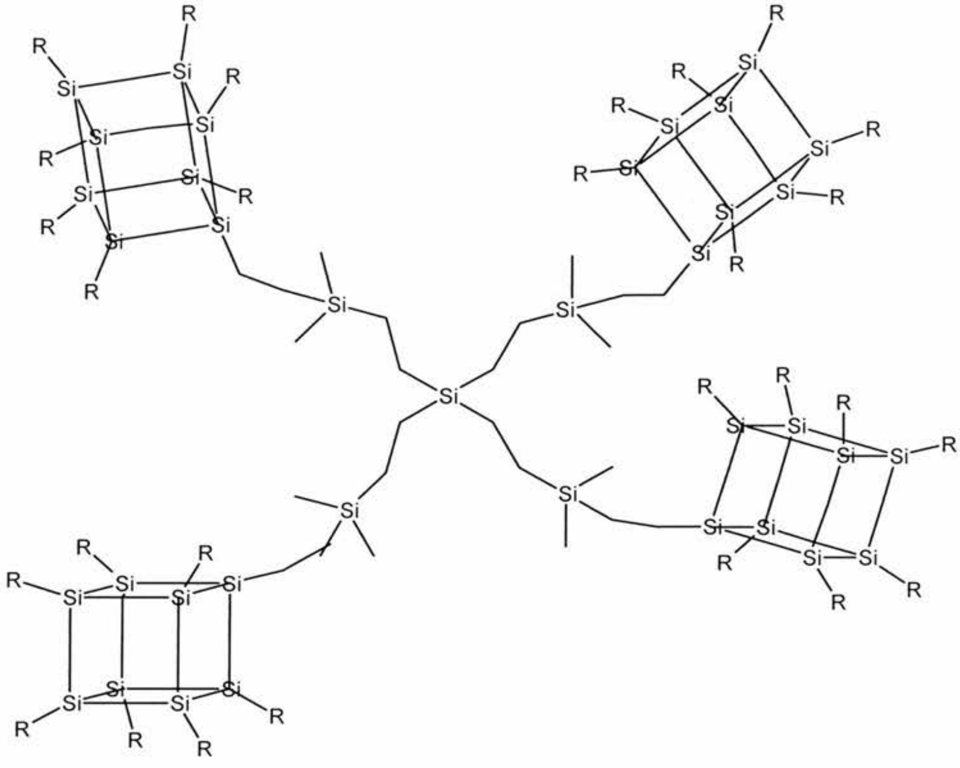
$Si(CH_2CH_2SiH_3)_4$ (0.007g, 0.0264mmoles) was added to the vinylheptacyclopentyl POSS (0.12g, 0.129mmoles) in dry THF (3.5ml). Karstedt's catalyst was added to the reaction mixture that was then stirred and heated for 5 hours. The solvent was left to evaporate off at room temperature, crystals were obtained which turned out to be vinylheptacyclopentyl POSS [14]. ^{13}C {^1H} NMR (75MHz, $CDCl_3$, 25°C): δ 135, 125, 26, 22. ^{29}Si NMR (59.6MHz, 50% v/v $CDCl_3/CHCl_3$, 25°C): δ -66, -80 [2]. Spectra appeared to contain vinylheptacyclopentylPOSS only.

Tetrakis{2-(2-heptacyclopentylPOSS)propyldimethylsilyl)ethyl]silane (57)



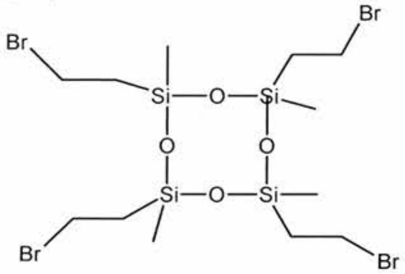
$Si(CH_2CH_2SiMe_2H)_4$ (0.1g, 0.265mmoles), allylheptacyclopentyl POSS (1g, 1.06mmoles), THF (4ml) and Karstedt's catalyst in xylene solution (2 drops) were refluxed for 2 hours. The volatile compounds were allowed to evaporate in air and analysis was carried out, but the material produced was starting material. So the mixture had more Karstedt's catalyst (3 drops) added to it and it was stirred at room temperature for 30 minutes and subsequently for 10 hours at 65°C. It still had not worked so more THF (24ml) was added to the mixture and it was stirred for 30 minutes at room temperature and subsequently at 65°C for 10 hours. Volatile compounds were removed on the rotary evaporator. In all three attempts vinyl groups appeared in the carbon NMR spectra δ 115 and 134 [2]. IR (KBr, cm^{-1}) 3454 (brm), 2954 (m), 2852 (m), 1263 (m), 1108 (vs), 496 (m).

Tetrakis{2-(2-heptacyclopentylPOSS)ethyldimethylsilyl)ethyl}silane (58)



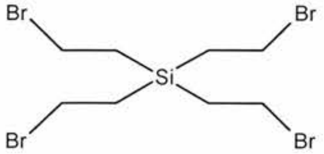
Vinylheptacyclopentyl POSS (1.18g, 1.27mmoles) in dry diethyl ether (30ml) with Karstedt's catalyst (12 drops) had $Si(CH_2CH_2SiMe_2H)_4$ (0.11g, 0.292mmoles) in diethyl ether (10ml) added to it under argon. The resulting mixture was refluxed overnight (vinylheptacyclopentyl POSS is not very soluble in diethyl ether). Volatile compounds were removed on the rotary evaporator but it looks like the starting material had deposited around the glassware. ^1H NMR spectra showed the presence of vinyl peaks. An IR spectra was run and showed no peaks around 2000cm^{-1} therefore there is no SiH present in the sample. A tlc was run on the sample and the two starting materials dissolved in THF. The tlc was eluted with hexane/diethyl ether 95/5 and the plate was developed in iodine. The product and the vinylheptacyclopentyl POSS had two spots (one of which was a faint spot at the baseline) and looked identical. The dendrimer had 3 spots (two faint ones, one at the baseline and one further up the plate at the same position as for the POSS species) the main spot was close to the solvent front. There was some non-dissolved solid present in the product. This was dissolved in THF and filtered, the NMR of the filtrate appears to be pure vinylheptacyclopentyl POSS. There are two peaks, one just above zero that could possibly be the dendrimer, but there doesn't appear to be any CH_2 groups that would indicate if the reaction was successful, or any SiH peaks, one of these peaks could be grease.

1,3,5,7-Tetramethyl-1,3,5,7-tetrakis[2-(bromo)ethyl]tetracyclosiloxane (59)



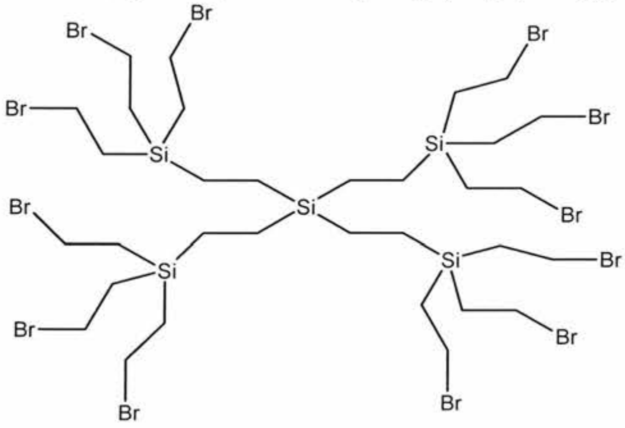
To a solution of dendrimer core (1ml, 1.0g, 2.89mmoles) in hexane (125 ml) was added benzoyl peroxide (0.1g, 0.537mmoles), the mixture was stirred until the peroxide was completely dissolved. The solution was saturated with anhydrous hydrogen bromide for 30 minutes using a gas dispersion tube. HBr is produced from the addition of bromine to tetrahydronaphtalene. The resulting mixture was stirred overnight at room temperature. The mixture was purged with argon to remove excess hydrogen bromide. The product was washed twice with a slightly basic aqueous solution and the volatile compounds were removed on the rotary evaporator. The product was a clear, colourless oil (1.42g, 2.12mmoles, 75.0%). $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 28.65, 23.33, -0.535. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 0.2 (m, 4H), 1.40 (m, 2H), 3.51 (m, 2H). There are peaks in the vinyl region of the spectra. In the repeat reaction the product was washed twice with K_2CO_3 solution (0.05M) and once with water instead of just washing twice with the basic solution [21].

Tetrakis[2-(bromo)ethyl]silane (60)



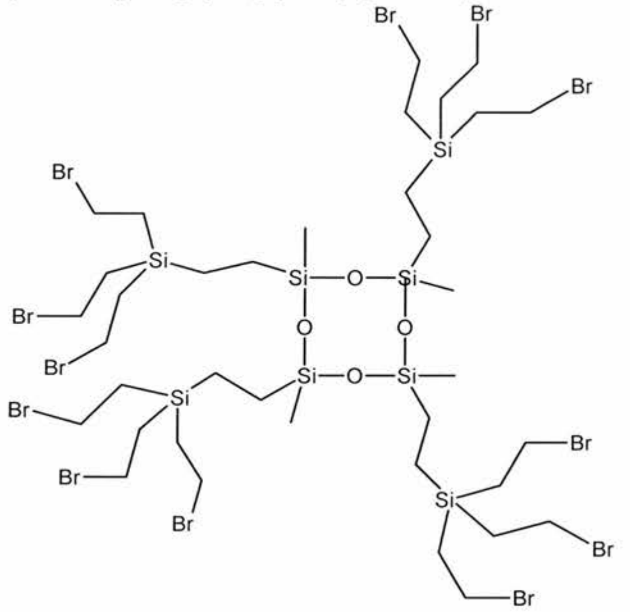
To a solution of dendrimer core (0.7ml, 0.56g, 4.11mmoles) in hexane (77 ml) was added benzoyl peroxide (0.01g, 0.0537mmoles), the mixture was stirred until the peroxide was completely dissolved. The solution was saturated with anhydrous hydrogen bromide for 30 minutes using a gas dispersion tube. The resulting mixture was stirred overnight at room temperature. The mixture was purged with argon to remove excess hydrogen bromide. The product was washed twice with slightly basic aqueous solution and the volatile compounds were removed on the rotary evaporator. $^{13}C\ \{^{1}H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 30.69, 29.69, 20.09, 19.45. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 3.6 (m, 2H), 1.6 (m, 2H). There were still some vinyl groups that had not been brominated. In the repeat reaction the product was washed twice with K_2CO_3 solution (0.05M) and once with water instead of just washing twice with the basic solution [21].

Tetrakis[2-tris(2-bromo)ethyl)silyl)ethyl]silane (61)



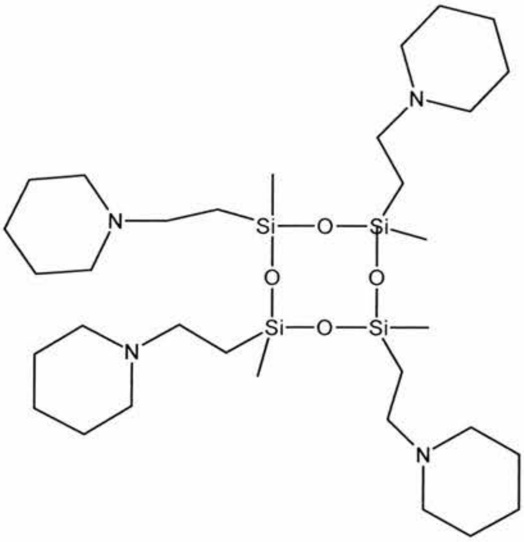
To a solution of dendrimer core (0.24g, 0.416mmoles) in hexane (75 ml) was added benzoyl peroxide (0.09g, 0.483mmoles), the mixture was stirred until the peroxide was completely dissolved. The solution was saturated with anhydrous hydrogen bromide for 30 minutes using a gas dispersion tube. The resulting mixture was stirred overnight at room temperature. The mixture was purged with argon to remove excess hydrogen bromide. The product was washed twice with K_2CO_3 solution (0.05M) and once with water and the volatile compounds were removed on the rotary evaporator. It was not obvious from the NMR that peaks were the important ones if any, but in the carbon NMR there are peaks in the vinyl region at δ 129 and 130 suggesting that benzoic acid was formed and therefore some of the radical reaction might have taken place [21].

1,3,5,7-Tetramethyl-1,3,5,7-tetrakis{2-(tris[2-(bromo)ethyl)silyl)ethyl]tetracyclosiloxane (62)



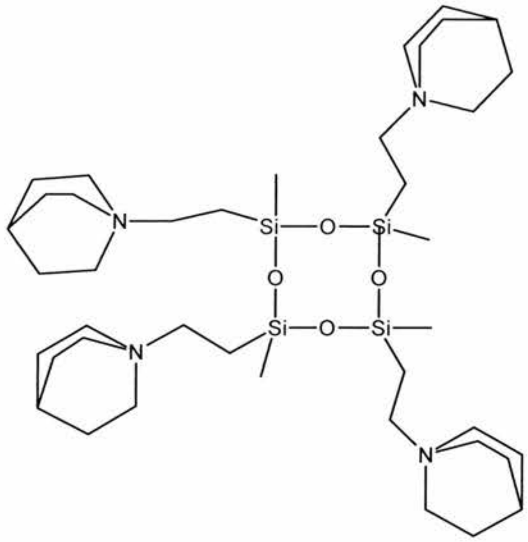
To a solution of dendrimer core (0.4g, 0.509mmoles) in hexane (150 ml) was added benzoyl peroxide (0.1g, 0.537mmoles), the mixture was stirred until the peroxide was completely dissolved. The solution was saturated with anhydrous hydrogen bromide for 30 minutes using a gas dispersion tube. The resulting mixture was stirred overnight at room temperature. The mixture was purged with argon to remove excess hydrogen bromide. The product was washed twice with K_2CO_3 solution (0.05M) and once with water and the volatile compounds were removed on the rotary evaporator. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25^{o}C): δ 29.11, 18.34, 0.81. ^1H NMR (300MHz, $CDCl_3$, 25^{o}C): δ 3.6 (m, 2H), 1.6 (m, 3H), 0.11 (s, 3H). There were vinyl peaks present in the spectra. There were some extra peaks in the carbon spectra that were not solvent peaks [21]. In the repeat reaction, the peaks mostly belong to the starting material but there are several smaller peaks in the ^{13}C that could belong to the product.

1,3,5,7-Tetramethyl-1,3,5,7-tetrakis[2-(cyclohexylamyl)ethyl]tetracyclosiloxane (63)



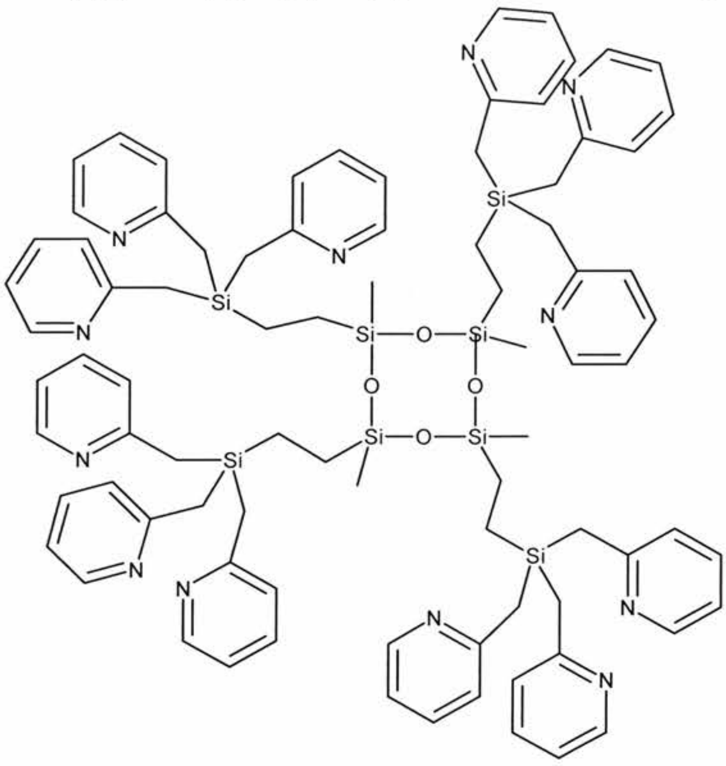
1,3,5,7-tetramethyl-1,3,5,7-tetrakis[2-(bromo)ethyl]tetracyclosiloxane **(59)** (1.23g, 1.84mmoles), cyclohexylamine (1.8ml, 1.6g, 18.5mmoles) and dry ethanol (40ml) were refluxed together for 6 days under argon. The mixture was filtered and the volatile compounds were removed on the rotary evaporator. The ^{13}C NMR only showed peaks corresponding to cyclohexylamine therefore it is possible that since cyclohexylamine is a primary amine and therefore not as reactive as other amines, this reaction may work with other kinds of amines.

1,3,5,7-Tetramethyl-1,3,5,7-tetrakis[2-(quinuclyl)ethyl]tetracyclosiloxane (64)



Dendrimer **(59)** (0.19g, 0.284mmoles), quinuclidine (0.12g, 1.08mmoles) and ethanol were refluxed together, under argon, for 5 days. Volatile compounds were removed on the rotary evaporator. To remove the excess quinuclidine, ethanol was added unfortunately there wasn't much product left after that. ^{13}C {^{1}H} NMR (75MHz, $CDCl_3$, 25°C): δ 46.06, 23.41, 22.40, 18.94, 18.40, 0.08 plus some extra peaks. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 3.71 (m), 3.34 (m), 2.16 (s), 1.96 (m), 1.17 (m), 1.0 (m), 0.17 (m), 0 (s). From the carbon and the hydrogen it appeared that there was too much quinuclidine present so that is why the product was washed with ethanol to get rid of the excess quinuclidine.

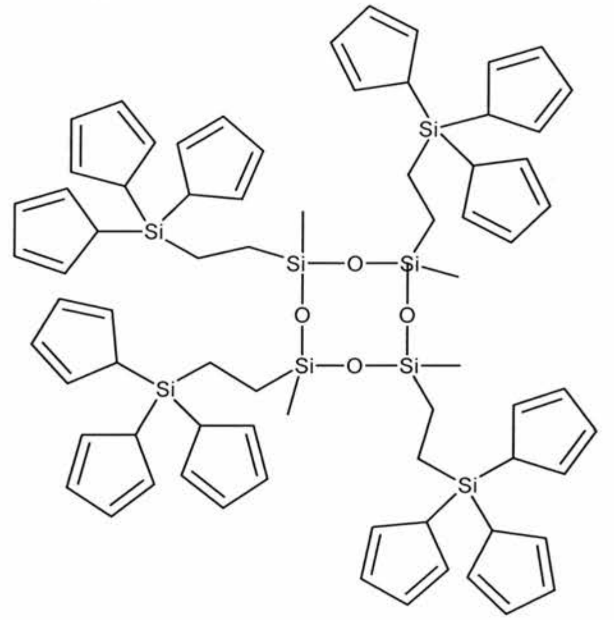
1,3,5,7-Tetramethyl-1,3,5,7-tetrakis{2-(tris[2-methylpyridinyl)silyl]ethyl}tetracyclosiloxane (65)



Butyllithium (48ml, 76.8mmoles) was added to 2-methylpyridine (7.6ml, 7.2g, 77.0mmoles) in THF (25ml) under argon. The solution changed colour immediately on addition at 0°C. The resulting mixture was stored in the freezer under argon overnight. The dendrimer **(14)** in THF (25ml) was added to the cooled mixture at 0°C. There was 10 times too much BuLi used in this reaction and a solid formed on addition of the dendrimer to the reagent so it is quite likely that this reaction hasn't worked. The solution was allowed to warm to room temperature over a period of several hours. Ethanol (350ml) was added to hydrolyse any remaining alkylating agent and Si-Cl bonds. The orange mixture was evaporated to dryness and it was stored in the fridge overnight. The solid was dissolved in CH_2Cl_2, filtered through celite, and the volatile compounds were removed on the rotary evaporator to leave a reddy/orange solid. Attempts to dissolve the product in CH_2Cl_2 didn't work and neither did dissolving it in ethanol [22]. $^{13}C\{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 134.6, 134.4, 4.6, 2.4. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 6.20 (m), 5.80 (m), 1.5

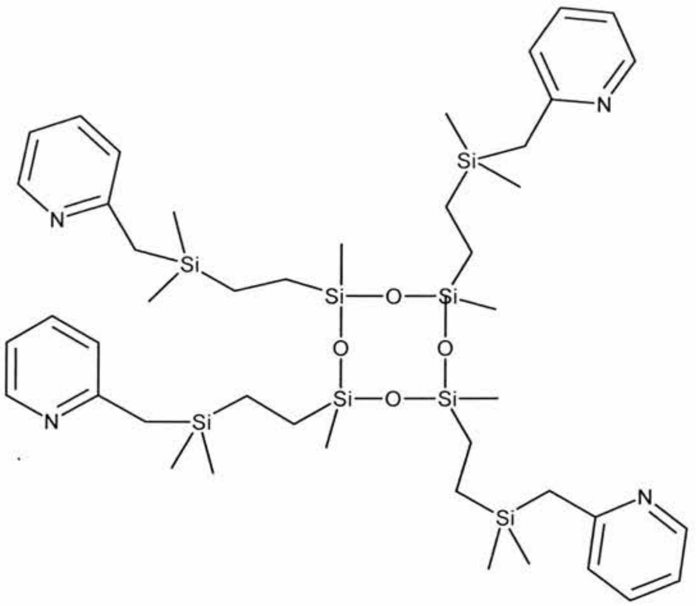
(s), 1.25 (s), 0.95 (m), 0.60 (m), 0.1 (s). There is little or no picoline present in the ^{1}H NMR spectra. The peak at 0.1 is not big enough to be the methyl peak. It is possible that there is not enough room around the silicon atom to place 3 picoline groups. There are not enough peaks in the carbon or hydrogen spectra to account for the picoline being present. Also in the hydrogen NMR spectra there does not appear to be a peak for the methyl protons on the dendrimer or in the carbon spectra.

1,3,5,7-Tetramethyl-1,3,5,7-tetrakis(2-(tris[2-cyclopentadienyl]silyl)ethyl)tetracyclosiloxane (66)



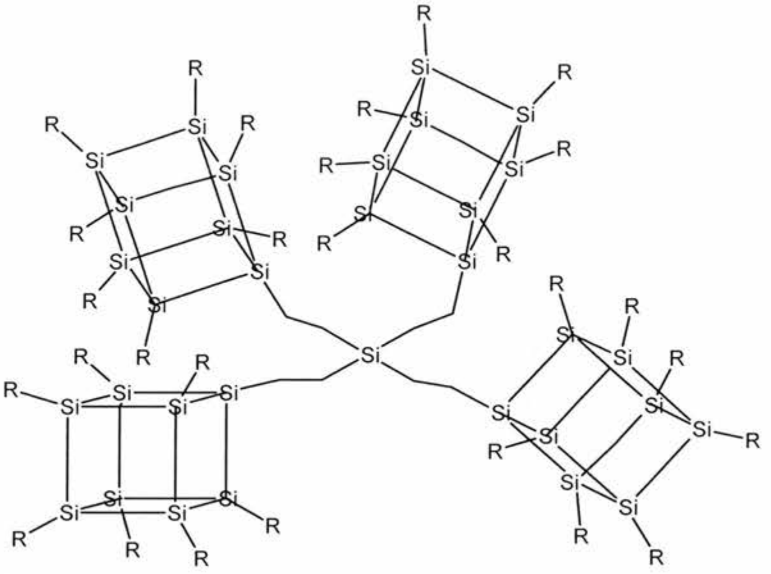
Dendrimer **(14)** in dry THF (30ml) was added to a mixture of lithium cyclopentadienylide (1.33g, 18.5mmoles) in dry THF (30ml), under argon at 0^{o}C. The resulting mixture was allowed to stir overnight whilst gradually warming to room temperature. The reaction mixture was quenched with ethanol (5ml) and the volatile compounds were removed on the rotary evaporator. The dried crude product and small amount of liquid were dissolved (at least partially since the filtrate was brown) in CH_2Cl_2 and then filtered through celite. The volatile compounds were removed on the rotary evaporator [22]. $^{13}C\{^{1}H\}$ NMR (75MHz, $CDCl_3$, 25^{o}C): δ 124, 22, 13, 0. ^{1}H NMR (300MHz, $CDCl_3$, 25^{o}C): δ 3.8 (m, 4H), 2.71 (s, 3H), 1.2 (m, 6H). It is possible that there is not enough room around the Si atom to place 3 cyclopentadienyl groups.

1,3,5,7-Tetramethyl-1,3,5,7-tetrakis{2-[2-methylpyridinyl)silyl]ethyl}tetracyclosiloxane (67)



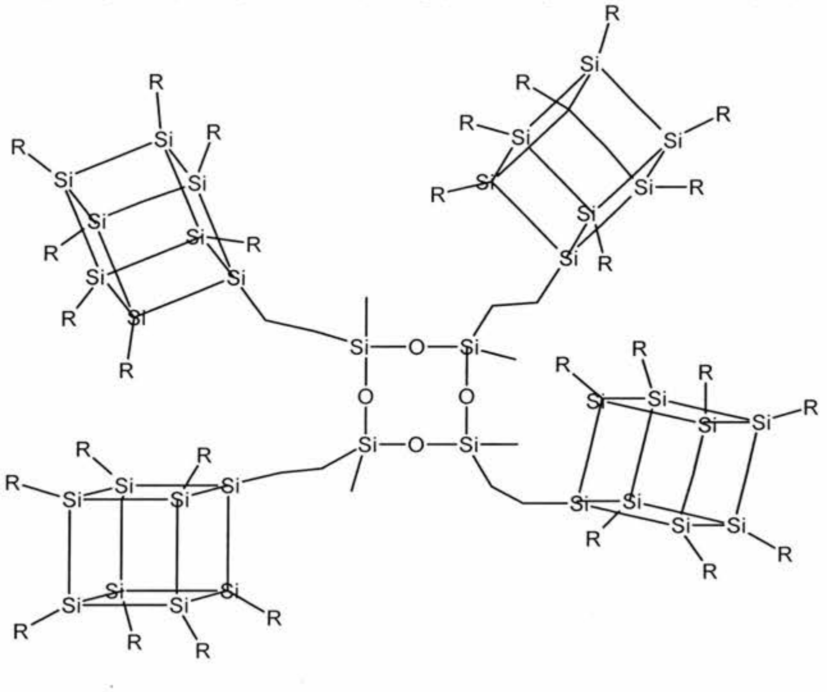
Butyllithium (10 ml, slight unintentional excess 2.5 M in hexane, 25.0mmoles) was added to 2-methylpicoline (1.8 ml, 1.7g, 18.2mmoles) in THF (20 ml) at 0°C. After stirring for a few minutes at 0°C giving a red solution, dendrimer 15 in THF (20 ml) was added. The solution was allowed to warm to room temperature over the weekend, whilst stirring under argon. Ethanol (12 ml) was added to hydrolyse any remaining alkylating agent and Si-Cl bonds. The light brown solution was evaporated to dryness to give a brown wax-like solid that was dissolved in CH_2Cl_2 and filtered through celite. The volatile compounds were removed on the rotary evaporator. A tlc run in CH_2Cl_2/ethanol mixture gave three spots (including the baseline spot). $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 148.99, 135.71, 122.07, 119.02, 23.17, 8.28, 7.22, -2.97, -4.16. There are more peaks present from the impurities. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 8.35 (m, 1H), 7.40 (m, 1H), 6.90 (m, 1H), 0.4 (m, 3H), 0 (m, 12H), 0.9 (m, 2H). There are possibly ethoxy groups present due to the quenching of Si-Cl bond by ethanol. The product would not dissolve into dichloromethane, dichloromethane/ethanol, diethyl ether and THF. Some of the product was dissolved in ethanol and placed in the freezer to re-crystallise. No product crystallised out.

Tetrakis(2-heptacyclopentylPOSS)ethyl)silane (68)



T7 cyclopentyltrisilanol (1.3g, 1.44mmoles) was stirred in toluene (200mL). To this suspension $Si(CH_2CH_2SiCl_3)_4$ (0.25g, 0.369mmoles) and triethylamine (0.5g, 4.94mmoles) were added. A white gas appeared. The mixture was stirred vigorously overnight then the hydrochloride salt was filtered off. The solvent was removed under vacuum leaving a white solid. This experiment was repeated using a longer reaction time, with heating and using BuLi as the base instead of triethylamine, the product in this case was a brown gel. This experiment has been repeated using dry THF, under nitrogen and letting the solvent evaporate in air. The original experiment gave ^{13}C NMR spectra the same as T7 cyclopentyltrisilanol, this implies that nothing had happened. Powder diffraction patterns were run that were essentially the same for this product and T7 cyclopentyltrisilanol. IR spectra were similar for this product and T7 cyclopentyltrisilanol except that there were peaks around 2500 cm^{-1} in the spectra of this product that were not in the spectra of T7 cyclopentyltrisilanol. IR (KBr, cm^{-1}) 3239 (brs), 2954 (vs), 2864 (vs), 2614 (m), 2591 (m), 2466 (m), 1474 (m), 1451 (s), 1383 (m), 1331 (s), 1251 (s), 1108 (brvs), 920 (s), 880 (s), 811 (m), 1400 (m), 502 (vs). The filtrate from this experiment was analysed by ^{13}C NMR and showed a trace similar to T7 cyclopentyltrisilanol. With heating the ^{13}C NMR pattern had a multiple signals between δ 28-29 and more between δ 23-24.5, this appears to be due to polymerisation of the T7 POSS molecule as a control experiment (i.e. an experiment with no dendrimer added) gave similar ^{13}C NMR data and a brown oil. ^{29}Si NMR (59.6MHz, 10-15% v/v C_6D_6/C_6H_6, 25°C): δ -53.10, -55.07, -64.01, -64.50, -65.63 plus other smaller peaks. BuLi experiment $^{13}C\{^1H\}$ NMR (75MHz, C_6D_6, 25°C): δ 30.86, 28.69, 28.58, 28.53, 28.22, 28.16, 24.14, 23.92, 23.40, -15.30. CHN analysis yielded %C 44.73 %H 7.09 whereas the theoretical was calculated as being %C 47.85 : %H 6.51 [23].

1,3,5,7-tetramethyl-1,3,5,7-tetrakis(2-heptacyclopentylPOSS)ethyl)tetracyclosiloxane (69)



Dendrimer **(14)** (0.29g, 0.327mmoles) was added to a solution of c-C_5H_9 trisilanol (1.167g, 1.29mmoles), triethylamine (2ml, 1.4g, 14.4mmoles) in THF (45ml) and left stirring overnight, under argon. This reaction may not have worked since the solvent and the trichlorosilane may not have been fully evaporated from the starting material. The hydrochloride was filtered off and the solution was left in air to let the volatile compounds evaporate off. ^1H NMR of the repeat reaction had peaks present for POSS box and a multiplet of peaks at 3 – 3.2 ppm but no dendrimer peaks were present.

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Chapter 3

Silanols and Aldehydes

3.1 Aims and objectives

One of the main aims of this project was to synthesise novel organosilicon dendrimers (covered in Chapter 2) and to functionalise the exteriors of the dendrimers in order to render them suitable for use as catalyst supports. This chapter explores the various ways tried to functionalise the branch ends of dendrimers to produce aldehydes and silanols. Both of these types of molecules could be used as catalytic supports. It was hoped that the silanols could be used as silica mimics (i.e. could mimic the catalytic properties of metals supported on silica (if they were combined with metals)) (see Figure 3.1) or as the building blocks of silsesquioxanes.

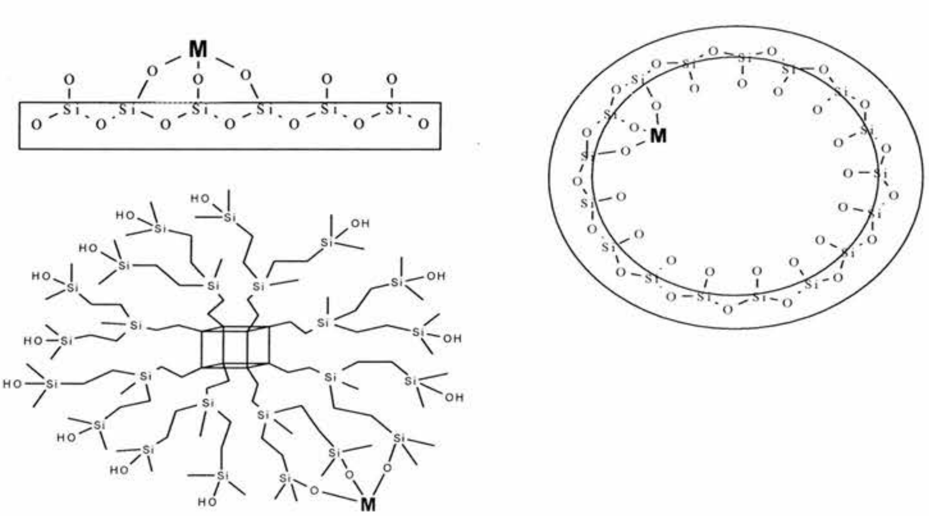


Figure 3.1 Silica mimics

Aldehydes are a good synthetic platform since there are a variety of compounds that can be made from them e.g. carboxylic acids, Schiff's bases and alcohols (see Figure 3.2). Carboxylic acids and alcohols are interesting since they can be used in crystal engineering and they can also be used as catalytic supports. Schiff's bases can be used to make catalytic supports.

Three different methods were found for making silanols, two of the methods used high dilution of the starting material, and either base or acid to hydrolyse, whereas the other method used catalytic means (Pd/C) to produce the silanols. It is important when making silanols to be careful as the chances of the product polymerising are quite high.

Both aliphatic and aromatic aldehydes were synthesised. The aliphatic aldehyde was made using a rhodium catalyst at high pressure and temperature on the core molecule 1,3,5,7,9,11,13,15-octavinylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane. The aromatic aldehyde was made by hydrosilating a protected silane aldehyde (which had been previously made by protecting bromobenzaldehyde with ethylene glycol then turning the resulting molecule into a Grignard reagent before reacting it with dimethylchlorosilane) unto 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane, followed by a deprotection step.

After the synthesis of the aldehydes attempts to make carboxylic acids from them using potassium permanganate as an oxidising agent were tried.

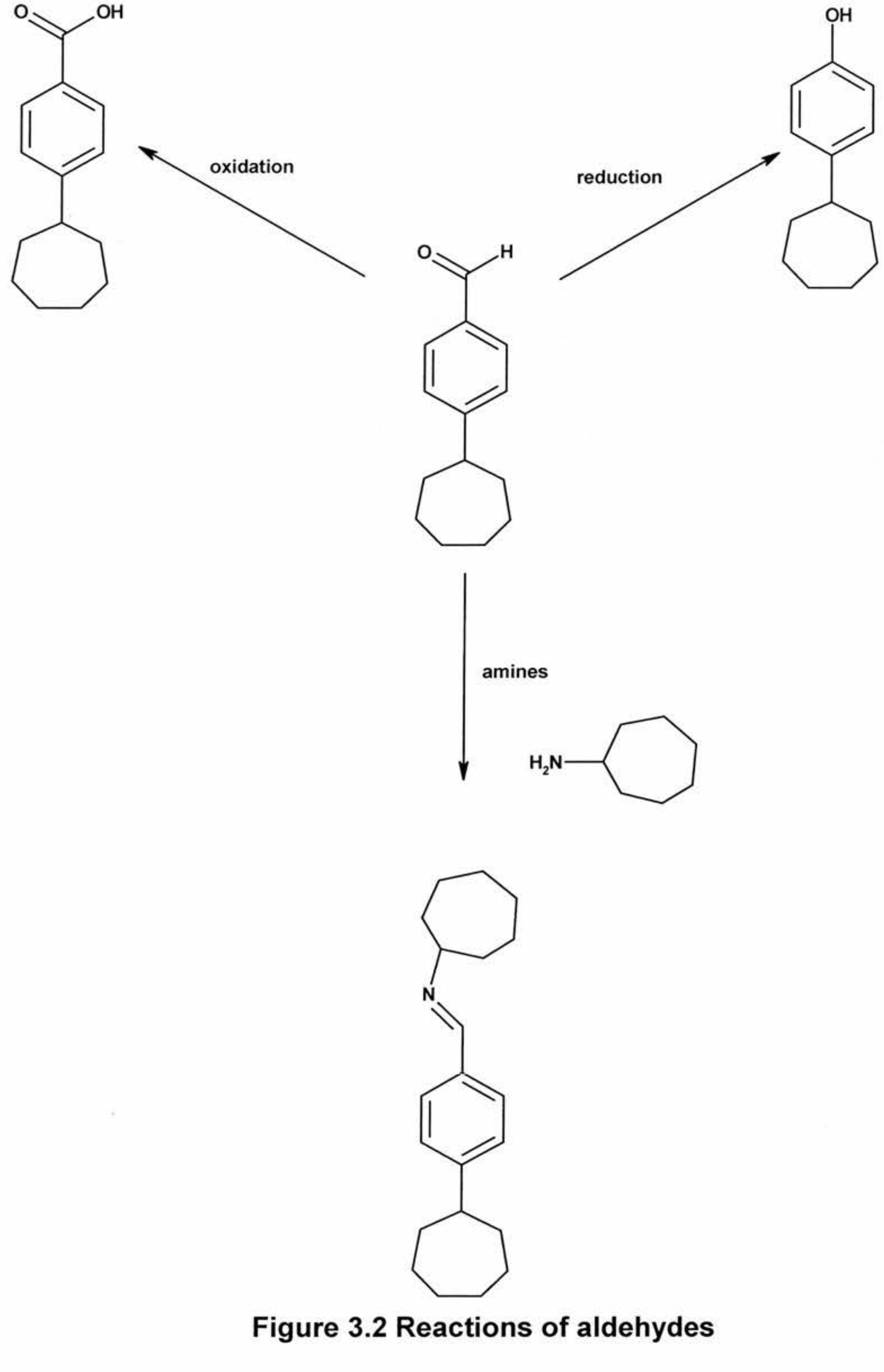


Figure 3.2 Reactions of aldehydes

3.2 Results and discussion

3.2.1 Silanols

Three different methods of hydrolysis were tried, two utilising high dilution, one with base and water on Si-Cl groups and the other with acid and water acting on Si-OMe groups. The other method used Pd on charcoal as a catalyst on Si-H groups. It was hoped that the dendritic silanol molecules could be used as supports for titanium catalysts or as silica mimics. The synthesis of some silantriols (Figure 3.3) was also tried since they could to hopefully be used as starting materials in a non-hydrolytic reaction to make mixed POSS species.

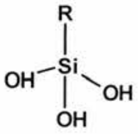


Figure 3.3 General trisilanol

There are other ways of functionalising dendrimers by placing phenol or aliphatic alcohol groups on the exterior rather than silanol groups. Using these strategies would mean that the molecules produced would not be models of silica. One such strategy, to make a phenol functionalised dendrimer, was attempted (as shown in Chapter 2, compound **(29)**) involving the formation of a dendritic ether (by hydrosilating 4-dimethylanisolesilane unto tetravinylsilane) followed by an ether cleavage reaction with BBr_3 that was unsuccessful.

Another possible strategy, leading to phenol functionalised dendrimers, is mentioned earlier in this chapter i.e. the reduction of the dendritic aromatic aldehyde to produce the dendritic phenol (see Figure 3.2).

All the strategies to produce dendrimers functionalised with either silanol or phenol groups involve the hydrosilation reaction to build the dendrimer. The main problem associated with hydrosilation reactions (as mentioned in Chapter 2) is the fact that there tends to be β-addition as well as the favoured α-addition of the silane unto the dendrimer core. There are a few ways of minimising this effect i.e. using sterically hindered core or branching molecules. The core materials which suffer less from β-addition are tetravinylsilane and 1,3,5,7,9,11,13,15-octavinylpentacyclo[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]octasiloxane. Another way of minimising β-addition (but not eliminating β-addition) is to carry out the addition of the reactants with the reaction vessel in an ice bath.

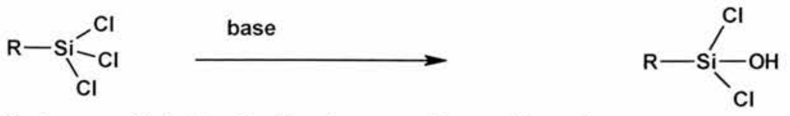
Another possible strategy would be to make dendrimers with aliphatic alcohol branch ends. This would involve using the hydrobrominated dendrimers (made in Chapter 2) and reacting them with aqueous sodium hydroxide and heat should give a dendrimer with alcohol groups on the exterior. Due to the fact that the starting dendrimer had bromine at the exterior means that the substitution reaction should be dominant over the elimination reaction [1]. The unknown factor in this reaction is whether there would be any attack at the Si-C bond from the nucleophiles.

Aliphatic alcohols could also be made from vinyl groups using the hydroboration reaction [2]. Borane adds to the less hindered side of the alkene group and reaction with alkaline hydrogen peroxide gives the aliphatic alcohol with the alcohol group at the same position as the previous borane group (α-addition of the borane molecule).

A problem that could be foreseen is that polar groups can direct where the addition of borane can occur. The examples cited in organic textbooks (i.e. [2]) involve groups that are more electronegative than carbon whereas silicon groups are less electronegative than carbon. Groups that are more electronegative than carbon, tend to direct the addition of the borane group onto the carbon that does not have the heteroatom group (the carbon which has the heteroatom group is slightly positive). This could mean that in a case where silicon is attached to a double bond, that the borane would add onto the carbon that is attached to the silicon (since the carbon with the silicon attached to it would be more negative than the other carbon in the double bond). The electronics of the reaction would be in competition with the sterics of the reaction (i.e. the sterics of the core molecule would be forcing α-addition of the borane group whereas the electronics of the reaction would be forcing β-addition of the borane group).

3.2.1.1 Hydrolysis using high dilution and base

High dilution is one way of ensuring that the silanol group, when it is made (see Scheme 3.1), is not in close proximity to another silanol group and therefore minimises the likelihood of condensation between the groups occurring (see Scheme 3.2).



Scheme 3.1 Hydrolysis reaction showing one group that has reacted

Scheme 3.2 Condensation reaction

The general reaction for hydrolysis using high dilution and base involved the trichlorosilane being added to a stirred emulsion of water, aniline and dry diethyl ether. The precipitated hydrochloride would be filtered off and the volatile compounds removed.

Hydrolysis using high dilution and a base was tried with several different trichlorosilanes: tetrakis[2-(trichlorosilyl)ethyl]silane, cyclohexyltrichlorosilane, cyclopentyltrichlorosilane and vinyltrichlorosilane. The dendritic trichloride (tetrakis[2-(trichlorosilyl)ethyl]silane) was tried in an effort to make dendritic hydroxides that could then be used as catalytic supports. The other reactions were tried since they could prove if the reaction could work and also it was hoped that they could be used as building blocks for POSS molecules.

3.2.1.1.1 Attempted synthesis of a dendritic trisilanol

Tetrakis[2-(trichlorosilyl)ethyl]silane was used in a hydrolysis reaction using aniline as base, water and a large quantity of diethyl ether as solvent [3]. The product made in this reaction was a polymer and not the expected hydrolysis product (see Figure

3.4). This is probably due to the solution not being dilute enough, the reaction not being carried out in an ice bath, and the dendrimer being added too quickly.

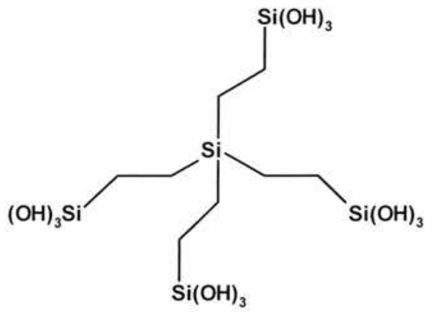


Figure 3.4 Diagram of the expected hydrolysis product

The reaction was repeated several times with no success (in the final attempt at making the product there was not enough product made to be analysed).

3.2.1.1.2 Hydrolysis of cyclohexyltrichlorosilane

Hydrolysis of cyclohexyltrichlorosilane [3] may not work first time as the reactants were reacted in the wrong quantities (i.e. at least 10 times the amount of water required was used). Cyclohexyltrichlorosilane was not very soluble in diethyl ether and at times more than a few drops were added. The reaction was repeated using the correct amount of water. The reaction was repeated several times. In one of the latter attempts a white residue was collected which gave CHN results %C 45.69 : %H 8.81 whereas the theoretical calculations gave %C 44.41 : %H 8.70. $^{13}C\ \{^1H\}$ NMR (75.4 MHz, CD_3OD, 25°C): δ 29.1, 28.1, 26.5. ^1H NMR (300 MHz, CD_3OD, 25°C): δ 1.87 (m, 2H), 1.77 (m, 3H), 1.33 (m, 5H), 0.77 (m, 1H). The multiplets were unresolvable.

This reaction was tried since the attempt to make a silsesquioxane using t-Bu(OH)3 and cyclohexyltrichlorosilane did not work due to the cyclohexyltrichlorosilane polymerising (see Chapter 4). It was believed that trying the reaction with t-BuCl3 and cyclohexylSi(OH)3 might work, since cyclohexylSi$(OH)_3$ should be more reactive than t-Bu$(OH)_3$ and t-BuCl_3 should be less reactive than cyclohexylSiCl_3. Also if it works then titanasiloxanes using this molecule and CpTiCl3 might be synthesised.

3.2.1.1.3 Hydrolysis of cyclopentyltrichlorosilane

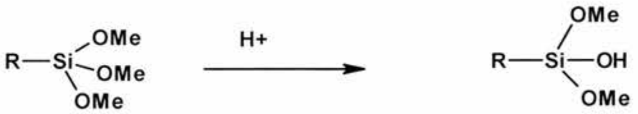
The hydrolysis of cyclopentyltrichlorosilane was also attempted. This reaction was repeated twice, for the first attempt the NMR spectroscopy showed no evidence that the correct product had been formed. The second attempt did not yield enough product to be analysed.

The hydrolysis of trichlorovinylsilane was also attempted by this method. The reaction was repeated twice. The first attempt produced no crystals and the second attempted did not produce enough product to be analysed by CHN but the proton NMR of this product did not show anything that was obviously the expected product.

From the condensation reactions of R$SiCl_3$ that produce POSS species there seems to be an obvious stability trend: cyclohexylsilanetriol is more stable than cyclopentylsilanetriol that is more stable than vinylsilanetriol. This assumption is based on the condensation reaction to produce POSS species. The fact that both cyclopentyl and cyclohexyl can be isolated as incompletely condensed POSS species whereas, as far as this author's knowledge extends, there has been no isolated incompletely condensed species of vinyl POSS. Also cyclohexyl incompletely condensed POSS takes a lot longer to form than its cyclopentyl counterpart therefore its silanetriol must be more stable than that of cyclopentyl.

3.2.1.2 Hydrolysis using acid

A reaction was found that made cyclohexyltrihydroxysilane from cyclohexyltrimethoxysilane (see Scheme 3.3). This reaction was tried using vinyltrimethoxysilane. The general reaction details follow: 10% by weight of a trimethoxysilane was hydrolysed by water at pH 3.5 adjusted by acetic acid. The non-hydrolysed silane formed oily droplets when first mixed with water. Rigorous agitation at room temperature for over an hour yielded a clear solution. The solution was allowed to stand whilst oily droplets floated to the surface. The solution was transferred to a conical flask and left in air to see if any crystals would form [4].

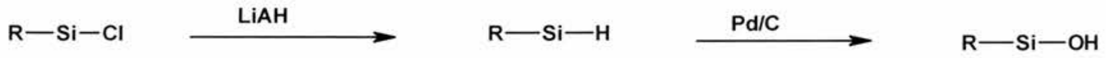


Scheme 3.3 Hydrolysis reaction showing the reaction of one group

When this procedure was tried with vinyltrimethoxysilane no crystals formed. This result could be due to the fact that the reaction was not left long enough to allow the oily droplets to form. Or it could be that vinyltrihydroxysilane is not stable enough to be isolated as crystals (in the paper, vinyltrihydroxysilane was made but it was not isolated as crystals instead it was attached to glass).

3.2.1.3 Hydrolysis using Pd/C

This reaction was tried with two dendritic cores. The cores were made by hydrosilating chlorodimethylsilane onto cores **(4)** and **(33)** before being reduced with LAH to form compounds **(48)** and **(50)** then the cores are ready to be hydrolysed using Pd/C (see Chapter 2 and Scheme 3.4).



Scheme 3.4 Hydrolysis using Pd/C

The general reaction is as follows: dendrimer in dioxane was added drop-wise to a stirring suspension of Pd/C in dioxane with buffer solution (the reaction mixture had previously been purged with argon otherwise no reaction takes place). On top of the reflux condenser was a gas collector filled with water and arranged so that the displaced water could be measured. The mixture was filtered through celite, washed through with diethyl ether and the volatile compounds were removed on the rotary evaporator. The product was then hopefully re-crystallised [5].

The hydrolysis reaction using Pd/C with 1,3,5,7-tetramethyl-1,3,5,7-tetrakis[2-(dimethylsilyl)ethyl]tetracyclosiloxane worked to give the desired product (see Figure 3.5) by NMR spectroscopy [6]. ^{13}C {^{1}H} NMR (75MHz, d^{4}-methanol, 25^{o}C): δ 10.0, 9.5, -0.1, -3.2. ^{1}H NMR (300MHz, d^{4}-methanol, 25^{o}C): δ 0.72 (m, 4H), 0.32 (m, 10H). CHN analysis yielded %C 38.82 : %H 8.78 whereas the theoretical values were calculated as being %C 36.99 : %H 8.69. The CHN analysis was out, this could be due to condensation of the cores by adventitious water [7].

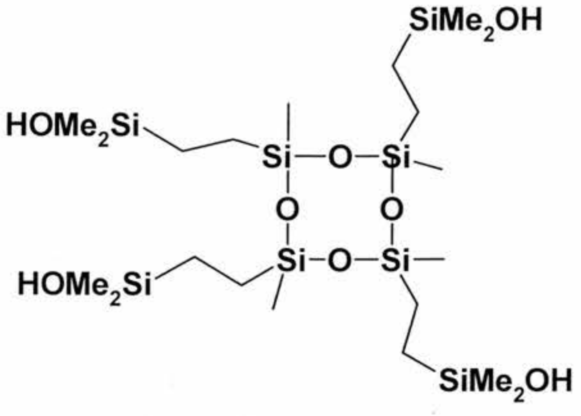


Figure 3.5 Expected structure of the hydrolysis product

When tried with a second generation dendrimer (see Figure 3.6) the product formed was an insoluble polymer.

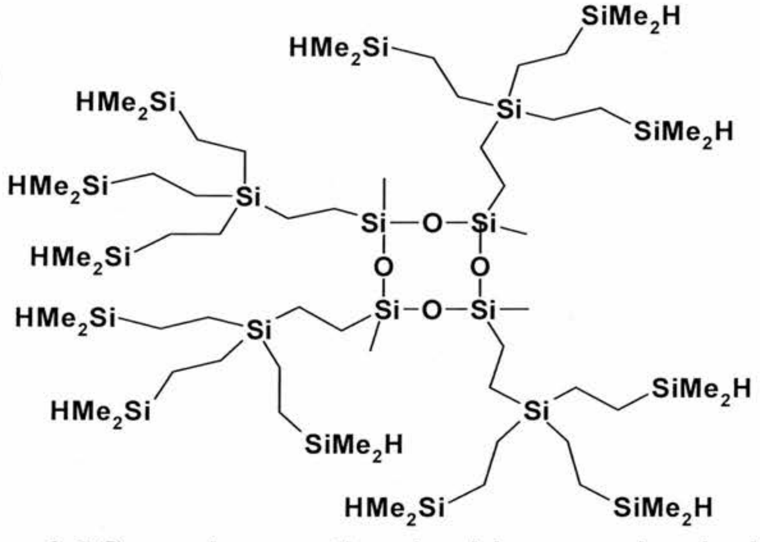


Figure 3.6 Second generation dendrimer used as hydrolysis core

The reason why the preparation of tetrakis{2-[tris-(hydroxy)]silylethyl}silane **(70)** by the Pd/C method was not investigated is that information given by another member of the group implied that this hydrolysis reaction works better when there is only one Si-H group at each branching site [6].

3.2.1.4 Conclusions about the hydrolysis reactions

The catalytic hydrolysis method (Pd/C) is more successful than using high dilution methods since another member of the group reported higher yields of silanol with the Pd/C method than with the hydrolysis with base on Si-Cl method [6]. Another advantage of the Pd/C method over either of the high dilution methods is that the amount of water that has been displaced by the production of hydrogen gas during the reaction denotes whether or not the reaction has gone to completion.

A benefit of using the high dilution with base on Si-Cl, over the other two reactions, is that the starting material for this reaction is made after the first stage of dendrimer production. To make the starting material for the reaction with Pd/C the Si-Cl bonds have to be reduced. The reaction using high dilution and acid is probably the least useful reaction currently since dendrimers with Si-OMe bonds at the periphery have not been synthesised. This could be accomplished by adding trimethoxysilane to a vinyl dendrimer core, although a similar reaction has been tried with triethoxysilane and requires more work (see Chapter 2).

Both the high dilution reactions require crystals to be formed from the reaction mixture. High dilution with acid catalysis led to removal of the crystals by filtering whereas the high dilution with base reaction had the crystals removed after the excess solvent had been distilled from the reaction mixture. Further it seems, from experience, the best way of accomplishing this is by distillation rather than evaporating the solvent off either on the rotary evaporator or in air. It seemed, when using the rotary evaporator, that no crystals were formed but they did appear on the sides of the reaction vessel when the solvent was distilled from the reaction mixture.

3.2.2 Aldehydes

Two different methods were found for making aldehydes. Aromatic aldehydes could be made using protected bromobenzaldehydes and using a Grignard reaction to turn them into silanes that could then be hydrosilated onto a core molecule (see Figure 3.7).

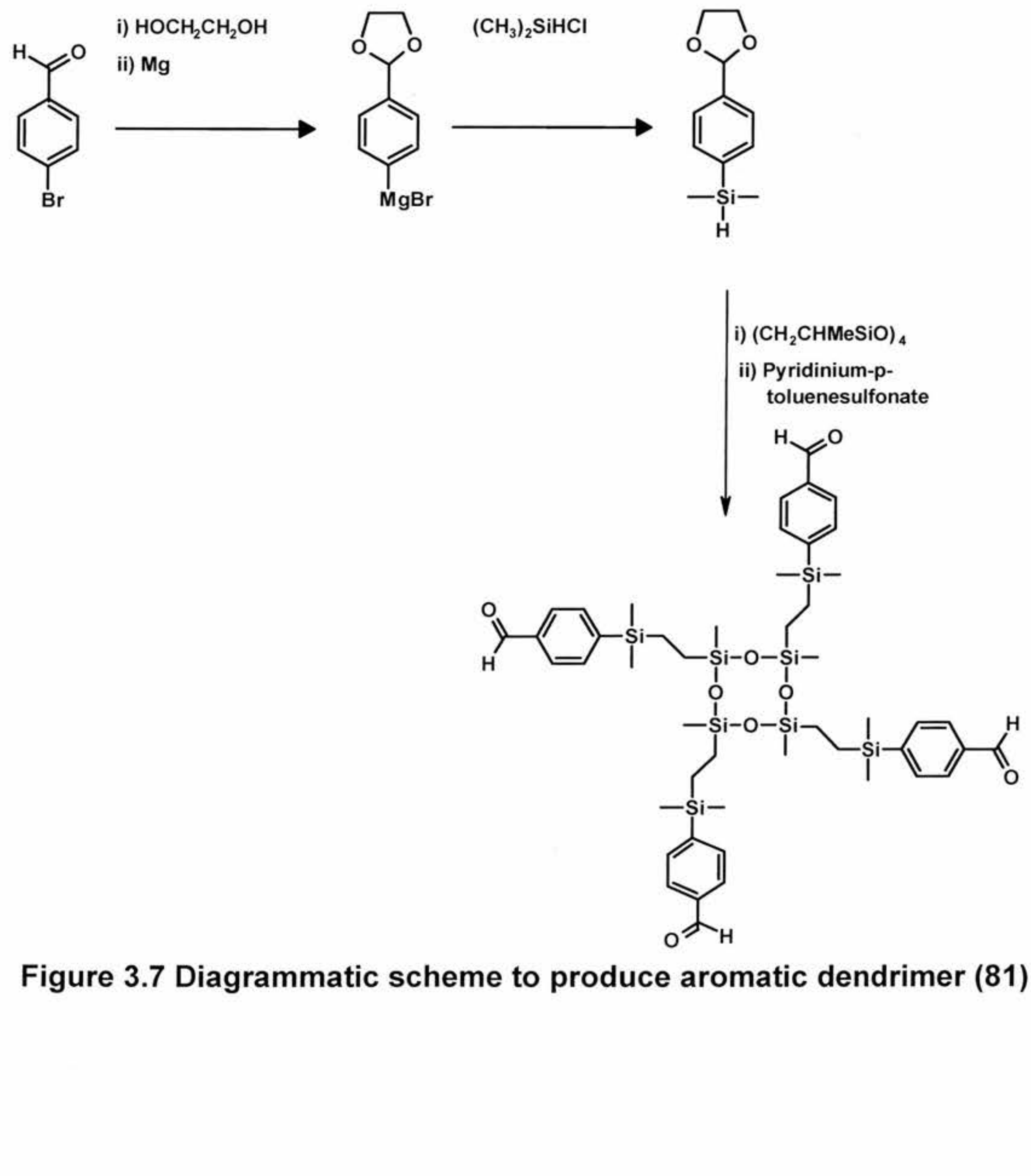


Figure 3.7 Diagrammatic scheme to produce aromatic dendrimer (81)

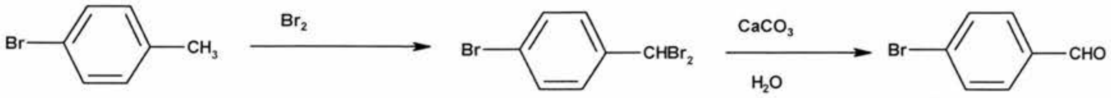
The second method, the hydroformylation reaction, used high-pressure autoclaves, a rhodium catalyst, triphenyl phosphine and syngas with a vinyl core to produce aliphatic aldehydes (see Scheme 3.5).

Scheme 3.5 Hydroformylation reaction

It was hoped that the aldehydes could be reacted further with potassium permanganate to produce carboxylic acids or reacted with Schiff bases to produce an amine site that could be used as a catalytic support.

There are other strategies to make both aromatic and aliphatic aldehydes. Aliphatic aldehydes can be made using Grignard reagents with dimethyl formamide or orthoformate esters (trialkoxymethanes) [2]. Aliphatic aldehydes can also be made using organoboranes or by the selective oxidation of alcohols [2]. Of course, alcohol functionalised dendrimers would have to be made before they could be converted to aldehydes. Also the reactions would have to be very high yielding to be useful in functionalising the periphery of a dendrimer.

To make aromatic aldehydes, the oxidation of a methyl group reaction could be used (see Scheme 3.6). This would work by making the 4-bromotoluene into a Grignard reagent and attaching it onto the dendrimer core then the methyl group would be converted into a aldehyde group. The reaction which makes aromatic aldehydes using protected bromobenzaldehyde is a better synthetic route to this compound since the de-protection step has a higher yield than the conversion of methyl groups to aldehyde groups.



Scheme 3.6 reaction to form aldehyde group from methyl group

3.2.2.1 Aromatic Aldehydes

Dendritic aromatic aldehydes were made by first protecting the aldehyde part of bromobenzaldehyde with ethylene glycol. This protected aldehyde was then converted to a Grignard reagent before being converted into a silane. The silane was hydrosilated onto a vinyl functionalised core molecule. Finally, the protection on the aldehyde group was removed (see Figure 3.7). These reactions were tried with 3- and 4-bromobenzaldehyde and with the core molecule 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane. These reactions were also tried without the protection on the bromobenzaldehyde to see if the protection was needed.

Prior to the reaction to form the Grignard reagents, 3-bromobenzaldehyde and 4-bromobenzaldehyde were protected using ethylene glycol with either p-toluenesulfonic acid or with the pyridine salt of the acid. The preparation and use of various Grignard reagents to make silanes was successful using 3-bromobenzaldehyde and 4-bromobenzaldehyde. During the initial attempt to make the Grignard of 4-bromobenzaldehyde, the Grignard solidified therefore becoming useless (it could be used but it was suspected not to be as good as the liquid Grignard). This was probably due to not enough solvent being used during the creation of the Grignard reagent or possibly water may have been present during the reaction.

There now follows the results gained at each intermediate on the way to the formation of the 1,3,5,7-Tetrakis{2-[4-(formylphenyldimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane. The results for the CHN analysis of protected 2-(4-bromophenyl)-1,3-dioxolane yielded %C 46.97 : %H 3.9 whereas the theoretical results were calculated as being %C 47.19 : %H 3.96. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ 7.6 (m, 2H), 7.4 (m, 2H), 5.9 (s, 1H), 4.1 (m, 4H). ^{13}C NMR (75.4MHz, $CDCl_3$, 25°C): δ 137.2, 131.4, 128.1, 124.2, 103.0, 65.2.

The results for the analysis of the protected 2-(4-(dimethylsilyl)phenyl)-1,3-dioxolane **(76)** were ^{13}C NMR (75.4MHz, $CDCl_3$, 25°C): δ 138.9 and 138.7 (2C, CSi and *C*CH), 134.1 (CH), 125.8 (CH), 103.7 (OCHO), 65.3 (2C, OCH_2CH_2O), -3.7 ($SiCH_3$). ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 7.61 (d, J = 8.0 Hz, 2H, CH), 7.51 (d, J = 8.0 Hz, 2H, CH), 5.86 (s, 1H, OCHO), 4.47 (sept, J = 3.8 Hz, 1H, SiH), 4.15 (m, 4H, OCH_2CH_2O), 0.38 (d, J = 3.8 Hz, 6H, $SiCH_3$). CHN analysis yielded %C 63.67 : %H 7.73 whereas the theoretical values were calculated as %C 63.41 : %H 7.74.

The results after addition to the core material to form 1,3,5,7-Tetrakis{2-[4-(1,3-dioxolan-2-yl)phenyldimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane **(79)** ^{13}C {^{1}H} NMR (75MHz, $CDCl_3$, 25°C): δ -3.79, -1.52, 6.74, 9.15, 65.32, 103.73, 125.66, 128.58, 133.68, 134.12, 136.57 plus extra aromatic carbon peaks, 192.53 plus extra peak at 63.72 possibly due to ethylene glycol. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 7.68 (m, 2.5H), 7.48 (m, 2.75H), 5.86 (s, 1H), 4.16 (m, 2.5H), 0.42 (m, 4.5H), 0.3 (m, 9.75H), 0.08 (s), 0 .04 (s, under TMS peak, the two final peaks have been integrated together, 27.25H). There are extra peaks present, some due to unprotected aldehyde and the acid from the oxidation of the unprotected aldehyde. The multiplets were unresolvable. CHN analysis yielded %C 54.53 : %H 7.28 whereas the theoretical values were calculated as %C 57.09 : %H 7.53. There is some THF present in the sample also some unprotected aldehyde that will make the %C too high.

The results for the 1,3,5,7-Tetrakis{2-[4-formylphenyldimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane **(81)** $^{13}C\ \{^{1}H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ -3.78, -1.52, 6.71, 9.10, 128.47, 128.58, 134.11, 192.58. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 10.0 (s, 1H), 7.82 (m, 1.8H), 7.68 (m, 2.5H), 0.4 (m, 3.1H), 0.28 (m, 5.6H), 0.08 (s), 0 (s, 10.8H, the last two peaks have been integrated together). There are other peaks present that would correspond to the acid being formed by oxidation of the aldehyde in the air. The multiplets are unresolvable although the peaks at 7.82 and 7.68 would be expected to be doublets.

The dendritic benzaldehydes might be oxidised to form carboxylic acids and therefore be reacted with metals to produce catalysts. A diagrammatic scheme (Figure 3.7) shows the stages involved in forming the aromatic aldehyde.

2-(3-Dimethylsilyl)phenyl)-1,3-dioxolane was reacted with 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane in a hydrosilation reaction using the Karstedt's catalyst in diethyl ether (see Figure 3.8). The product was put through a silica column to remove the catalyst. The NMR spectra indicated that most of the vinyl groups had reacted.

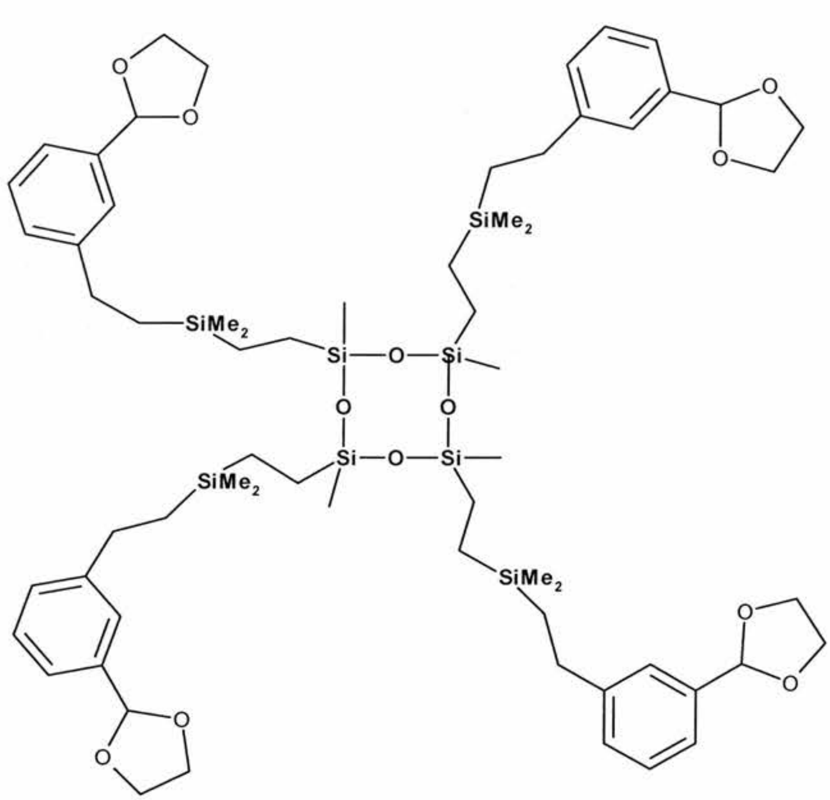


Figure 3.8 Expected product (78) from the reaction of 2-(3-dimethylsilyl)phenyl)-1,3-dioxolane (77) and 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane (4).

Problems that were encountered during this reaction were that: complete de-protection does not necessarily occur if the acetone is not wet enough. Also the aromatic aldehyde is very reactive and can undergo oxidation to the corresponding carboxylic acid in air, so collecting a pure sample of the aldehyde seemed very difficult.

A test was done to see if protection of the aldehyde was necessary at the hydrosilation stage. Since a product made with unprotected aldehydes could possibly be cleaner than one in which the aldehyde groups had to be de-protected once attached to the dendrimer. In both reactions vinyl groups were present and there were some small peaks in the CH_2 region but they were not in the right place and there were no SiH peaks.

3.2.2.2 Aliphatic aldehydes

3.2.2.2.1 OctavinylPOSS hydroformylation with syngas and rhodium acetate

The hydroformylation reaction (see Scheme 3.5) was used to produce aliphatic aldehydes from a T_8 vinyl POSS core. The hydroformylation reaction adds carbon monoxide and hydrogen across a double bond using a rhodium catalyst, temperature and high pressure.

The hydroformylation reaction of vinyl groups attached to an electron-withdrawing core (T_8 vinyl POSS should be electron withdrawing) should add to the molecule at the β position (the labelling of α and β positions is with respect to the edge of the dendrimer, branched isomer, i). Since the T_8 vinyl POSS is more sterically hindered than the usual substrates for this reaction it was hoped that mostly α addition (straight isomer, n) would occur and this was found to be the case (see Figure 3.9). The results for the aliphatic aldehyde were as follows ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 9.82 (s, CHO, 1H), 2.59 (m, CH_2, 2.5H). There are extra peaks present due to the branched product being present. $^{13}C\{^1H\}$ NMR (75.4MHz, $CDCl_3$, 25°C): δ 202 (CHO), 201 (CHO), 37 (CH_2), 7.7 (CH), 7 (CH_3), 3.7 (CH_2). There was a shoulder present on the aldehyde peak at 9.77 plus peaks in the region 7.4 – 7.8

corresponding to triphenylphosphineoxide. The CHO resonance should be a triplet but it looks like a singlet, this could be due to exchange broadening. The reaction went to completion since there are no vinyl peaks present in the NMR spectra. The n:i ratio gained for this reaction was 4:1 i.e. this means that every molecule has either one or two branched arms.

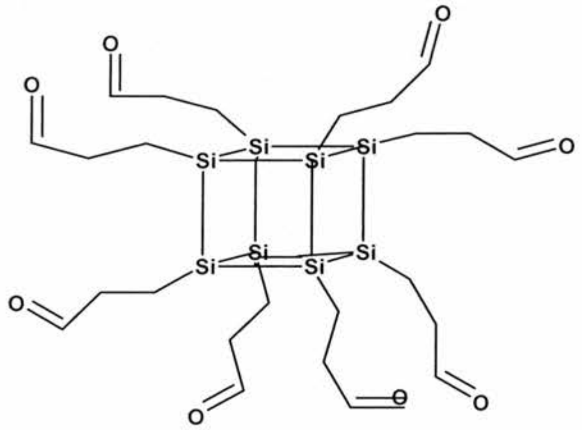


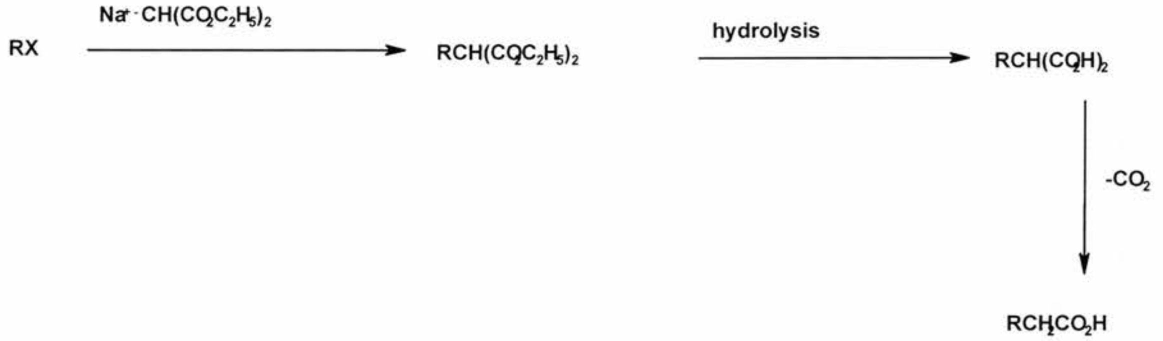
Figure 3.9 Expected aliphatic aldehyde product

3.2.3 Oxidation of aldehyde

Several of the aldehydes made were oxidised to hopefully make carboxylic acids. The oxidation agent used was potassium permanganate.

An alternative strategy is to catalytically hydrocarboxylate directly onto the T_8 vinyl POSS using $[PdCl_2(PPh_3)_2]$-$SnCl_2$ then $[PdCl_2(PPh_3)_2]$ in the presence of excess PPh_3. This should give fully hydrocarboxylated product with hopefully the carboxylate group attached to the α carbon [8]. Although this is a reaction carried out in a similar manner to the hydroformylation reactions and so will probably have similar n:i ratio problems (only by trying the reaction could the extent of the problem be determined) as the Si-O withdrawing properties of the POSS structure should force the β substitution but the steric constraints of the molecule should force the α substitution.

Other possible strategies include substitution of the dendritic halide (made after the hydrobromination reaction, see Chapter 2) with a sodium ester salt and then hydrolysis, using base and water followed by acid, to the carboxylic acid [2] (see Scheme 3.7). A possible problem with this reaction would be nucleophilic attack of the Si-C bonds depending on the strength of the base as a nucleophile.



Scheme 3.7 Reaction to form acid from alkylhalide

Another possible strategy to making an acid would involve making a Grignard reagent from a dendrimer with halide functional groups. The Grignard reagent would then be reacted carbon dioxide. The Grignard reagent would undergo carboxylation, giving carboxylate ions, then an acid would be used to protonate the ions to make the carboxylic acids. The possible problem with this reaction would be that the formation of the Grignard would have to be very high yielding. There are other ways of going from vinyl groups to carboxylic acids but these involve the use of potassium permanganate which seems to oxidise the Si-C bonds as well as the group that it is meant to be oxidising.

It was found that using potassium permanganate as the oxidising agent can cause the Si-C bond to be oxidised to Si-O it was decided to abandon potassium permanganate as the oxidising agent. Since oxidation to the carboxylic acid went too far, it could be tried using a milder oxidising agent like Ag^{2+} or Cu^{2+}. It has since been found, by another member of the group [9], that the carboxylic acid can be made from the aromatic aldehyde by allowing the aldehyde sit in the air.

3.3 Conclusions

The attempted synthesis to make vinyl silanetriols for the synthesis of mixed POSS molecules may have been a flawed idea since it could be that the vinyltrihydroxysilane may be too reactive to be isolated as crystals. The synthetic schemes that were followed for the production of crystals of trihydroxysilanes were done using more stable R groups (i.e. cyclohexyl and t-butyl). Certainly in the synthetic method which made vinyl silanetriol from vinyltrimethoxysilane, the paper from which the synthetic method came, the authors [4] only isolated crystals of cyclohexyltrihydroxysilane and not crystals of vinyltrihydroxysilane. Instead, the solution of vinyltrihydroxysilane was reacted onto a glass fiber. It would probably be better, if this work was continued, to make more stable trihydroxysilane products (i.e. cyclohexyltrihydroxysilane).

For the most part the production of hydroxysilanes from either trimethoxysilane or trichlorosilanes was unsuccessful. It is true to say that the high dilution method using acid on trimethoxysilane wasn't attempted enough and certainly wasn't tried on any other substrate than vinyltrimethoxysilane. It could be that it would work a lot better if it were to make a more stable product.

The high dilution method with base acting on Si-Cl bonds never seemed to make a lot of product. The only success with this method was when some product was made from one of the cyclohexytrichlorosilane reactions. There was no success with collecting enough sample for analysis from the reactions with the trichlorodendritic silane or the trichlorovinylsilane.

The attempted synthesis of a trihydroxydendritic silane may not have worked since the starting dendrimer may not have been pure enough to form crystals for collection. This is in regard to the Si-Cl end groups going off rather than a mixture of α and β products being formed (the tetravinylsilane core usually only produced α product due to possible steric strain). Another member of the group [6] managed to synthesise a monohydroxydendritic silane using this method.

The synthesis of a first generation dendritic silane using Pd/C was successful although the synthesis of the second-generation dendritic silane using this method was not successful. This could be due to the second-generation dendritic silane material not being pure enough. It looks from the ^{1}H NMR that there were not enough Si-H peaks in the spectra for the molecule of the starting material. If the reaction were to be repeated with purer starting material then it would probably be more successful. Other dendritic hydroxy silanes were made by another member of the group [6] using this method [5]. Of all the methods to make dendrimers with silanol groups attached to the outside of them, this is the most promising since it does not require the production of crystals of the product. This reaction is only good for producing silanols with one Si-OH group per branch and therefore if silanols with more than one Si-OH group per branch are to be made then the other reactions using high dilution would have to be utilised.

The reaction to produce aromatic aldehydes is successful but it suffers from the same problems of partial β substitution that most hydrosilations suffer from. If care is taken during the initial stages of the reaction (i.e. the reaction is cooled whilst the catalyst is initially added) then the amount of β product is minimised but not eliminated. The use of a more sterically hindered core molecule or a more sterically hindered branching material might limit this. Further work in this area would be trying to perfect the hydrosilation reaction to minimise the amount of β addition.

The hydroformylation reaction was successful with full reaction at the vinyl groups. It's only drawback is the n:i ratio being 4:1. It could have its n:i ratio improved (in favour of the n product) by using more triphenylphosphine but this will probably not totally eliminate the production of the β product, only minimise the amount of it which is formed.

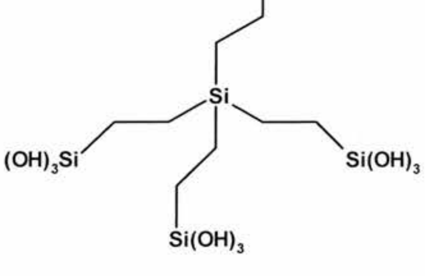
The reaction to form carboxylic acids from the aldehydes was unsuccessful since the reaction went too far, some of the Si-C bonds were oxidised to Si-O bonds. Since the current concentration of potassium permanganate is too high, it may just be the question of using less to get the desired product. Failing that, it may be prudent to use a milder oxidising agent like silver or copper. It was later discovered that the aromatic aldehyde reverted to the carboxylic acid if it was left in air.

In general, the hydroformylation is a good reaction but n:i will never reach infinity. Hydrosilation to produce aromatic aldehydes is a good reaction but there are still problems with the production of α/β mixtures. Silanols are difficult to handle (condensation), two of the synthetic methods show this by using high dilution, the third method gets around the problem by using a catalyst. The catalytic formation of silanols seems to be the best way, especially for larger molecules.

3.4 Experimental

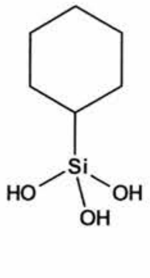
^{1}H (300MHz) and ^{13}C (75MHz) NMR spectra were recorded on a Brucker AM 300. Some of the ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300. The ^{1}H and ^{13}C NMR solutions were placed in 5mm glass tubes. The spectra were recorded at room temperature and in either d^6 benzene, d^4 methanol or $CDCl_3$ (Apollo Scientific/Aldrich). All CHN measurements were made on a Carlo-Erba Modell 1106.

Tetrakis{2-[tris-(hydroxy)]silylethyl}silane (70)



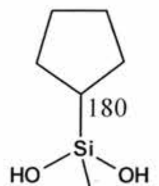
$Si(CH_2CH_2SiCl_3)_4$ (2.2g, 3.24mmoles) was added to a stirred emulsion of water (0.8ml, 44.0mmoles), aniline (3.6ml, 3.7g, 39.5mmoles) and dry diethyl ether (55ml). This mixture had turned white during the addition and was left to stir overnight. The precipitated hydrochloride was filtered off, and the clear filtrate was left standing to allow the volatile compounds to evaporate off [3]. If this reaction doesn't work it could be due to several factors: addition of the dendrimer was to quick, the addition was not carried out in an ice bath, the reaction mixture was too concentrated. The solid produced gave many peaks in ^{13}C NMR δ 71.4, 71, 70.3, 70.1, 63.3, 62.2, 45, 31.9, 30.6, 30, 29.4, 29.2, 26.9, 26.6, 26.4, 26.1, 19.7, 14.2. The product was dissolved in excess diethyl ether and had excess hexane added to it before being placed in the freezer to see if anything would crystallise out. It is possible that the dendrimer polymerised on addition to the reaction mixture. The ^{1}H NMR did not have any peaks in the region where OH groups are expected only aniline peaks. This reaction was repeated and instead of the volatile compounds evaporating in air they were removed on the rotary evaporator until there was only a small amount of diethyl ether left and some white powder was filtered off from the solution. The rest of the solution had hexane added to it to see if any crystals would form, this was unsuccessful. More recently this was repeated and the product was sent for CHN analysis but the analysis couldn't be carried out since there was not enough product present. ^{1}H NMR (300MHz, d^4 methanol, 25°C): δ 5.05 (m, 2.2H), 3.5 (m, 1H). The multiplets are unresolvable.

Cyclohexyltrihydroxysilane (71)



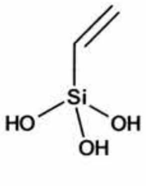
$C_6H_{11}SiCl_3$ (2.84g, 13.0mmoles) in dry diethyl ether (13ml) was added drop-wise over a period of 40 minutes to a vigorously stirred emulsion of water (7ml, 380mmoles) and aniline (7ml, 7.1g, 76.8mmoles) in dry diethyl ether (150ml) cooled in ice, under argon. After the addition the mixture was left stirring overnight at room temperature. The mixture was filtered through a medium glass filter funnel to remove the hydrochloride. The volatile compounds were allowed to evaporate off in air. After most of the volatile compounds had evaporated off, the mixture was placed in the fridge to aid crystallisation. A solid was filtered off and the filtrate was returned to the flask and placed back into the fridge to see if any more product would appear, no more product was formed. The ^{13}C NMR spectra gave many peaks. ^{13}C $\{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C):. δ 27.4, 27.1, 23.8, 23.2, 22.8, 22.4, 22.2 [3]. This reaction has been repeated using cyclohexyltrichlorosilane (2.82g, 13.0mmoles) in dry diethyl ether (8.5ml) being added to a stirring solution of water (0.7ml, 38.0mmoles), aniline (3.5ml, 3.6g, 38.4mmoles) and dry diethyl ether (150ml) in ice, under argon. The resulting mixture was allowed to stir overnight. The hydrochloride was filtered off and the filtrate was distilled at atmospheric pressure at 35°C. A white residue appeared on the sides of the flask during the distillation and this was filtered off whilst there was still 20ml of solvent left in the flask. CHN analysis yielded %C 45.69 : %H 8.81 whereas the theoretical calculations gave %C 44.41 : %H 8.70. Attempts were made to crystallise the product from diethyl ether/hexane. ^{13}C $\{^1H\}$ NMR (75.4 MHz, CD_3OD, 25°C): δ 29.1, 28.1, 26.5. ^1H NMR (300 MHz, CD_3OD, 25°C): δ 1.87 (m, 2H), 1.77 (m, 3H), 1.33 (m, 5H), 0.77 (m, 1H). The multiplets were unresolvable.

Cyclopentyltrihydroxysilane (72)



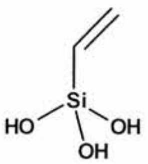
$C_5H_9SiCl_3$ (2.66g, 13.1mmoles) in dry diethyl ether (12ml) was added drop-wise over a period of an hour to a vigorously stirred emulsion of water (0.7ml, 38.0mmoles) and aniline (3.6ml, 3.7g, 39.5mmoles) in dry diethyl ether (150ml) cooled in ice, under argon. After the addition the mixture was left stirring overnight at room temperature. The mixture was filtered through a medium glass filter funnel to remove the hydrochloride. The volatile compounds were allowed to evaporate off in air. After most of the volatile compounds had evaporated off, the mixture was placed in the fridge to aid crystallisation [3]. ^{13}C {^1H} NMR (75MHz, $CDCl_3$, 25°C): δ 30, 28, 27, 24. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 1.77 (s, 4H), 1.53 (m, 1H), 1.27 (m, 4H), 0.8 (s, 2H). The multiplets in the spectra are unresolvable. There are also peaks in the spectra due to aniline. The repeat reaction did not produce enough product for any analysis to take place.

Vinyltrihydroxysilane (73)



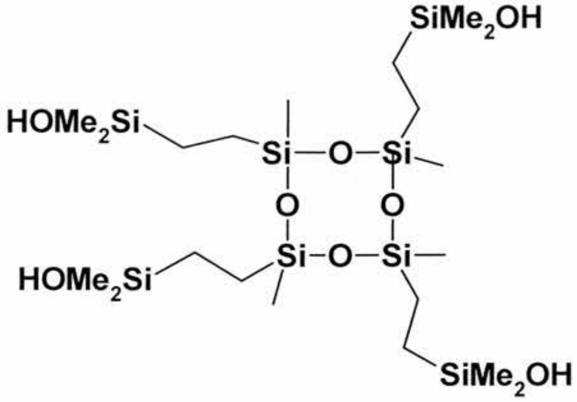
Trichlorovinylsilane (10.5ml, 13.3g, 82.6mmoles) in dry diethyl ether (42ml) was added drop-wise slowly to a stirring suspension of water (3.5ml, 190mmoles), aniline (17.8ml, 18.2g, 195mmoles) and dry diethyl ether (750ml) in an ice bath, under argon. The resulting mixture was allowed to stir overnight. The hydrochloride was filtered off and the diethyl ether was distilled off but possibly to far since no crystals were filtered off after most of the diethyl ether had been driven off. This could be because the water bath was to hot and any crystals that were formed were taken off with the diethyl ether. So the residue that was left was washed with brine and diethyl ether, this produced two similarly coloured solutions. The organic layer had hexane added to it and both layers were left to see if any crystals would form. The second attempt at this reaction had a sample, a yellow solid, sent for CHN analysis but this couldn't be performed since there was not enough sample present. The proton NMR of the repeat reaction in d^4 methanol showed some small bumps in the baseline but nothing obviously product.

Vinyltrihydroxysilane (73) using acid hydroysis



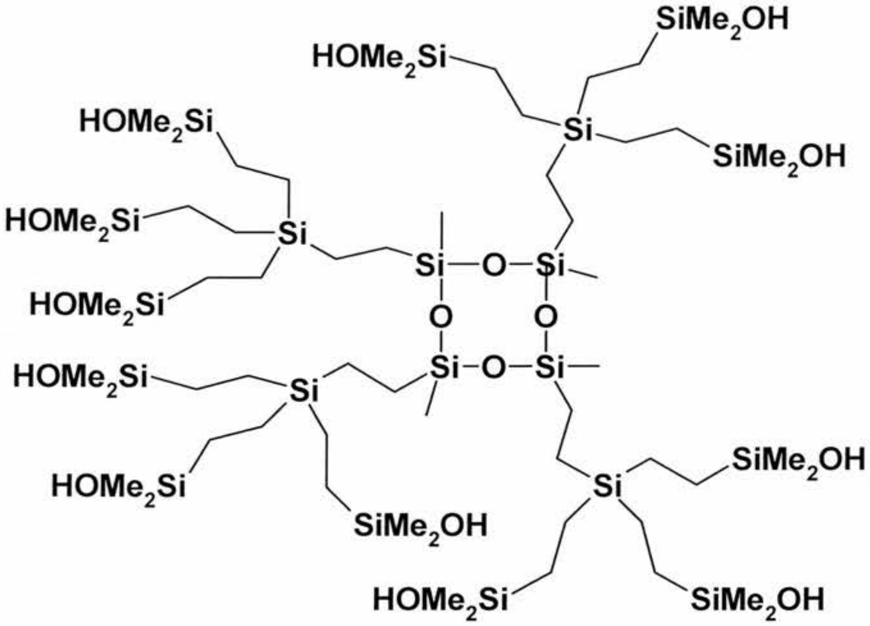
Another method found to produce vinylsilanetriol was as follows: 10% by weight of vinyltrimethoxysilane (10g, 67.5mmoles) was hydrolysed by water at pH 3.5 adjusted by acetic acid. The non-hydrolysed silane formed oily droplets when first mixed with water. Rigorous agitation at room temperature for over an hour yielded a clear solution. The solution was allowed to stand but no oily droplets floated to the surface (was possibly not allowed to stand long enough). The solution was transferred to a conical flask and left in air to see if any crystals would form [4]. Attempts were made to filter this, but it had a gel at the bottom of the flask so the product was separated by washing with diethyl ether into aqueous and organic fractions and the gel was dissolved in diethyl ether. Both solutions in diethyl ether had hexane added to them, the one obtained by washing with aqueous solution turned cloudy on addition of hexane, the other one did not. All three of them were left to see if crystals would form.

1,3,5,7-tetrakis{2-[dimethylhydroxysilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane(74)



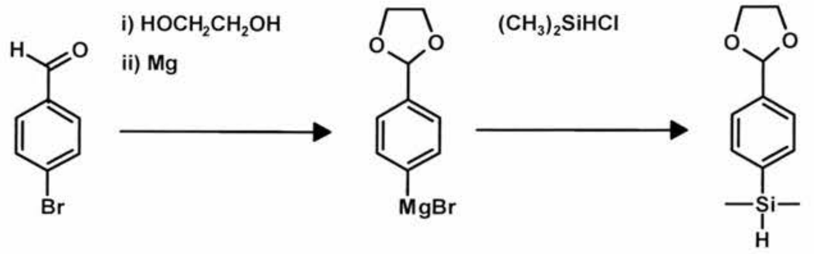
The dendrimer (0.3g, 0.512mmoles) in dioxane (10ml) was added drop-wise to a stirring suspension of Pd/C (0.1g) in dioxane (5ml) with buffer solution (0.4ml) (the reaction mixture had previously been purged with argon otherwise no reaction takes place). On top of the reflux condenser was a gas collector filled with water and arranged so that the displaced water could be measured. Water (45ml) had been displaced, which is nearly the correct amount of water that should be displaced, by the gas coming off. The mixture was filtered through celite, washed through with diethyl ether and the volatile compounds were removed on the rotary evaporator. A colourless oil was produced and this was dissolved in diethyl ether and hexane and placed in the fridge to see if it would produce crystals. This did not work and a mixture of THF and hexane was also tried which also failed to produce crystals. Another mixture of diethyl ether and hexane was tried but this time the volatile compounds were allowed to evaporate off in air, still no crystals. Carbon and hydrogen NMR spectra were run in $CDCl_3$ but produced strange spectra since the chloroform did not dissolve the product properly but the hydrogen spectra did show a signal at δ 2.2 - 2.3 which could correspond with an OH group. More spectra were run in d^4-methanol that gave more expected spectra. The only problem with using methanol as the NMR solvent is that the OH groups on the molecule do not appear since they exchange with the OH groups in the solvent. ^{13}C {^{1}H} NMR (75MHz, d^4-methanol, 25^{o}C): δ 10.0, 9.5, -0.1, -3.2. There were some other peaks also present. ^{1}H NMR (300MHz, d^4-methanol, 25^{o}C): δ 0.72 (m, 4H), 0.32 (m, 10H). The peaks overlap each other and this makes the multiplets unresolvable. The peak at 0.32 has a smaller peak beside it probably due to the other methyl environment but the peaks have been integrated together. There are other peaks present in the spectra. An IR was run but the area where OH stretches appear i.e. 2700 - 3650 cm^{-1} was obscured. There were broad peaks in the area associated with Si-O stretches i.e. 767 - 900 cm^{-1} and 1044 - 1144 cm^{-1}. This reaction can be unreliable since it has been repeated twice and once no water was displaced and the second time only half the volume of water was displaced that ought to have been displaced [5]. CHN analysis yielded %C 38.82 : %H 8.78 whereas the theoretical values were calculated as being %C 36.99 : %H 8.69. It appears that some condensation has occurred at some point either during the reaction or during the work up. The buffer solution is made up of 0.1N NaOH and $NaH_2PO_4.2H_2O$. IR (KBr, cm^{-1}) 2966 (vs), 2920 (vs), 1406 (s), 1263 (vs), 1143 (vs), 1086 (brvs), 874 (brvs), 840 (vs), 788 (brvs), 697 (s), 640 (m) and 571 (m).

1,3,5,7-tetrakis{2-[tris-(2-(dimethylhydroxysilyl)ethyl)silyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane(75)



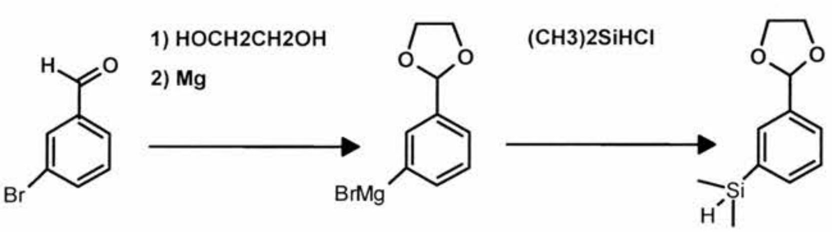
Dendrimer (0.33g, 0.219mmoles) in dioxane (10ml) was added to a mixture of Pd/C (0.13g), buffer solution (0.4ml) and dioxane (5ml) that had been under argon. Gas (20ml) was produced, the mixture was filtered and the volatile compounds were removed on the rotary evaporator. The product formed was an insoluble polymer since it did not dissolve in methanol and therefore could not be analysed by NMR [5].

2-(4-(Dimethylsilyl)phenyl)-1,3-dioxolane (76)



To a solution of 4-bromobenzaldehyde (5.07g, 27.4mmoles) in toluene (20ml), ethylene glycol (8.28g, 133mmoles), pyridinium tosylate (2.03g, 8.08mmoles) are added and the resulting mixture is refluxed for several hours and the water produced was collected in a Dean Stark trap. Volatile compounds were removed on the rotary evaporator. Excess diethyl ether was added to the solution and the mixture was washed with excess sodium hydrogen carbonate solution and excess saturated sodium chloride solution. The organic phase was dried over magnesium sulfate. The mixture was filtered and the volatile compounds were removed on the rotary evaporator [10]. This experiment was repeated using toluenesulfonic acid instead of pyridinium tosylate as the catalyst [11]. CHN analysis yielded %C 46.97 : %H 3.9 whereas the theoretical results were calculated as being %C 47.19 : %H 3.96. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ 7.6 (m, 2H), 7.4 (m, 2H), 5.9 (s, 1H), 4.1 (m, 4H). ^{13}C NMR (75.4MHz, $CDCl_3$, 25°C): δ 137.2, 131.4, 128.1, 124.2, 103.0, 65.2. The multiplets in ^{1}H spectra were unresolvable. There were some other peaks present that could be due to non-reacted aldehyde and excess ethylene glycol. Literature data %C 46.92 : %H 4.15 : %Br 35.06 [12].The products from both the reactions were distilled together under high vacuum at 87°C. The water in the condenser was turned off since the product's melting point was just below room temperature and the product solidified in the condenser if the water was on. The product was a clear, colourless liquid. This product in THF (20ml) was added drop-wise to a mixture of magnesium turnings (3.03g, 125mmoles), a small crystal of iodine and THF (30ml) under argon at a rate at which reflux was attained and the colour of the solution changed, then more solvent (10ml) was added. The reaction mixture was left stirring to cool down to room temperature. The Grignard had solidified and could not be used in the rest of the reaction. This could have happened if water had entered the system or if not enough solvent was used to prepare the Grignard. These reactions were repeated using more solvent at the Grignard stage and the Grignard formed was added drop-wise to chlorodimethylsilane (7ml, 6.0g, 63.0mmoles) in dry THF (18ml), under argon, and was left stirring at room temperature overnight. Sodium bicarbonate (aqueous solution) was added and diethyl ether was used to extract the product. The product was washed with brine (aqueous solution) and dried over $MgSO_4$. This was filtered and the volatile compounds were removed on the rotary evaporator. The product was a clear, colourless oil (3.01g, 14.4mmoles, 52.7%). ^{13}C NMR (75.4MHz, $CDCl_3$, 25°C): δ 138.9 and 138.7 (2C, CSi and *C*CH), 134.1 (CH), 125.8 (CH), 103.7 (OCHO), 65.3 (2C, O*C*H$_2$*C*H$_2$O), -3.7 ($SiCH_3$). ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 7.61 (d, J = 8.0 Hz, 2H, CH), 7.51 (d, J = 8.0 Hz, 2H, CH), 5.86 (s, 1H, OCHO), 4.47 (sept, J = 3.8 Hz, 1H, SiH), 4.15 (m, 4H, OCH_2CH_2O), 0.38 (d, J = 3.8 Hz, 6H, $SiCH_3$). IR (neat, cm^{-1}) 3073 (m), 3021 (m), 2959 (m), 2886 (s), 2118 (vs, Si-H), 1411 (s), 1388 (s), 1309 (m), 1250 (s), 1221 (s), 1184 (m), 1082 (s), 1022 (m), 970 (m), 944 (m), 881 (s), 817 (s), 767 (s), 706 (m), 627 (m). CHN analysis yielded %C 63.67 : %H 7.73 whereas the theoretical values were calculated as %C 63.42 : %H 7.74.

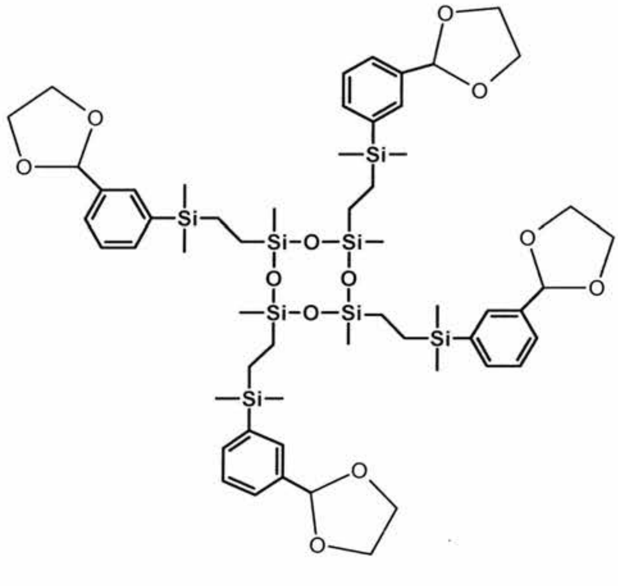
2-(3-(Dimethylsilyl)phenyl)-1,3-dioxolane (77)



3-Bromobenzaldehyde (35.17g, 190mmoles), ethylene glycol (14g, 226mmoles), toluenesulfonic acid (0.56g, 3.25mmoles) and toluene (225ml) were refluxed together overnight. The water produced was collected in a Dean Stark trap [11]. Diethyl ether (140ml) was added and the product was washed twice with excess sodium bicarbonate and once with excess sodium chloride solutions (both aqueous), then the organic layer was dried over $MgSO_4$. This was filtered and the volatile compounds were removed on the rotary evaporator. The product was vacuum distilled at 96°C. $^{13}C\{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 140.8, 132.1, 129.9, 129.4, 125.1, 122.4, 102.6, 65.2 plus several smaller peaks. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 7.80 (s, 1H), 7.63 (m, 1.1H), 7.53 (m, 1.1H), 7.4 (m, 1.4H), 5.93 (s, 1H), 4.2 (m, 4.4H) plus several other smaller peaks. The multiplets in ^1H spectra were unresolvable. Magnesium turnings (4.7g, 193mmoles), a small crystal of iodine and dry THF (200ml), under argon, had the product (20ml) in dry THF (50ml) added to it drop-wise. The indication that the reaction had started was the reaction mixture changing colour and heat being evolved. The reaction mixture was allowed to stir and cool to room temperature for over 2 hours. The Grignard reagent was added drop-wise to a solution of chlorodimethylsilane (14ml, 11.9g, 126mmoles) in dry THF (25ml) under argon. This was left stirring over the weekend. Volatile compounds were removed on the rotary evaporator. Diethyl ether (140ml) and ammonium chloride were added to extract the salt and the organic phase was dried over $MgSO_4$. This was filtered and the volatile compounds were removed on the rotary evaporator. The product was vacuum distilled without a vacuum and unfortunately this destroyed the product. This has been repeated several times but there have been some problems in working up the silane. It was discovered that ammonium chloride solution should not be added to the protected aldehyde since this de-protects the protected aldehyde function. Instead of adding ammonium chloride to the mixture sodium bicarbonate was added and then this mixture was extracted with diethyl ether and the organic layers were washed with brine. The product was vacuum distilled at 130°C at 7mmHg. The product was a clear, colourless liquid (14.48g, 69.6mmoles, 36.6%). $^{13}C\{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 137.7 and 137.1 (2C, CSi and *C*-CH), 135.0 (CH), 132.0 (CH), 127.9 (CH), 127.3 (CH),

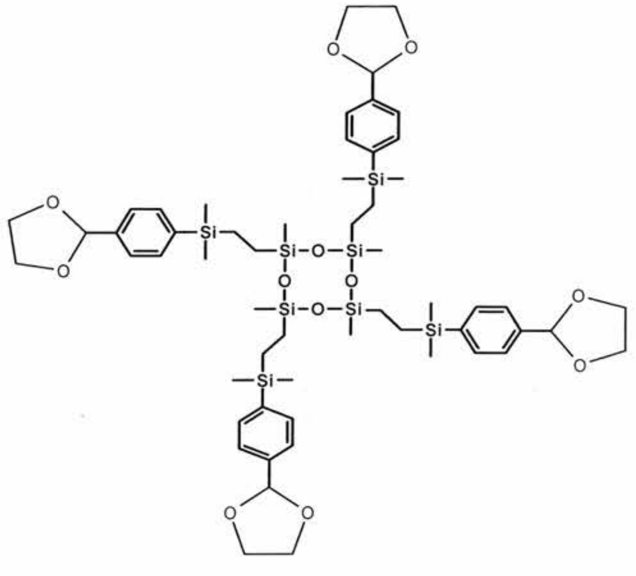
103.9 (OCHO), 65.4 (2C, O*C*H_2*C*H_2O), -3.7 ($SiCH_3$). ^{1}H NMR (300MHz, $CDCl_3$, 25^{o}C): δ 7.68 (s, 1H, CH), 7.58 (m, 1H, CH), 7.54 (m, 1H, CH), 7.41 (m, 1H, CH), 5.85 (s, 1H, OCHO), 4.47 (sept, J = 3.7 Hz, 1H, SiH), 4.16 (m, 4H, OC*H_2*C*H_2*O), 0.38 (d, J = 3.7 Hz, 6H, $SiCH_3$). IR (neat, cm^{-1}) 2969 (s), 2887 (s), 2119 (vs, Si-H), 1475 (m), 1423 (s), 1368 (s), 1251 (s), 1222 (s), 1121 (s), 1093 (vs), 1030 (m), 888 (s), 837 (m), 797 (m), 764 (m), 735 (m), 652 (m). CHN analysis yielded %C 63.05 : %H 7.76 whereas the theoretical values were %C 63.42 : %H 7.74.

1,3,5,7-Tetrakis{2-[3-(1,3-dioxolan-2-yl)phenyldimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane (78)



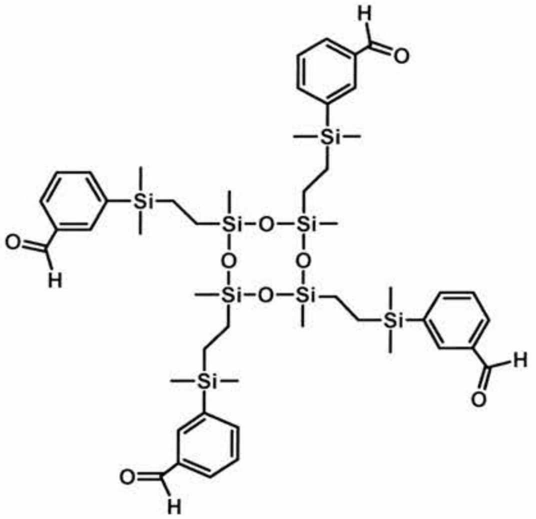
1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane (1g, 2.90mmoles), Karstedt's catalyst (12 drops) and dry diethyl ether (25ml) had the silane (3.03g, 14.5mmoles) in dry diethyl ether (10ml) added to it, under argon, whilst stirring. The resulting mixture was refluxed overnight. The volatile compounds were removed on the rotary evaporator. A 30cm silica pad in diethyl ether was used to filter the product from the catalyst. Tlc plates were checked under UV to see if the product was present in the fraction, only two spots were present. The product was placed on the Kugelrohr, under vacuum at 100°C for 1 hour. The temperature was increased to 120°C to remove the silane. The product was a clear, colourless oil (2.48g, 2.10mmoles, 72.5%). $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ -3.70, -1.51, 6.80, 9.14, 65.30, (63.70 could be ethylene glycol), 103.98, 126.86, 127.71, 128.34, 131.61, 134.54, 139.67 plus extra peaks due to some unprotected aldehyde being present. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 7.6 (s, 1H), 7.45 (m, 2H), 7.4 (m, 1.3H), 5.85 (s, 1H), 4.1 (m, 3.3H), 0.75 (m, 2.2H), 0.5 (m), 0.3 (s), 0.1 (s, under TMS peak). There are extra peaks present due to the present of the unprotected aldehyde, the last few peaks in the 1H NMR spectra have not been integrated due to the interference from other peaks in the sample. CHN analysis was carried out yielding %C 51.41 : %H 6.99 the theoretical values were %C 57.09 : %H 7.53. The best fit for this data is one unprotected branch and one molecule of THF associated with each dendrimer %C 50.3 : %H 6.5. To minimise α addition the reaction was tried in an ice/brine bath. This gave a slight improvement to the α:β ratio from 1:5.8 to 1:5.6 but it was not as impressive as was hoped.

1,3,5,7-Tetrakis{2-[4-(1,3-dioxolan-2-yl)phenyldimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane (79)



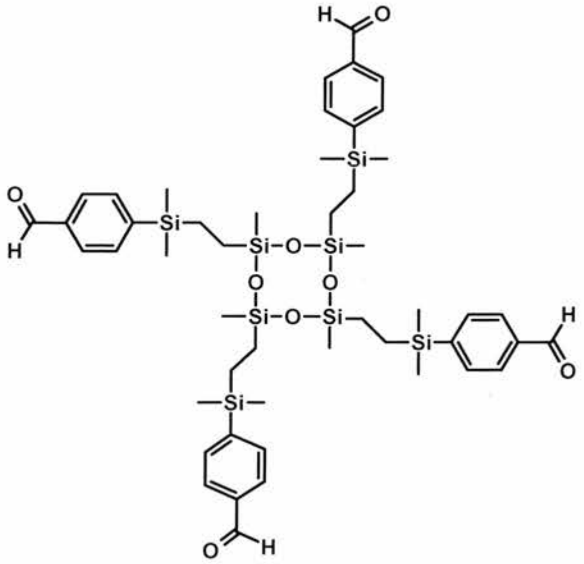
Core material (1g, 2.90mmoles), silane (3.01g, 14.4mmoles), dry diethyl ether (20ml) and Karstedt's catalyst (12 drops) were refluxed together overnight. Volatile compounds were removed on the rotary evaporator. The dark green product was placed on a 15cm silica gel plug to filter off the catalyst (in diethyl ether) (3.99g). (3.93g) of the product were retrieved from the silica plug. The product was placed on the Kugelrohr, under vacuum at 100°C for an hour (the product was placed in the flask using diethyl ether that was removed on the water pump). The temperature was increase to 120°C to remove the excess silane. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ -3.79, -1.52, 6.74, 9.15, 65.32, 103.73, 125.66, 128.58, 133.68, 134.12, 136.57 plus extra aromatic carbon peaks, 192.53 plus extra peak at 63.72 possibly due to ethylene glycol. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 7.68 (m, 2.5H), 7.48 (m, 2.75H), 5.86 (s, 1H), 4.16 (m, 2.5H), 0.42 (m, 4.5H), 0.3 (m, 9.75H), 0.08 (s), 0 .04 (s, under TMS peak, the two final peaks have been integrated together, 27.25H). There are extra peaks present, some due to unprotected aldehyde and the acid from the oxidation of the unprotected aldehyde. The multiplets were unresolvable. There should have been doublets for the 7.48 and 7.68 peaks but these appeared to be multiplets due to the fact that there were peaks for aromatic carbons next to acid and aldehyde groups also present. CHN analysis yielded %C 54.53 : %H 7.28 whereas the theoretical values were calculated as %C 57.09 : %H 7.53. There is some THF present in the sample also some unprotected aldehyde that will make the %C too high. There was not an obvious fit for the data. These reactions were repeated but a small peak was appearing in the spectra around the vinyl area. It has been concluded that there is a problem with the core material since this doesn't occur with the T_8 vinyl core as tried by other members of the group and the catalyst had been changed. It also seems possible that there is slight de-protection of the aldehyde group during the reaction. The aldehyde can also de-protect during the formation of the silane from the protected bromobenzaldehyde but at this stage it can be separated on the Kugelrohr. Catalytic traces of acid cause the de-protection reaction to occur.

1,3,5,7-Tetrakis{2-[3-formylphenyldimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane (80)



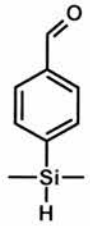
The dendrimer (2.85g, 2.84mmoles), acetone (wet, 50ml) and pyridinium p-toluenesulfonate (0.64g, 2.55mmoles) were refluxed together overnight [10]. Forgot to remove the solvent before trying to re-crystallise from ethanol so had to remove the volatile compounds and then attempt to re-crystallise from ethanol, the product was a yellow-like coloured oil. The second attempt at this reaction was dissolved in diethyl ether once the volatile compounds had been removed and the product was washed with sodium bicarbonate and brine aqueous solutions, dried over magnesium sulfate. This was filtered and the volatile compounds were removed on the rotary evaporator. The product was a yellow oil (2.04g, 2.04mmoles, 71.8%). ^{13}C $\{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ -3.81, -1.61, 6.69, 9.01, 128.24 (this peak was double intensity possibly due to overlapping peaks), 130.11, 134.80, 139.56, 135.45, 192.74. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 10.06 (s, 1H), 8.00 (s, 1.5H), 7.86 (m, 1.2H), 7.78 (m, 1.3H), 7.52 (m, 1.7H), 0.68 (m, 2H), 0.4 (m), 0.36 (s, 10.3H this integration also covers the previous peak since the peaks are close together), 0.08 (s, 6.5H) plus some impurities caused either by not completely deprotected aldehyde or of the oxidation of the aldehyde to the acid. The multiplets are unresolvable. Attempts to re-crystallise the product using diisopropyl ether with a few drops of ethanol in it were unsuccessful. Tlc run in hexane/diethyl ether 50/50 showed 3 main spots. A sample was dissolved in diethyl ether/hexane and methanol and run through a diethyl ether/hexane 50/50 vacuum packed column. Tlc was used to identify fractions. The end fractions had 3 spots not far removed from the baseline. An earlier fraction had 2 spots believed to be protected and deprotected silane reacted with methanol.

1,3,5,7-Tetrakis{2-[4-formylphenyldimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane (81)



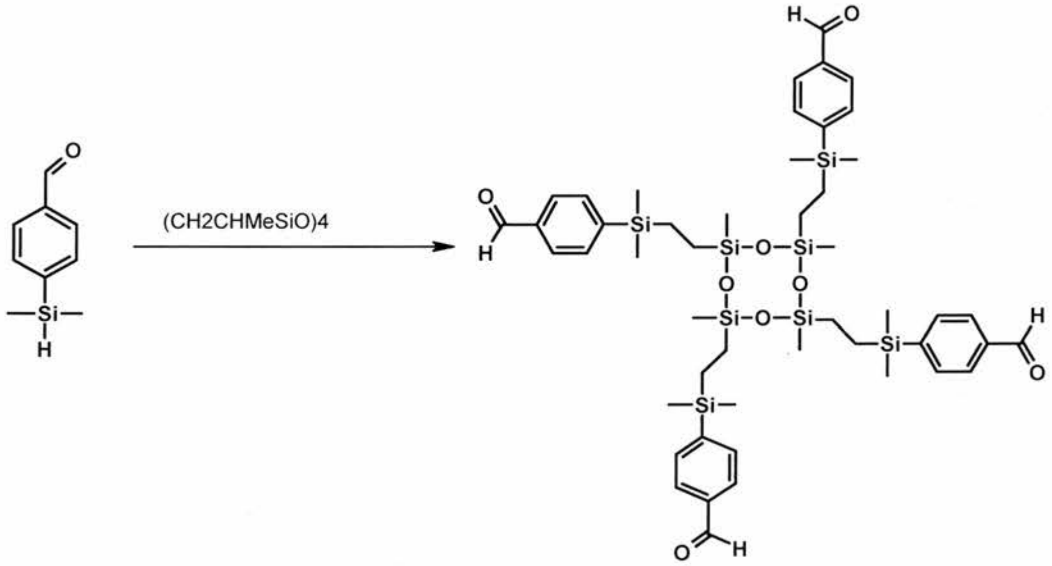
Dendrimer (2.96g, 2.95mmoles), acetone (wet, 50ml) and pyridinium p-toluenesulfonate (0.68g, 2.70mmoles) were refluxed together overnight. Volatile compounds were removed on the rotary evaporator and ethanol was added to crystallise the product, the product was a yellowy oil. The second attempt at this reaction had diethyl ether added to the product once the volatile compounds had been removed and this was washed with sodium bicarobonate and brine aqueous solutions, dried over magnesium sulfate. This was filtered and the volatile compounds were removed on the rotary evaporator. The product was a yellow oil. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ -3.78, -1.52, 6.71, 9.10, 128.47, 128.58, 134.11, 192.58. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 10.0 (s, 1H), 7.82 (m, 1.8H), 7.68 (m, 2.5H), 0.4 (m, 3.1H), 0.28 (m, 5.6H), 0.08 (s), 0 (s, 10.8H), the last two peaks have been integrated together). There are other peaks present that would correspond to the acid being formed by oxidation of the aldehyde in the air. The multiplets are unresolvable although the peaks at 7.82 and 7.68 would be expected to be doublets. Attempts to crystallise the product using diisopropylether with a few drops of ethanol were unsuccessful. Tlcs were ran in hexane/diethyl ether 50/50 on the repeat reaction that had many spots, the reason appears to be that the Karstedt's catalyst was going off. The original product had only 3 spots.

4-formyldimethylsilane (82)



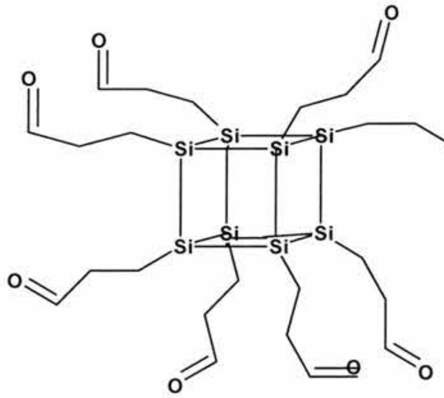
The silane (0.22g, 1.06mmoles), pyridinium p-toluenesulfonate (0.07g, 0.278mmoles) and acetone (10ml) were stirred and refluxed overnight. Volatile compounds were removed on the rotary evaporator. Diethyl ether was added and this was washed with sodium hydrogen carbonate and brine aqueous solutions before being dried over sodium sulfate. This was filtered and the volatile compounds were removed on the rotary evaporator. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ 10.07 (s, 1.2H), 7.88 (d, 2.6H), 7.75 (d, 2.3H), 4.53 (m, 1H), 0.27 (m, 7.2H). There were some extra peaks present. There are no blow-ups of the NMR, so J values could not be accurately measured and the peak at 4.53 could not be properly described pattern wise. It appears as though some of the silane may have condensed since the ratios are a bit high

1,3,5,7-Tetrakis{2-[4-formylphenyldimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane (81)



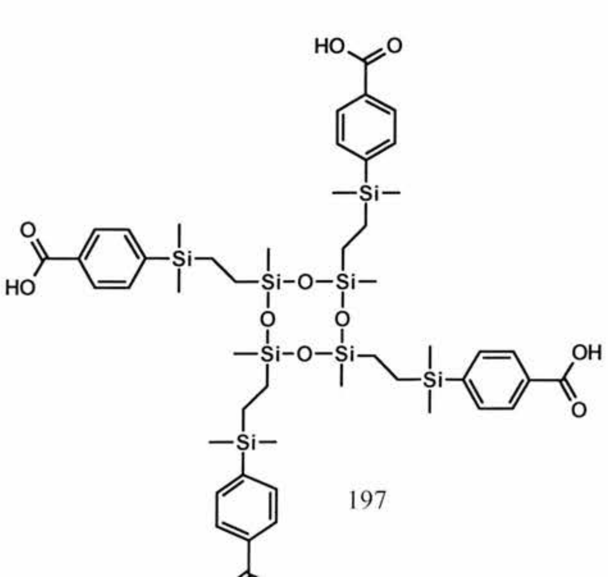
1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane (1ml, 1.0g, 2.89mmoles), Speiers catalyst (12 drops), dry diethyl ether (10ml) were stirred, under argon, whilst addition of silane (0.69g, 4.17mmoles) in dry diethyl ether (5ml). The resulting solution was stirred for half an hour at room temperature before being refluxed overnight. Volatile compounds were removed on the rotary evaporator. Dark coloured liquid was obtained dissolved into $CDCl_3$ to produce an orange solution. The reaction hadn't refluxed convincingly so it was repeated. In both reactions vinyl groups were present and there were some small peaks in the CH_2 region but they were not in the right place and there were no SiH peaks.

1,3,5,7,9,11,13,15-octakis{2-[formyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane(83)



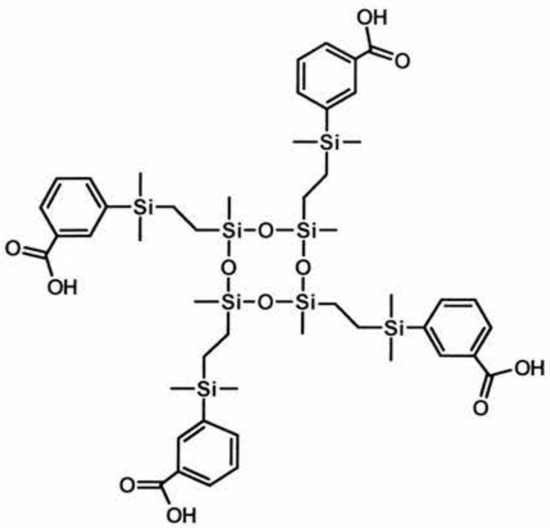
Carried out in a high pressure autoclave, vinyl POSS (0.5013g, 0.792mmoles), was in a glass liner fitted with a funnel, had added to it the catalytic solution $Rh_2(OAc)_4.MeOH$ (0.025g, 0.0527mmoles) in toluene (11ml) and PPh_3 (0.05g, 0.191mmoles). The autoclave was flushed with nitrogen prior to addition of the syngas. The autoclave is pressurised to 20 bar of syngas at 100°C for 4 hours. After reaction the autoclave is cooled down in a cold water bath for 20 minutes. The gases are vented and the solution is removed. There was a dark solid present in the autoclave lining plus some more liquid that was under the glass liner. n.b. rhodium turns black during reactions, it had previously been a rusty orange/brown colour. This reaction was repeated with the catalytic precursors being placed in the glass liner and the vinyl POSS being dissolved in the toluene [13]. Liquid samples had their volatile compounds removed on the rotary evaporator and all samples were allowed to dry on the vacuum line all day. The supernat liquid (solid when dried) was run through a silica plug to remove the Rh (some of the silica was discoloured but the solution was still dark brown, this was carried out in dichloromethane). Hexane was added to this. The product was a black solid. ^{1}H NMR (300MHz, CDCl$_3$, 25^{o}C): δ 9.82 (s, CHO, 1H), 2.59 (m, CH$_2$, 2.5H). There are extra peaks present due to the branched product being present. ^{13}C {^{1}H} NMR (75.4MHz, CDCl$_3$, 25^{o}C): δ 202 (CHO), 201 (CHO), 37 (CH$_2$), 7.7 (CH), 7 (CH$_3$), 3.7 (CH$_2$). There was a shoulder present on the aldehyde peak at 9.77 plus peaks in the region 7.4 – 7.8 corresponding to triphenylphosphineoxide. The CHO resonance should be a triplet but it looks like a singlet, this could be due to exchange broadening. No non-reacted vinyl peaks were present therefore the reaction went to completion. In the carbon spectra there were extra peaks present in the aromatic region, only some of which were triphenylphosphineoxide, plus an extra peak at 39.3. It appears that the n:i ratio is 4:1, this means that every molecule has either one or two branched arms. This ratio could be improved by adding excess triphenyl phosphine as this should favour the linear product but there will never be 100% pure linear product. It seems that if the pressure is too high in the reaction i.e. 40 bars then there is no reaction. There also needs to be found a way of separating the catalyst and the by-product from the product.

1,3,5,7-Tetrakis{2-[4-carboxylphenyldimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane (84)



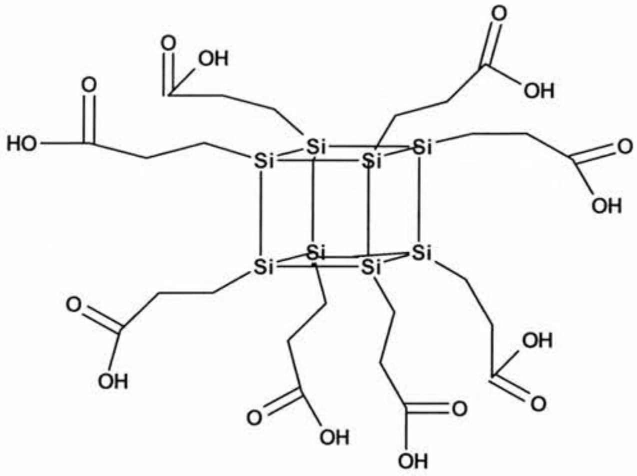
4-Aldehyde dendrimer (1g, dissolved in diisopropylether and acetone, 0.994mmoles) had potassium permanagante (1g, 6.33mmoles) in acetone (50ml) added to it drop-wise, the resulting solution was stirred overnight. Some heat evolved during addition. It was filtered through a sintered glass funnel. This was first washed with acetone to remove excess unused potassium permangante then it was washed with methanol. Both of the washings were vacuumed down. The methanol washings were dissolved in methanol and had some acetone added to them to aid crystallisation. ^{1}H NMR (300MHz, CD_3OD, 25°C): δ 6.4 (d, J = 5.33 Hz, 2H), 5.93 (d, J = 5.33 Hz, 2H), -0.8 (m, 1H), -1.1 (m, 1H), -1.26 (d, J = 10.67 Hz, 6H), -1.53 (s, 4H) plus extra peaks. Possibly some siloxane dimer has been formed from non-reacted silane. No aldehyde was present. The acetone washings in $CDCl_3$ had some aldehyde peaks present so obviously not enough potassium permangante had been used, probably due to siloxane dimer being present. The repeat reaction's acetone washings NMR had a little murmur in the aromatic region but nothing in the aldehyde region and several large peaks in the alkyl region, therefore no starting material. The methanol washings had some peaks in the aromatic region, no aldehyde groups, some peaks in the alkyl region therefore could be product but there are other peaks present so needed to crystallise the product and attempted to do so from hot methanol. The re-crystallisation failed. CHN analysis yielded %C 40.63 : %H 5.56 and the repeat reaction gave %C 54.09 : %H 6.81. IR run in KBr had a strong absorption just below 1600cm^{-1} that could be due to a carbonyl stretch. IR (KBr, cm^{-1}) 3443 (brs), 3068 (m), 3000 (m), 2943 (m), 1588 (vs), 1543 (s), 1400 (s), 1268 (s), 1143 (s), 1108 (s), 1086 (brs), 840 (s), 800 (s), 777 (s), 731 (m), 651 (m), 623 (m).

1,3,5,7-tetrakis{2-[3-carboxylphenyldimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane (85)



3-Aldehyde dendrimer (1.51g, 1.50mmoles) in acetone (10ml) had potassium permanganate (1.57g, 9.93mmoles) in acetone (15ml) added to it. The resulting mixture was stirred overnight. This was filtered through a sintered glass funnel and washed with acetone to remove non-reacted potassium permanganate and then with methanol and the two portions were evaporated. The acetone washing's hydrogen NMR had no aromatic peaks just some alkyl peaks therefore no product or starting material appeared to be present. The methanol washings had aromatic peaks, no aldehyde peaks plus some alkyl peaks therefore possibly contains product along with some other material so tried to re-crystallise it from hot methanol. The recrystallisation was unsuccessful. CHN analysis yielded %C 39.70 : %H 6.37 compared to the theoretical values %C 54.09 : %H 6.81. The CHN analysis results of both 3- and 4-aldehyde dendrimer lie between a fully hydrolysed dendrimer and one with one non-hydrolysed group i.e. %C 36.99 : %H 8.69 compared to %C 43.04 : %H 8.03.

1,3,5,7,9,11,13,15-octakis{2-[carboxyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (86)



Octaaldehyde (0.16g, 0.183mmoles) in acetone (10ml) had potassium permangate (0.19g, 1.20mmoles) in acetone (20ml) added to it drop-wise. The resulting solution was stirred overnight. The mixture was filtered on a medium sintered glass filter funnel and washed with acetone to remove excess potassium permanganate. This was then washed with methanol. The methanol washings were evaporated on the rotary evaporator. Attempts were made to re-dissolve the product in hot methanol, was filtered prior to adding acetone to it and allowing it to stand. The methanol washings, a brown powder, ^{1}H NMR had one main peak (run in $CDCl_3$) at 1.931 (m). In the acetone washings were peaks at 7.4 – 7.8 relating to triphenylphosphineoxide. There were other smaller impurities present in both samples. The acetone washings were reduced with vacuum to reveal triphenylphosphine peaks plus a few other peaks. Attempts were made to re-crystallise the methanol washings from hot methanol. An IR KBr disc was run which showed absorption above 1600cm^{-1} that could be due to carbonyl groups (several peaks). The CHN analysis yielded %C 13.79 : %H 1.35 compared to the theoretical values %C 28.79 : %H 4.03. The result of the CHN analysis lies between the calculated results for cubes with 5 hydrolysed groups %C 16.06 : %H 2.99 and cubes with 6 hydrolysed groups %C 11.68 : %H 2.61. IR (KBr, cm^{-1}) 3420 (brvs), 2977 (s), 2750 (s), 2386 (m), 2341 (m), 2273 (m), 1851 (brm), 1697 (s), 1651 (s), 1628 (s), 1577 (vs), 1411 (vs), 1371 (m), 1000 (m), 966 (m), 828 (m), 703 (m), 668 (m).

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Chapter 4

Silsesquioxane synthesis

4.1 Aims and objectives

There are different kinds of silsesquioxane molecules that can be synthesised. Molecules that are fully condensed or partially condensed can be readily synthesised. The partially condensed silsesquioxane can be used as mimics of silica and can be corner capped with metals to be mimics of metals on silica or as catalysts. Some groups are trying to make silsesquioxanes with alternating groups on each corner by using the electronic properties of the cube as this could be used as dentist filling material. Silsesquioxanes have also found use as hard blocks in polymers and could be used as viscosity modifiers.

This chapter is concerned with the attempted synthesis of cubic silsesquioxanes, both incompletely condensed polyhedral oligomeric silsesquioxanes (POSS) and fully condensed POSS molecules. Some cubic silicates were also synthesised. Attempts were made to synthesise fully condensed and partially incompletely condensed silsesquioxanes with alternating R groups on them.

4.2 Results and discussion

4.2.1 Silsesquioxane synthesis

The following section is split into smaller subsections which comprise the synthesis of partially condensed silsesquioxanes, reactions of partially condensed silsesquioxanes, attempted synthesis of mixed POSS species using heterofunctional and homofunctional groups.

The most common method of making polyhedral oligomeric silsesquioxanes is by the hydrolytic condensation of trifunctional monomers, $XSiY_3$. The trifunctional part of the monomer can be groups like Cl or alkoxy. Other methods of synthesising polyhedral oligomeric silsesquioxanes are condensation of Si-functional oligoorganylcyclosiloxanes $[XYSiO]_m$, co-condensation of organosilicon monomers and/or oligomers of different structure and composition or by thermolysis of polyorganylsilsesquioxanes [1].

This chapter has mostly utilised the hydrolytic condensation method using trifunctional monomers although the reaction of incompletely condensed POSS molecules are mentioned by Voronkov and Lavrent'yev as being co-condensation reactions of organosilicon monomers and/or oligomers of different structure and composition [1]. Thermolysis of polyorganylsilsesquioxanes and condensation of Si-functional oligoorganylcyclosiloxanes were not investigated.

The synthesis of polyhedral oligomeric silsesquioxanes via the hydrolytic condensation of trifunctional monomers depends on 8 factors: concentration of the initial monomer in the solution, nature of the solvent, character of substituent X in the initial monomer, nature of the functional group Y in the initial monomer, type of catalyst employed, temperature, rate of addition of water and quantity of water added and the solubility of the polyhedral oligomers formed [1].

4.2.1.1 Partially condensed silsesquioxanes

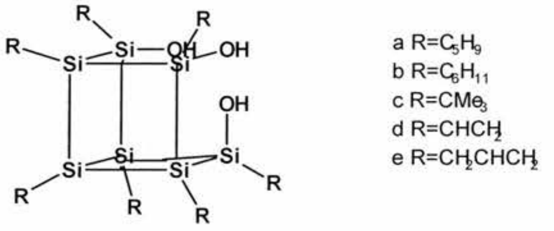
The synthesis of cyclopentyltrisilanol is carried out by adding distilled water cautiously and with vigorous stirring to a solution of c-$C_5H_9SiCl_3$ and acetone and then refluxing the solution for 70 hours. This is followed by washing with acetone and a work-up with pyridine to produce the final product. The reaction using c-

$C_6H_{11}SiCl_3$ is carried out in a similar fashion except it is allowed to stand for at least 3 months as opposed to refluxing for 70 hours.

The synthesis of the partial cage T7 cyclopentyltrisilanol POSS **(87)** molecule and the partial cage T7 cyclohexyltrisilanol POSS molecule **(88)** have both been accomplished and have been repeated to give reproducible results (see Figure 4.1.1a, 4.1.1b) [2, 3]. The T7 cyclopentyltrisilanol POSS molecule reaction has advantages over the reaction to form the more soluble partial cage T7 cyclohexyltrisilanol POSS molecule since it only takes a week whereas the quickest time in which to collect POSS molecules made with cyclohexyltrichlorosilane is several months. Also reactions to form partial cages with t-butyl **(89)**, vinyl **(90)** and allyl **(92)** groups were tried (see Figure 4.1.1c,d,e). The partial cage vinyl reaction produced a completely condensed vinyl POSS molecule. The reaction to produce $^{t\text{-}}$Bu POSS molecule yielded very little product of which there was not enough to be analysed. The reaction to produce allyl POSS molecule did not yield any product at all. In the literature there are reports of fully condensed T_8 allyl POSS and a tetranuclear silsesquioxane $[^{t\text{-}}BuSiO]_4$ [4].

Later, the reaction used to produce T_8 hydridoPOSS molecules was used in an effort to make T_8 vinyl POSS cubes **(91)**. This was in part done as a test to see how much T_8 the reaction would yield (since it takes a month to produce the T_8 by the commonly used method), and also to see if it was possible to make mixed POSS cubes by this method. The reaction uses $FeCl_3$, concentrated HCl with methanol and adds hexane and toluene to it to set up a biphasic mixture, the trichlorosilane is added dropwise over many hours (depending on the quantities used) [5].

The reaction yielded more product when the addition of the vinyltrichlorosilane had not been constant (i.e. the addition had stopped at some point) which made it appear that some of the reaction was occurring in the dropping funnel as well as in the reaction flask. Therefore the reaction to produce mixed POSS molecules by this method would have to be carefully monitored to ensure that the addition of organotrichlorosilane to the reaction mixture was constant so as to minimise the chance of reaction occurring in the dropping funnel.

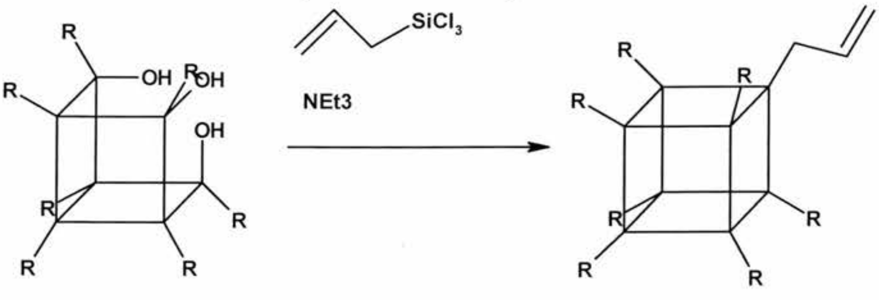


a R=C_5H_9
b R=C_6H_{11}
c R=CMe_3
d R=$CHCH_2$
e R=CH_2CHCH_2

Figure 4.1.1 Partially condensed silsesquioxane
The Si-Si bonds, in this diagram, are actually Si-O-Si bonds, the oxygens have been left out for clarity.

4.2.1.2 Reactions of incompletely condensed POSS molecules

The reaction usually carried out on incompletely condensed POSS molecules is to "corner cap" them with a trichlorospecies. This species can be either a silicon species or a metallic species that has a functional group so that further reactions can be carried out on them (see Scheme 4.1).



Scheme 4.1 Corner capping reaction

4.2.1.2.1 Corner capping with vinyl and allyltrichlorosilanes

The corner capping reaction is carried out in solvent with T_7 cyclopentyltrisilanol and triethylamine being vigorously stirring whilst the trichlorsilane (to cap the incompletely condensed POSS molecule) is being added. The hydrochloride is filtered off and the solvent is removed, before the product is washed with acetone [6].

The corner capping reaction using vinyltrichlorosilane and T_7 cyclopentyltrisilanol **(93)** was originally tried in toluene but only the starting materials were found after analysis. This reaction was repeated in dry THF with the stirring carried out in a nitrogen atmosphere [6]. ^{29}Si NMR on the recovered product showed the expected 2 resonances (see Figure 4.1.2). Crystals were produced from the T_8 vinylheptacyclopentyl POSS molecules **(93)** and a partial X-ray crystal structure was obtained with an R-centered lattice type (see appendix and Figure 4.1.3 for more details). Figure 4.1.3 shows that the POSS molecule is fully condensed. Corner capping the POSS molecules with allyltrichlorosilane has also been achieved **(94)**.

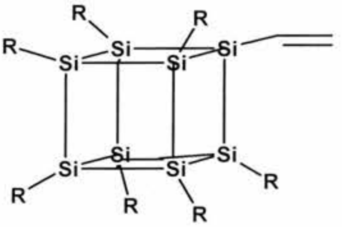


Figure 4.1.2 a POSS molecules which has been corner capped by a vinyl group

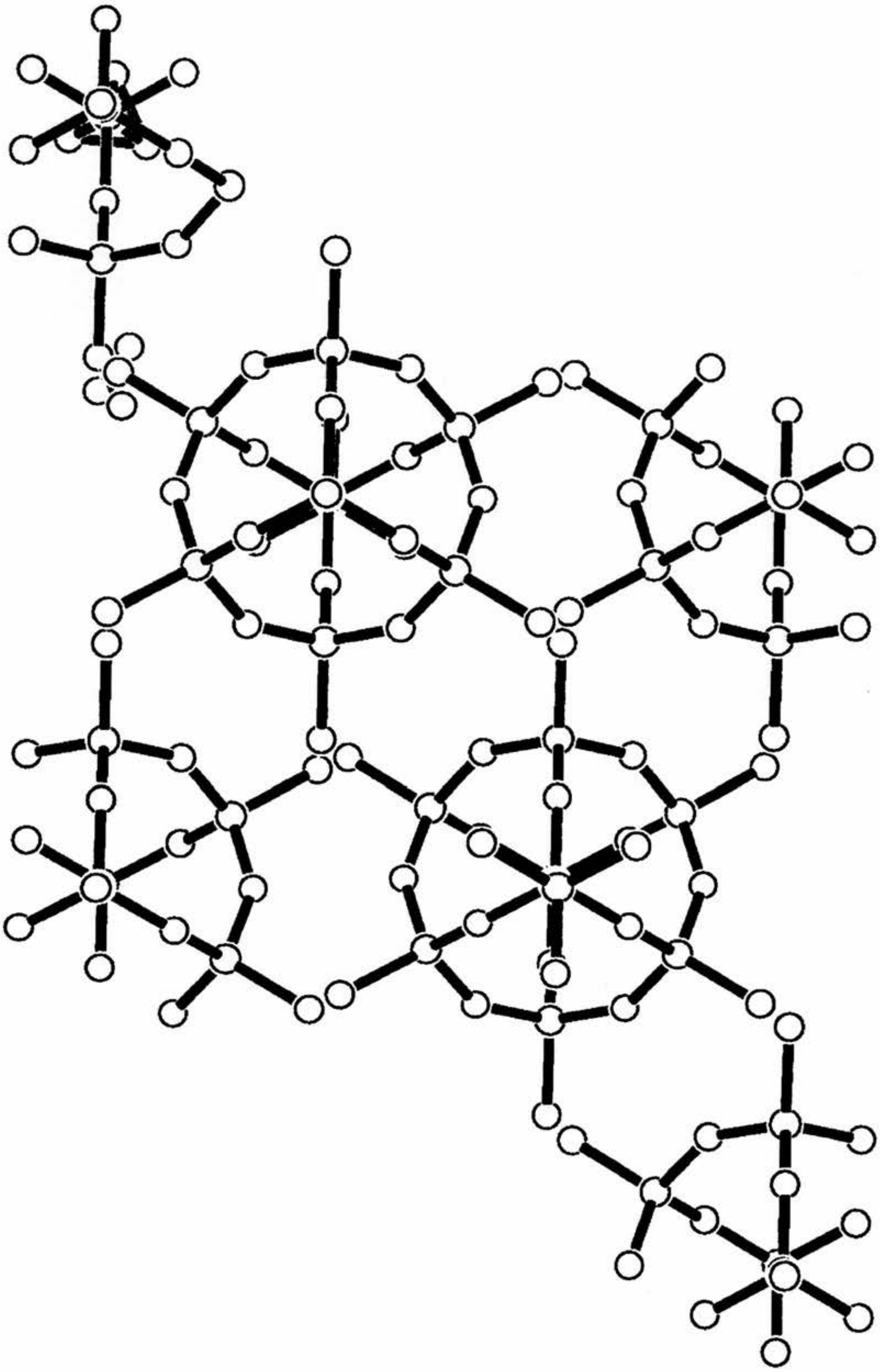


Figure 4.1.3 Crystal structure of vinylheptacyclopentylPOSS (93)

4.2.1.3 Attempted synthesis of mixed fully condensed POSS molecules using heterofunctional condensation

Heterofunctional condensation involves reacting two species together which have different Y components i.e. reacting $RSiCl_3$ with $R'Si(OH)_3$. Several different reactions were tried to try and synthesise a mixed cubic POSS molecule. Originally the reactions were tried using $^{t-}BuSi(OH)_3$ and either cyclohexyltrichlorosilane **(95)** or cyclopentyltrichlorosilane **(96)** using the conditions of the corner capping reaction. The next attempt involved $^{t-}BuSi(OH)_3$ and vinyltrichlorosilane **(97)** in a non-hydrolytic condensation. Although none of these reactions were successful, this author believes that if it is possible for a pure, mixed POSS species to be made it can only be formed using a non-hydrolytic condensation of heterofunctional species.

A final attempt was to be made using the hydrido POSS method to form cubes in a non-hydrolytic fashion using vinyltrichlorosilane and cyclohexylsilanetriol [5]. This method would have involved substituting the methanol for cyclohexylsilanetriol. Since this would probably just be used as a source of scarce water (like the methanol is in the hydrido POSS reaction) and the loss of the biphasic nature of the mixture, it was decided that this would probably not work. Another possibility was using the same method with vinyltrimethoxysilane and organyltrichorosilane but it was unclear what would happen under these conditions plus there would still be the loss of the biphasic nature of the mixture since vinyltrimethoxysilane would be substituted for methanol in the reaction. It may be a better idea to try various conditions when attempting to synthesis the mixed POSS molecules i.e. by placing the vinyltrimethoxysilane and organyltrichlorosilane together and letting them stand or by using these reactants with refluxing for 70 hours (both reactions would be without the presence of water).

This method could still have a serious disadvantage due to homocondensation. Although it would be less likely for the chloro species to condense in the absence of water, the alkoxy species could condense (see Schemes 4.2 and 4.3), these reactions are speculated to occur during the production of hydrolytically produced silsesquioxanes.

Scheme 4.2 Heterocondensation between silicon species

Scheme 4.3 Homocondensation between silicon species

Another possible problem could be group switching on the silicon atom i.e. H-Si Vi-Si swapping has been reported to happen during the hydrosilation reaction.

There have been reports that mixed tetracyclosiloxanes can be synthesised [7] from a silanediol and a dichlorosilane (see Figure 4.1.4). Maybe by looking at the way in which this reaction was carried out, it may shed some light upon how cubic mixed POSS species can be made.

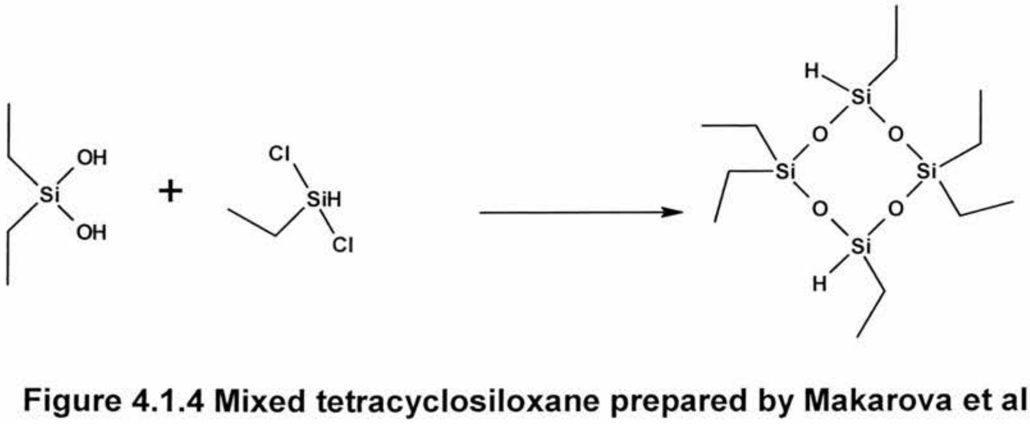
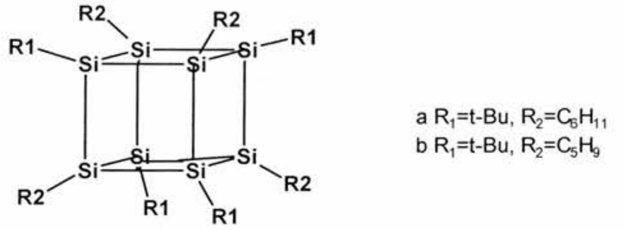


Figure 4.1.4 Mixed tetracyclosiloxane prepared by Makarova et al [7]

With the hydrolytic condensation of trifunctional monomers, it has been reported that low pH values of the medium favour cyclisation whereas high pH values facilitate polymerisation [1], with the exception of the condensation of phenyltrichlorosilane when a high pH favours a higher yield of the product than low pH.

The synthesis of a silsesquioxane using $^{t-}BuSi(OH)_3$ and $RSiCl_3$ was tried because Laine et al. [8] were trying to functionalise four of the corners of the silsesquioxane cube using the electronic effects of the cube. It seemed to me to be more obvious, at the time, to build a cube with alternating functionalities. This reaction has been repeated using dry solvents, under a nitrogen atmosphere. The silsesquioxane product was polymeric possibly due to $RSiCl_3$ being added too quickly or the reactant concentration being too high or opportunistic water being present.

The reaction was also tried in a two phase system since the $^{t-}BuSi(OH)_3$ is not soluble in hexane but $RSiCl_3$ is. The two-phase system was tried but it also gave polymer. The only way not tried was with higher dilution and slower addition of $RSiCl_3$, with the reaction vessel in ice, conditions which might stop the formation of the polymer. Also using dry triethylamine or pyridine may make the $^{t-}$butylsilanetriol more reactive. This reaction was tried originally with cyclohexyltrichlorosilane (see Figure 4.1.5a) and then with cyclopentyltrichlorosilane, just in case the less soluble cyclopentyl would work, but it did not (see Figure 4.1.5b). The cyclopentyl reaction was only carried out in dry THF under nitrogen using dry solvents (i.e. not tried in a two phase system). In both cases, as the trichlorosilane dropped from the dropping funnel, puffs of white smoke appeared. To stop the trichlorosilane hydrolysing, maybe addition by catheter tube is required. It is now hoped that if $^{t-}BuSiCl_3$ is added to $RSi(OH)_3$ that may be the reaction will work. $^{t-}BuSi(OH)_3$ is exceptionally stable compared to other silanetriols which undergo self condensation [9]. Possibly the way to react it with $RSiCl_3$ is to use the protective group $trisOSnMe_3$ which has been used to prepare titanosilsesquioxanes from $^{t-}BuSi(OH)_3$ and $CpTiCl_3$ [10]. Another possibility is making ^{t}BuSi(OLi)$_3$ as the lithiated ^{t}Bu silanediol has been reacted with a metal dichloride to form a mixed tetracyclo metalsiloxane [11].



a R_1=t-Bu, R_2=C_6H_{11}
b R_1=t-Bu, R_2=C_5H_9

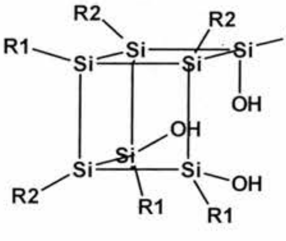
Figure 4.1.5 Fully condensed mixed silsesquioxane

4.2.1.4 Attempted synthesis of partial mixed POSS molecules using homofunctional copolymerisation

Since the hydrolytic condensation of cyclopentyltrichlorosilane worked so well and the other reaction using $RSiCl_3$ and $^{t-}$Bu(OH)$_3$ did not give the desired product, a series of reactions were tried to see if mixed partial cage silsesquioxanes could be made. The mixtures tried are shown in Table 4.1(see Figure 4.1.6).

After these reactions had been tried, a paper was found in which a variety of methods were used to make mixed silsesquioxanes. This paper describes three main methods: "homofunctional copolymerisation of alkyl- and alkenyl- trichlorosilanes as well as of alkyl- and alkenyl- triacetoxysilanes; heterofunctional copolymerisation of organyltrichloro- and organyltriacetoxy- silanes; and the interaction reaction of chlorine-containing cyclosiloxanes and alkenyltrichlorosilanes" [12].

It was reported that the homofunctional copolymerisation method yielded products with the formula $(RSiO_{1.5})_m(R'SiO_{1.5})_{8-m}$ where m ranged from 0-8. Although the quantities in which the trichlorosilanes were mixed produced the highest yield of product i.e. equal molar quantities of $RSiCl_3$ and $R'SiCl_3$ would give the highest yield of $(RSiO_{1.5})_4(R'SiO_{1.5})_4$ there would be no control as to what R group would be adjacent to another. Also the homofunctional condensation reaction using trichlorosilanes gave less reproducible results than the other methods due to the production of HCl.



a $R_1=C_5H_9$, $R_2=C_6H_{11}$
b $R_1=C_5H_9$, $R_2=CMe_3$
c $R_1=C_6H_{11}$, $R_2=CMe_3$
d $R_1=C_5H_9$, $R_2=CHCH_2$
e $R_1=C_6H_{11}$, $R_2=CHCH_2$
f $R_1=CMe_3$, $R_2=CHCH_2$
g $R_1=C_5H_9$, $R_2=CH_2CHCH_2$
h $R_1=C_6H_{11}$, $R_2=CH_2CHCH_2$
i $R_1=CMe_3$, $R_2=CH_2CHCH_2$

Figure 4.1.6 Partially condensed mixed silsesquioxanes

	cyclopentyl	cyclohexyl	t-butyl	vinyl	allyl
cyclopentyl		**(98)**	**(99)**	**(101)**	**(104)**
cyclohexyl	**(98)**		**(100)**	**(102)**	**(105)**
t-butyl	**(99)**	**(100)**		**(103)**	**(106)**

Table 4.1 Mixed homofunctional reactions tried (functional group used was chlorine).

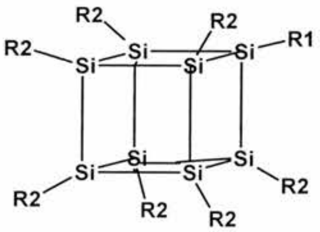
4.2.2 Silicate synthesis

This section describes the synthesis of several different silicates. Trimethyl **(112)**, vinyldimethyl **(109)** and hydridodimethyl **(110)** silicates are well known. Also mentioned is the attempted synthesis of a silicate with silsesquioxane arms **(113)** that would have comprised of a silicate core surrounded by 8 silsesquioxane cubes had it been successful.

4.2.2.1 Synthesis of silicate molecules

Two methods were found that produced silicate molecules. The first method involved the synthesis of tetramethylammonium silicate that then had an R group reacted onto it. Tetramethylammonium silicate **(108)** is made by reacting tetramethylammonium hydroxide with silicic acid. The second attempt at the preparation of the tetramethylammonium silicate reaction was successful, since crystals were formed from all the reactions tried using it as a starting material [11].

Cubic silicate molecules can be made whereby the alkenyl substituent is reacted onto a silicate anion. This is formed using tetramethylammonium silicate, dimethylformamide, and dimethylvinylchlorosilane and heptane **(109)** (see Figure 4.1.7a) [12]. This reaction was also tried with trimethylsilane **(112)** (see Figure 4.1.7b) instead of dimethylvinylsilane and with a mixture of dimethylvinylsilane and trimethylsilane **(111)** (see Figure 4.1.7c). Crystals were produced in all three reactions. Single crystal data was collected on some of the crystals. It was discovered that the structures made with only trimethylchlorosilane and the mixed structure had the same unit cell which implied that these structures were the same i.e. the mixed structure did not have every box with one vinyl substituent on it. The crystal system of these structures was triclinic with a primitive lattice type (see appendix and Figure 4.1.8 for more details).



a $R_1=R_2=OSiMe_2CHCH_2$
b $R_1=R_2=OSiMe_3$
c $R_1=OSiMe_2CHCH_2$, $R_2=OSiMe_3$
d $R_1=R_2=OSiMe_2H$

Figure 4.1.7 Cubic silicate where the alkenyl substituent is added onto a cubic silicate anion

The other experimental method found used tetraethoxysilane with tetramethylammonium hydroxide in methanol and water. It was used to make octakis(vinyldimethylsiloxy)octasilicate **(109)**. Octakis(dimethylsiloxy)octasilicate **(110)** (see Figure 4.1.7d) was also made via this method but the crystals formed were gel-like. Octakis(dimethylsiloxy)octasilicate has been reported and used, it was synthesised using the tetramethylammonium silicate method [13].

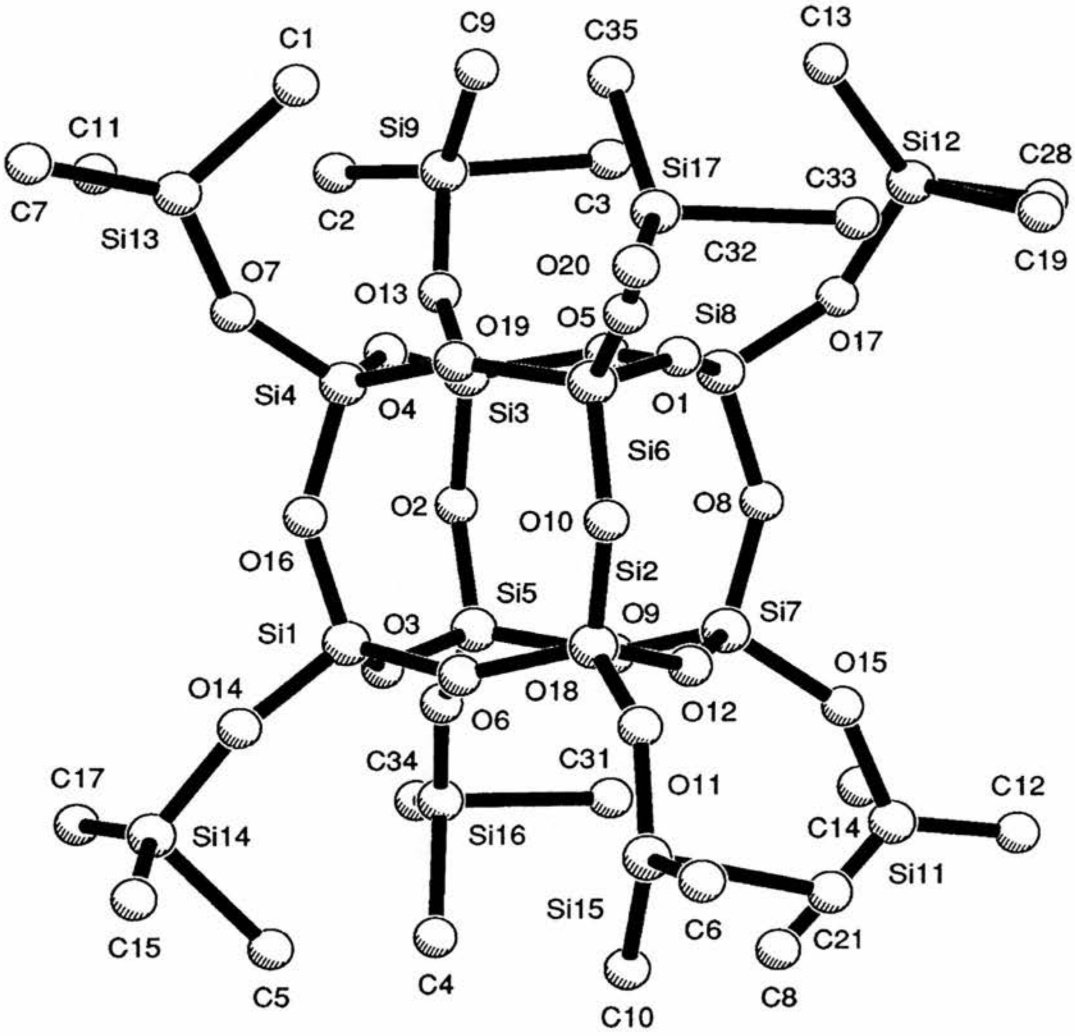


Figure 4.1.8 Crystal structure of trimethyl silicate (112)

4.2.2.1.1 Production of silicate with silsesquioxane arms

A way of making a dendrimer with silsesquioxane arms was attempted by combining several of the different reactions already used. For example, corner capping the T_7 cyclopentyl POSS molecules with vinyltrichlorosilane, hydrosilating $HSiMe_2Cl$ onto the vinyl T_7 cyclopentyl POSS molecules and finally reacting this with tetramethylammoniumsilicate and water to produce a silicate with silsesquioxane arms **(113)**. This reaction should work better than the corner capping reactions with T_7 cyclopentyl POSS molecules and dendrimers (see Chapter 2), since there is a longer chain between the focal point of the dendrimer (i.e. the silicate box) and the branch ends (i.e. the POSS molecules). This reaction was tried but there were some non-reacted vinylheptacyclopentyl POSS molecules present in the mixture used. It was decided that since there were so many unwanted compounds present and that there was nothing present in the NMR spectra that was obviously product, this experiment was abandoned. Concentration of the reacting species is crucial in the silicate forming reactions. It may be more advantageous to try the reaction again but using already formed octakis(dimethylsiloxy)octasilicate and hydrosilating vinylheptacyclopentyl POSS onto it. Alternatively, hydridoheptacyclopentyl POSS could be hydrosilated onto octakis(vinyldimethylsiloxy)octasilicate.

4.3 Conclusions

Reactions to produce incompletely condensed POSS molecules with cyclopentyl **(87)** and cyclohexyl **(88)** groups were successful. Reactions to produce other incompletely condensed POSS molecules were not successful (although the reaction with vinyl groups produced a fully condensed POSS molecule **(90)**).

Corner capping incompletely condensed POSS molecules with vinyl- **(93)** and allyltrichlorosilane **(94)** was successful. The vinyl corner capped product was successfully hydrosilated with dimethylchlorosilane (see Chapter 2).

Synthesising mixed T_7 or T_8 POSS molecules using either homo- or heterofunctional condensation reactions was unsuccessful **(95)-(107)**. It would be better to make POSS molecules using heterofunctional condensation reactions as they should have more control over the placement of the R groups than homofunctional condensation reactions.

Cubic silicates were produced which either had dimethylvinyl groups **(109)**, trimethyl groups **(112)** or dimethyl groups **(110)**. The cubic silicates with dimethylvinyl groups were used as dendrimer cores (see Chapter 2). Cubic silicates with dimethyl groups have been used to make octopus molecules [13]. It is possible that the silicates with trimethyl groups could be used in further reactions since the hydrogens on the trimethyl groups should be slightly acidic.

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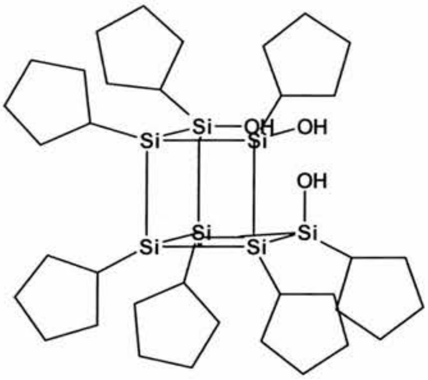
4.4 Experimental

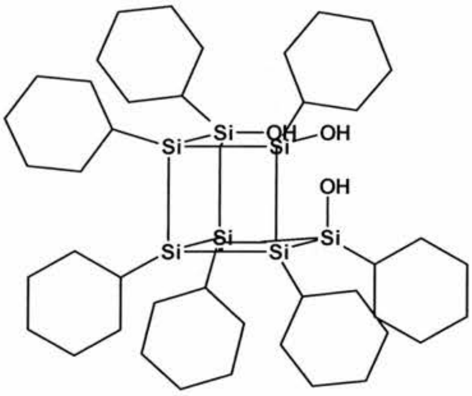
^{1}H (300MHz), ^{13}C (75MHz) and ^{29}Si (59.6MHz) NMR spectra were recorded on a Brucker AM 300. Some of the ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300. The ^{1}H and ^{13}C NMR solutions were placed in 5mm glass tubes whereas the ^{29}Si NMR solutions were placed in 10mm tubes. The spectra were recorded at room temperature in one of the following: d^6 benzene, d^4 methanol or $CDCl_3$ (Apollo Scientific/Aldrich) the ^{29}Si NMR samples were either in C_6D_6/C_6H_6 or $CDCl_3/CHCl_3$ solutions. The infra red spectra were recorded on a Perkin Elmer 1710. Liquid samples were placed between sodium chloride plates. Solid samples were made into potassium bromide (Aldrich) plates. Powder diffraction was carried out on a STOE Stadi/P uses copper radiation that has a wavelength of 1.54056 Å and has a motion sensitive detector. Single crystal diffraction was carried out on a Rigaku AFC7S diffractometer with graphite monochromated Mo-Kα radiation. All CHN measurements were made on a Carlo-Erba Modell 1106.

T7 hepta(cyclopentyl)trisilanol POSS (87)



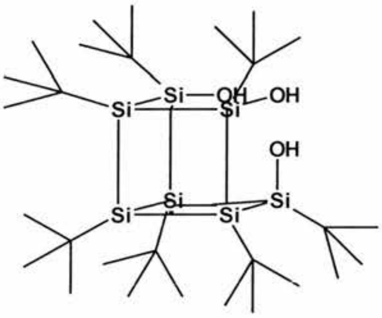
Distilled water (120ml, 6.59moles) was added cautiously and with vigorous stirring to a solution of $c\text{-}C_5H_9SiCl_3$ (16g, 78.6mmoles) and acetone (400mL) in a 1-L round-bottomed flask, before the solution was refluxed for 70 hours. The resulting white solid was collected on a Buchner funnel and washed with acetone. In order to remove any remaining resinous material the filter cake was broken up and suspended in acetone (100mL, 2h with stirring). The suspension was filtered and dried overnight (40-50°C). The crude product was suspended in 20 times its weight of pyridine and stirred overnight. Any insoluble compounds were removed by filtration through a medium sintered glass Buchner funnel with Hyflo; before the pyridine solution was carefully poured into an equal volume of concentrated HCl mixed with crushed ice. The precipitated product was collected on a medium sintered glass Buchner funnel and washed with copious amounts of water. It was left in an oven overnight (40-50°C), the final product was a white solid (3g, 3.43mmoles, 30.5%) [2]. ^1H NMR (300MHz, C_6D_6, 25°C): δ 1.95 (m), 1.4 (s), 0.7 (s), 0.5 (s). ^{13}C $\{^1H\}$ NMR (75MHz, C_6D_6, 25°C): δ 27.8, 27.3. The peaks were very broad since the product was not very soluble in C_6D_6. The peaks in the ^1H NMR spectra were not assigned or integrated since they were broad and not well defined. CHN analysis yielded %C 48.04 : %H 7.79 the theoretical values were calculated at %C 48.01 : %H 7.60. IR (KBr, cm^{-1}) 3193 (brm), 2966 (s), 2875 (s), 1440 (m), 1251 (m), 1120 (brvs), 1040 (s), 908 (m), 874 (s), 490 (s). Literature data ^{1}H NMR (500.1MHz, $CDCl_3$, 25°C): δ 6.00 (br s, 3H), 1.79 (m, 20H), 1.56 (m, 36H), 0.97 (m, 7H). ^{13}C {^{1}H} NMR (125.03MHz, 25% v/v pyridine/$CDCl_3$, 25°C): δ 26.72, 26.64, 26.56, 26.28, 26.26 (s, for CH_2); δ 23.30, 21.95, 21.57 (s, 3:3:1 for CH). ^{29}Si {^{1}H} NMR (99.35MHz, 25% v/v pyridine/$CDCl_3$, 25°C): δ -57.73, -65.90, -67.31 (s, 3:1:3). CHN analysis yielded %C 47.75 : %H 7.53 the theoretical values were calculated at %C 48.00 : %H 7.60 [2].

T_7 hepta(cyclohexyl)trisilanol POSS(88)



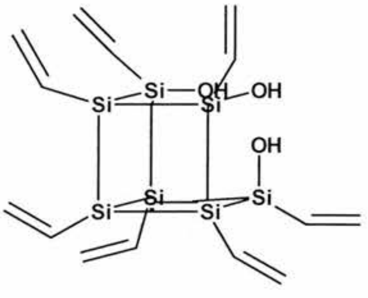
Distilled water (160ml, 8.79moles) was carefully added, with stirring, to a solution of $CySiCl_3$ (32.5g, 149mmoles) in acetone (300ml). The flask was stoppered and allowed to stand. After some time had elapsed, a considerable amount of solid had formed so this was filtered off and the filtrate was returned to the flask. A powder diffraction pattern was run on the sample and it had peaks which suggests the sample was crystalline. ^{13}C {^{1}H} NMR (75MHz, $CDCl_3$, 25°C): δ 27.47, 26.57, 23.81, 23.47, 23.03 plus some extra peaks. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 0.84 (m, 1H), 1.27 (m, 5H), 1.77 (m, 5H). The crystals were crushed in a mortar and pestel and suspended in acetone (30ml) and stirred for 1 hour. The powder was filtered off and placed in an oven (40-50°C) to dry overnight. The crude product was stirred in pyridine (25ml) for 30 minutes. It was filtered through a medium sintered glass funnel. The pyridine extract was added carefully to ice-cooled concentrated aqueous HCl (45ml). The solid was collected on a Buchner funnel. To remove any mechanically entrained pyridine, pyridinium hydrochloride, or HCl before continuing, the solid was stirred in a large excess of water for 1 hour, the product was collected on a very large Buchner funnel, before being washed with copious amounts of water. The solid was dried overnight in an oven (40-50°C). The sample was dissolved in hot diethyl ether and filtered to remove particulates. The volume was reduced on the rotary evaporator and by evaporating in air. Some solid had formed so this was filtered off and the rest was returned to the flask [3]. CHN analysis yielded %C 52.37 : %H 8.60 the theoretical values were %C 51.8 : %H 8.28. Literature data $^{13}C\ \{^1H\}$ NMR (62.5MHz, $CDCl_3$, 25°C): δ 27.554 (br s), 26.886 (br s), 26.656 (br s, 2:1:2 for CH_2); 23.881 (s), 23.542 (s), 23.112 (s, 3:3:1 for SiCH). $^{29}Si\ \{^1H\}$ NMR (49.7MHz, $CDCl_3$, 25°C, 0.02M $Cr(acac)_3$): δ -60.159 (s), -67.993 (s), -69.544 (s, 3:1:3) [14].

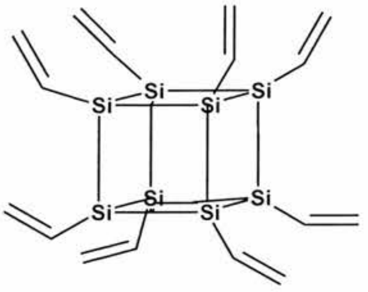
T_7 hepta(tert-butyl)trisilanol POSS(89)



Distilled water (30ml, 1.65moles) was added drop-wise (under nitrogen) to a solution of ^{t}butyltrichlorosilane (5.08g, 26.5mmoles) in acetone (110ml). The resulting solution was refluxed over the weekend. Very little, if any, solid had formed so the solution was transferred to a conical flask, stoppered and left to stand. After some time there was a considerable amount of solid so this was filtered and the filtrate was returned to the flask to see if any more would form [2]. It was filtered again but as before there was not enough product for analysis.

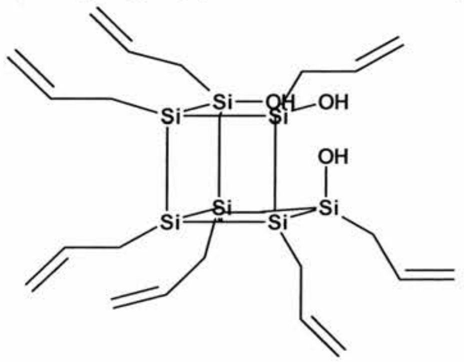
T$_7$hepta(vinyl)trisilanol POSS(90) and octakis(vinyl)silsesquioxane(91)





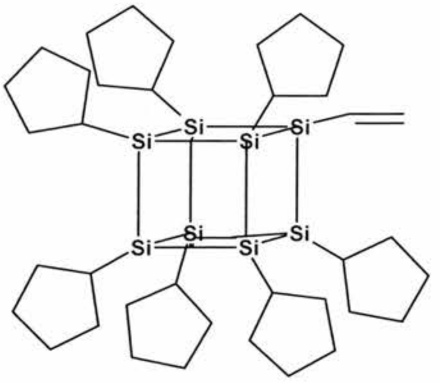
Vinyltrichlorosilane (1.44g, 8.92mmoles) in acetone (35ml) had distilled water (10ml, 549mmoles) added drop-wise to it, with stirring. The resulting mixture was stoppered and left to stand. Large cubic crystals were filtered off from this solution and the filtrate was returned to the flask in case more product would crystallise out. In the centre of some of the larger crystals were traces of solvent [2]. It turned out to be cubic vinyl POSS that is very well known. The most useful synthesis of this compound takes about a month so attempts were made using the hydrido POSS synthesis method using trichlorovinylsilane to see what kind of yield, in the time period of the synthetic method would produce T_8 vinyl POSS. $FeCl_3$ (anhydrous, 50.228g, 310mmoles) was placed in a 1 litre round bottomed flask, and concentrated HCl (20ml) was added followed by methanol (40ml). Hexane (mixture of isomers, 350ml) and toluene (50ml) were then added, and the biphasic mixture was stirred. A solution of vinyltrichlorosilane (20ml, 25.4g, 157mmoles) in hexane (150ml) was added drop-wise by using a pressure-equalising dropping funnel over a period of 9 hours before stirring overnight. The upper hexane layer was transferred to a conical flask with some suspended yellow solid. K_2CO_3 (14.138g) and $CaCl_2$ (10.037g) were added to the flask and the contents were stirred overnight [5]. The mixture was filtered, and the filtrate volume was reduced by evaporation. The first crop was filtered off, a white powder (0.798g, 1.26mmoles, 12.8%) and left on top of the oven to dry. The volatile compounds were removed down to 10ml. A second crop of solid was filtered off and the volatile compounds were removed to leave a residue. The second crop was also a white powder (0.087g, 0.137mmoles, 1.4%). Tlc's were run in a mixture of hexane and diethyl ether of both crops, the residue and a pure sample made by the month long method. They all had spots in the same place but the first crop had extra spots as did the residue. During the repeat reaction the addition was not all added within the 9 hour period and the first crop was not as soluble as the previous reaction had been. First crop (1.31g, 2.07mmoles, 21.0%) and the second crop (0.104g, 0.164mmoles, 1.7%) were both white powders. The residue was also a white powder (3.491g, 5.52mmoles, 56.1%). Tlc gave similar results as before except the first crop only showed one spot. Attempts to re-crystallise the residue from dichloromethane proved to be fruitless since there were too many by-products present. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 5.92 – 6.2 (m) appeared in both first and second crops of the reactions plus some other smaller peaks. In the residue spectra there were lots of extra peaks between 0.8 – 3.4 as well as a not very well defined peak at 5.8 – 6.2 [5].

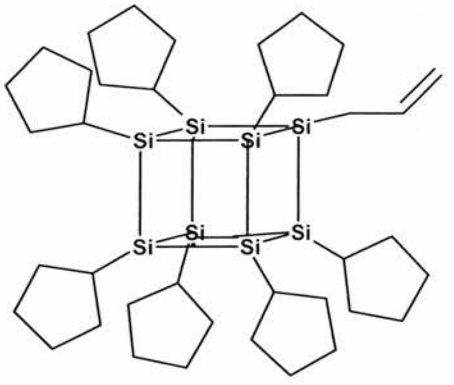
T7 hepta(allyl)trisilanol POSS(92)



Allyltrichlorosilane (1.56g, 8.89mmoles) in acetone (35ml) had distilled water (10ml, 549mmoles) added to it, with stirring. The resulting mixture was stoppered and left to stand [2]. No solid product formed.

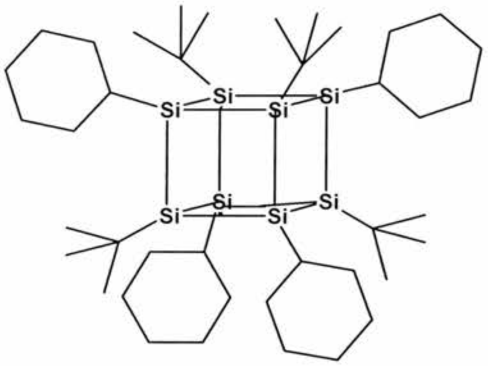
T_8 vinylheptacyclopentyl POSS(93) and T_7 allylheptacyclopentyl POSS (94)

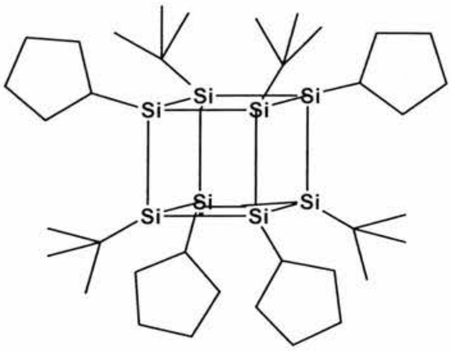




T7 cyclopentyltrisilanol (1.3g, 1.44mmoles) and triethylamine (0.5g, 4.94mmoles) were dissolved in toluene (200ml). Vinyltrichlorosilane (0.23g, 1.42mmoles) was added with vigorous stirring and the resulting mixture was stirred overnight. The hydrochloride was filtered off and the solvent was removed under vacuum. The white solid product was washed with acetone and left to dry in the oven (40 - 50 ^{o}C) over the weekend. This experiment was repeated using dry THF as solvent and the stirring carried out in a nitrogen atmosphere [6]. POSS molecules were also capped with an allyl substituent in dry THF. Original experiment: IR spectra essentially the same as T7 (cyclopentyl)trisilanol. The final product was a white powder (0.965g, 1.04mmoles, 72.2%). IR (KBr, cm^{-1}) 3204 (brs), 2954 (vs), 2875 (vs), 2375 (m), 2341 (m), 1451 (s), 1320 (s), 1246 (vs), 1114 (brvs), 1046 (s), 926 (s), 880 (s), 743 (m), 496 (s), 461 (s). ^{13}C {^{1}H} NMR (75MHz, C_6D_6, 25^{o}C): δ 28.59, 28.23, 28.17, 24.13, 23.75. ^{1}H NMR (300MHz, C_6D_6, 25^{o}C): δ 1.96 (m, 1H), 1.375 (m, 2H), 0.625 (s, 2H), 0.52 (s), 0.22 (s) plus a few extra peaks. Vinyltrichlorosilane ^{13}C {^{1}H} NMR (75MHz, $CDCl_3$, 25^{o}C): δ 139.14, 131.06. Experiments using dry solvents under nitrogen: ^{13}C {^{1}H} NMR (75MHz, $CDCl_3$, 25^{o}C): δ 135.50, 130.03, 27.19, 27.17, 26.89, 26.84, 22.11 plus several smaller peaks. ^{1}H NMR (300MHz, $CDCl_3$, 25^{o}C): δ 5.85 (m, 1H), 3.7 (m, 4H), 1.55 (m, 12H), 0.9 (m, 1H). ^{29}Si NMR (59.6MHz, 50% v/v $CDCl_3$/$CHCl_3$, 25^{o}C): δ -66.36, -66.53, -80.74 plus several smaller peaks. CHN analysis yielded %C 47.92 : %H 7.44 the theoretical values were calculated as %C 47.9 : %H 7.17. A partial X-ray diffraction pattern was obtained for this species, it was only a partial due to the motion of the organic groups stopping the formation of a good crystal structure. The crystal system was trigonal with an R-centred lattice type. The crystal was a colourless block. Literature data ^{29}Si NMR (49.70MHz, $CDCl_3$, 25°C): δ -68.467 (3Si), -68.603 (3Si), -68.623 (1Si), -80.602 (1Si) [15]. Allyltrichlorosilane $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 127.14, 119.46, 30.64. Allyl corner capped POSS molecule, a white solid gave $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 132.49, 114.46, 27.18, 26.90, 22.12 plus some smaller peaks. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 0.95 (m, 4H), 1.5 (m, 29H), 1.725 (s, 10H), 4.925 (m, 2H), 5.775 (m, 1H). CHN analysis yielded %C 40.72 : %H 7.16 : %N 3.07 the theoretical values were calculated as %C 48.47 : %H 7.28. The values of CHN results corrected for the presence of triethylamine yielded %C 42.00 : %H 5.10. From the integration of the ^1H NMR spectra it appears that there is too much allyl present in the sample but this could be due to not washing the product enough or maybe different separation techniques need to be employed to clean up the product. ^{29}Si NMR (59.6MHz, 50% v/v $CDCl_3$/$CHCl_3$, 25°C): δ -66.53 (7Si), -71.13 (1Si). The allylsilane capped box had a sample dissolved in hexane to see how pure it was when it hadn't been washed with acetone. The tlc had two main spots one at the baseline and one near the solvent front and it had a third weaker spot half way up the tlc plate.

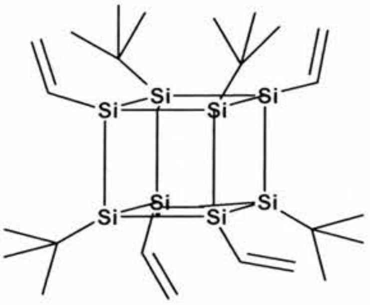
1,5,9,13-tetrakis(tert-butyl)-3,7,11,15-tetrakis(cyclohexyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane(95) and 1,5,9,13-tetrakis(tert-butyl)-3,7,11,15-tetrakis(cyclopentyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane(96)





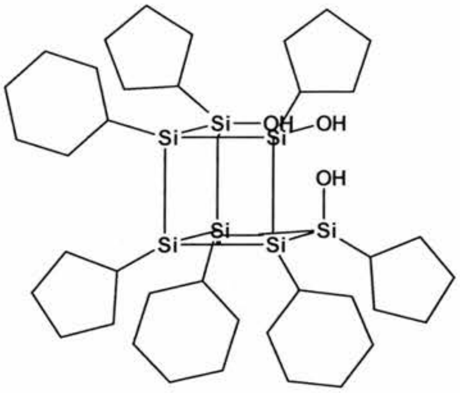
To a suspension of $^{t\text{-}}$BuSi(OH)$_3$ (0.41g, 3.01mmoles) in hexane (20ml) cyclohexyltrichlorosilane (0.8ml, 0.98g, 4.53mmoles) and triethylamine (0.22ml, 0.16g, 1.59mmoles) were added. The reaction mixture was left to stir at room temperature for 4 hours. The suspension was filtered to remove the hydrochloride salt. The filtrate was reduced on the rotary evaporator and placed in a desiccator overnight under vacuum. This reaction was repeated in dry THF, under a nitrogen atmosphere but the cyclohexyltrichlorosilane was added to quickly and the product was a red/brown polymer. The reaction was also tried using cyclopentyltrichlorosilane instead of cyclohexyltrichlorosilane but it again produced a polymeric mess. The reaction was also tried in dry THF/hexane and dry methanol /hexane systems but these did not work either [16]. The original experiment: ^{13}C {^{1}H} NMR (75MHz, C_6D_6, 25^{o}C): δ 28.54, 27.90, 26.98, 25.21, 17.92. ^{29}Si NMR (59.6MHz, 10-15% v/v C_6D_6/C_6H_6, 25^{o}C): no peaks. Reaction using cyclopentyltrichlorosilane instead of cycloyhexyltrichlorosilane: ^{13}C NMR (75MHz, C_6D_6, 25^{o}C): δ 27.31, 26.84, 25.90, 25.74, 25.28, 22.59 plus other smaller peaks.

1,5,9,13-tetrakis(tert-butyl)-3,7,11,15-tetrakis(vinyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (97)



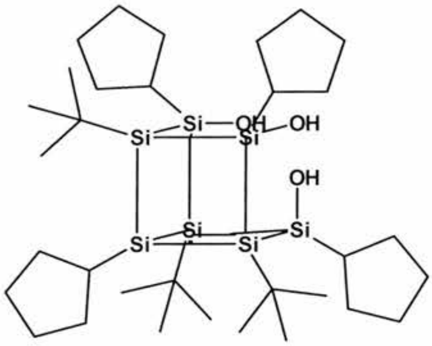
^{t}Butylsilanetriol (0.21g, 1.54mmoles), triethylamine (1.8ml, 1.3g, 13.0mmoles) in THF (100ml) had trichlorovinylsilane (0.13ml, 0.16g, 1.02mmoles) in THF (80ml) under argon, which was added drop-wise. The resulting mixture was allowed to stir overnight. The hydrochloride was filtered off and the volatile compounds were removed on the rotary evaporator. The product was extracted several times with petroleum ether (40 – 60) (the product was a yellowy gel substance) but accidentally flooded the filtrate with water so this was separated to see if anything could be salvaged if it had indeed worked at all. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 0.05 (m, 6H), 6.0 (m, 1H) plus some other smaller peaks. The vinyl peak was a small bump. ^{13}C {^{1}H} NMR (300MHz, $CDCl_3$, 25°C): δ 0.824. The multiplet at 5.9-6.1 was not sharp plus there were peaks in the region 0.9 – 1.7 that were not expected. This was repeated, but won't work since t-butylsilanetriol is very stable and would probably only work if activated by $SnMe_3$. Definitely an excess of vinyltrichlorosilane was used since the product began smoking during the filtering process to produce a polymer. Volatile compounds were removed on the rotary evaporator, the hydrochloride and polymer were kept. ^{1}H NMR spectra had plenty of peaks certainly a methyl peak but no obvious vinyl peaks (although there were a few peaks in the vinyl region).

T7 tetrakis(cyclopentyl)tris(cyclohexyl)trisilanol POSS (98)



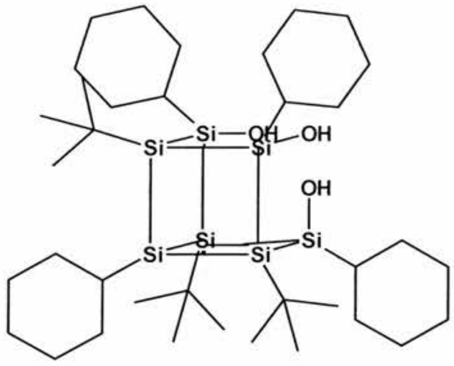
Cyclohexyltrichlorosilane (1.26g, 5.79mmoles), cyclopentyltrichlorosilane (1.55g, 7.61mmoles) and acetone (55ml) were placed in a flask under nitrogen. Distilled water (15ml, 824mmoles) was added slowly to the mixture. The resulting mixture was refluxed over the weekend. The reaction mixture was filtered and the solid collected was suspended in acetone (12.5ml) and stirred over 3 hours. The mixture was filtered and the solid collected was placed in an oven overnight. The crude product (0.03g) was suspended in pyridine (25ml). The mixture was filtered through a medium sintered glass funnel and the filtrate was poured into HCl (25ml) mixed with ice. The mixture was filtered through a medium sintered glass funnel and washed with copious amounts of water. There was very little product. This reaction was repeated with more material and instead of refluxing the mixture after the hydrolysis, it was placed in a stoppered conical flask and allowed to stand. After some time a considerable amount of solid had formed and this was filtered off and the filtrate was placed back into the flask. The sample had a powder diffraction pattern run on it, which had peaks and this suggests that the sample was crystalline. $^{13}C\ \{^{1}H\}$ NMR (75MHz, $CDCl_3$, 25^{o}C): δ 27.44, 27.22, 26.98, 26.50, 23.81, 23.43, 22.82, 22.39 plus other smaller peaks. ^{1}H NMR (300MHz, $CDCl_3$, 25^{o}C): δ 0.70 (s, 2H), 0.95 (s, 3H), 1.2 (s, 10H), 1.5 (m, 15H), 1.725 (s, 15H) [1]. CHN analysis yielded %C 49.72 : %H 7.72 the theoretical values were %C 51.51 : %H 7.86. The product was dissolved in THF along with partial cage cyclopentyl and cyclohexyl POSS and spotted on a tlc plate eluted with hexane/diethyl ether 95/5 and developed in iodine. There was only one spot from each of the solutions spotted at roughly the same height on the tlc plate.

T7 tetrakis(cyclopentyl)tris(tert-butyl)trisilanol POSS (99)



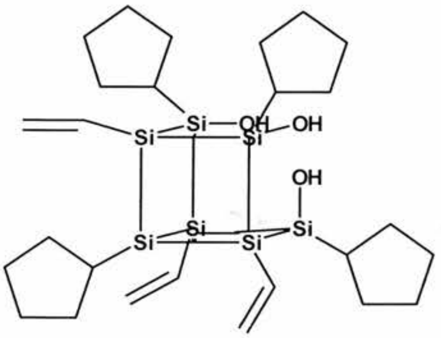
Cyclopentyltrichlorosilane (3.09g, 15.2mmoles), t-butyltrichlorosilane (2.20g, 11.5mmoles) and acetone (108ml) were placed in a round-bottomed flask. Distilled water (30ml, 1.65moles) was added drop-wise (under nitrogen) and the resulting solution was refluxed over the weekend. Very little solid, if any, had formed so the solution was transferred to a conical flask, stoppered and left to stand. After some time, a considerable amount of solid had formed and so this was filtered off and the filtrate was placed back into the flask to see if more product would form. The sample had a powder diffraction pattern run on it, which had peaks and this suggested that the sample was crystalline. $^{13}C\ \{^{1}H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 27.19, 26.94, 25.58, 22.80, 22.40, 22.13 plus other smaller peaks. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 0.05 (s, 2H), 0.95 (s, 1H), 1.6 (m, 3H) plus other smaller peaks [2]. CHN analysis yielded %C 46.38 : %H 8.09, the theoretical values were calculated as %C 46.91 : %H 7.87. A sample was dissolved in THF and a tlc was run, eluted in hexane/diethyl ether 95/5 and developed in iodine. One spot was present other than the baseline spot.

T_7 tetrakis(cyclohexyl)tris(tert-butyl)trisilanol POSS (100)



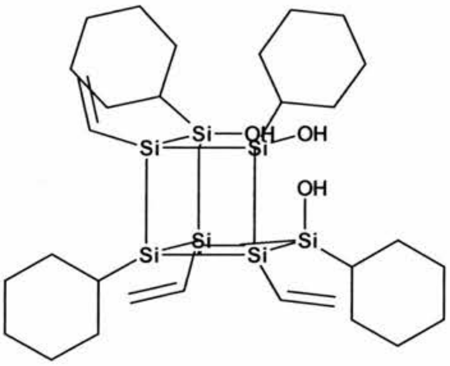
Cyclohexyltrichlorosilane (3.35g, 15.4mmoles) and $^{t-}$butyltrichlorosilane (2.20g, 11.5mmoles) were placed in a 250ml conical flask in acetone (110ml) with stirring. Distilled water (30ml, 1.65moles) was added drop-wise to the mixture and when the addition was complete the conical flask was stoppered and allowed to stand [2]. No solid was formed.

T_7 tetrakis(cyclopentyl)tris(vinyl)trisilanol POSS (101)



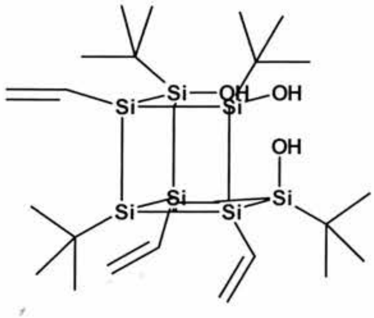
Vinyltrichlorosilane (0.62g, 3.84mmoles) and cyclopentyltrichlorosilane (1.27g, 6.24mmoles) in acetone (35ml) had distilled water (10ml, 549moles) added to it, with stirring. The resulting mixture was stoppered and left to stand. Some crystals appeared in the solution and were filtered off but they turned to mush during filtering. The filtrate was placed back into the flask to see if more product would crystallise out [2]. No more product crystallised. $^{13}C\ \{^{1}H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 136.29, 136.07, 135.97, 27.20, 26.90, 26.85, 26.79, 22.05 plus other smaller peaks.

T7 tetrakis(cyclohexyl)tris(vinyl)trisilanol POSS (102)



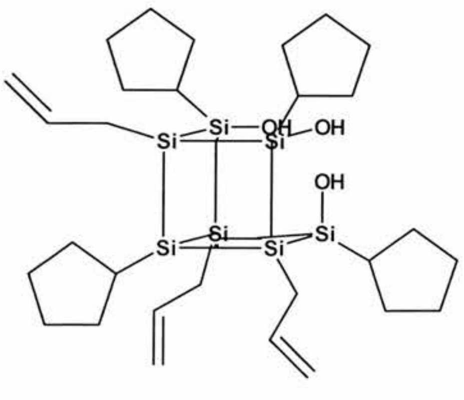
Vinyltrichlorosilane (0.63g, 3.90mmoles) and cyclohexyltrichlorosilane (1.19g, 5.47mmoles) in acetone (35ml) had distilled water (10ml, 549mmoles) added to it, with stirring. The resulting mixture was stoppered and left to stand [2]. No solid formed.

T7 tetrakis(tert-butyl)tris(vinyl)trisilanol POSS (103)



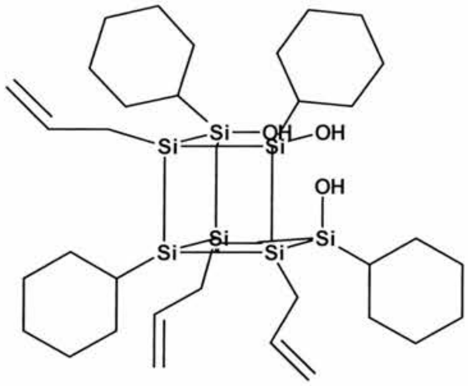
Vinyltrichlorosilane (0.67g, 4.15mmoles) and $^{t-}$butyltrichlorosilane (1.02g, 5.32mmoles) in acetone (35ml) had distilled water (10ml, 549mmoles) added to it, with stirring. The resulting mixture was stoppered and left to stand [2]. No solid formed.

T7 tetra(cyclopenty)tris(allyl)trisilanol POSS (104)



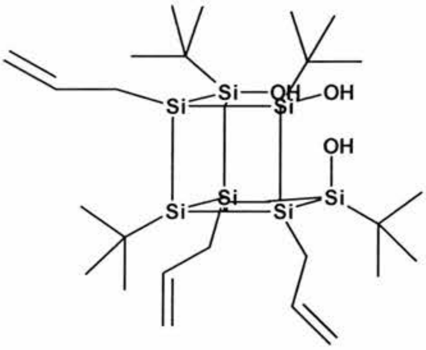
Allyltrichlorosilane (0.67g, 3.82mmoles) and cyclopentyltrichlorosilane (1.03g, 5.06mmoles) in acetone (35ml) had distilled water (10ml, 549mmoles) added to it, with stirring. The resulting mixture was stoppered and left to stand. Solid was filtered off and the filtrate was returned to the flask to see if any more solid would form [2]. No more solid formed.

T7 tetrakis(cyclohexyl)tris(allyl)trisilanol POSS (105)



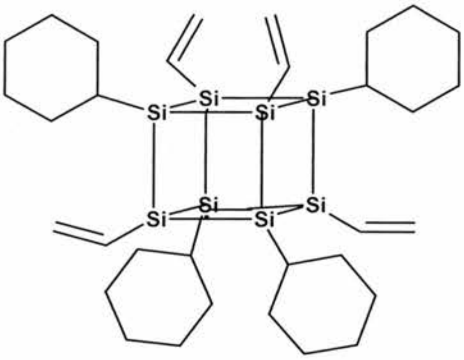
Allyltrichlorosilane (0.67g, 3.82mmoles) and cyclohexyltrichlorosilane (1.10g, 5.06mmoles) in acetone (35ml) had distilled water (10ml, 549mmoles) added to it, with stirring. The resulting mixture was stoppered and left to stand [2]. No solid formed.

T7 tetrakis(tert-butyl)tris(allyl)trisilanol POSS (106)



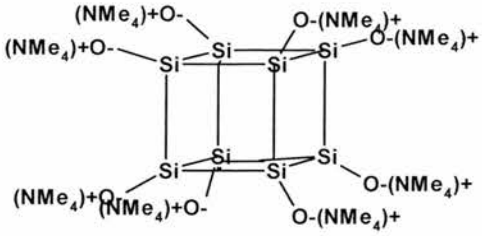
Allyltrichlorosilane (0.68g, 3.87mmoles) and ^{t}-butyltrichlorosilane (0.97g, 5.06mmoles) in acetone (35ml) had distilled water (10ml, 549mmoles) added to it, with stirring. The resulting mixture was stoppered and left to stand [2]. No solid formed.

1,5,9,13-Tetrakis(cyclohexyl)-3,7,11,15-tetrakis(vinyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (107)



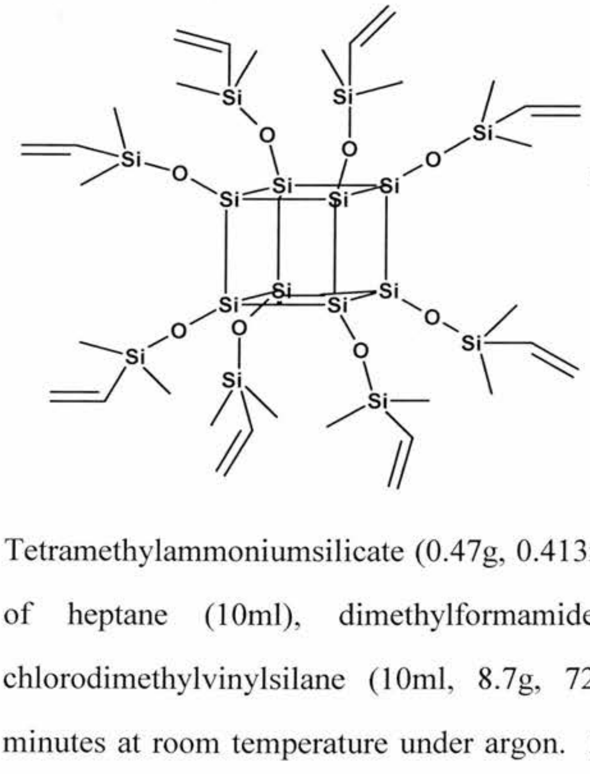
Cyclohexyltrihydroxysilane **(71)** (0.25g, 1.15mmoles), triethylamine (1ml, 0.7g, 7.21mmoles), THF (20ml) in ice had vinyltrichlorosilane (0.2ml, 0.25g, 1.57mmoles) in THF (20ml) added to it under argon. The resulting solution was stirred overnight. This was filtered twice, second time through a sintered glass funnel and celite. During filtering white smoke appeared indicating that the vinyltrichlorosilane hadn't entirely reacted. It was filtered a third time through celite and a sintered glass funnel before the volatile compounds were removed on the rotary evaporator. ^{1}H NMR revealed that only cyclohexyl groups were present. Due to the lack of success, two reactions were tried one using water, the other using acetic acid and water to condense the products. It was hoped that the acetic acid might show some selectivity. These reactions were carried out as follows: trimethoxyvinylsilane (1.5ml, 1.4g, 9.70mmoles) in ethanol (10ml) had trichlorocyclohexylsilane (1.7ml, 2.1g, 9.62mmoles) added to it drop-wise with stirring, under argon. Water (0.54g, 30mmoles) was added followed by more ethanol (15ml) and stirred over the weekend. The second reaction was the same except acetic acid (1.8ml) was added at the same time as the water. Both were allowed to stand to see if some product would form. No solid formed in either reaction.

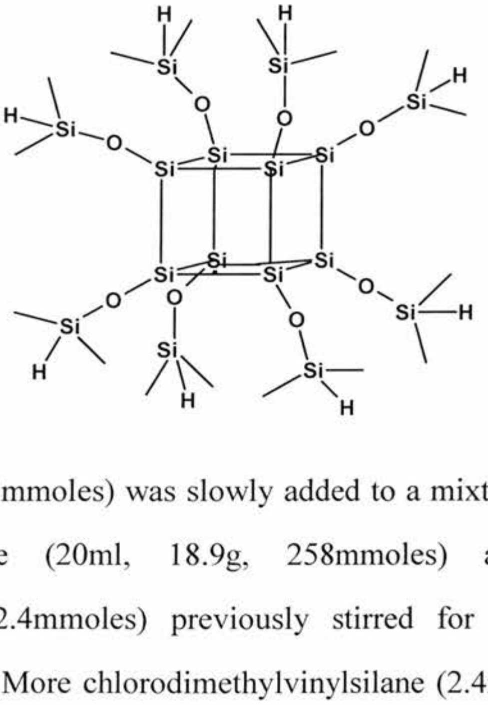
Tetramethylammonium silicate (108)



Tetramethylammonium hydroxide (10% aqueous solution, 87ml, 95.4mmoles) and silicic acid (5.7g, 10.3mmoles) were stirred at room temperature over the weekend. The reaction mixture was refluxed at 60°C for 10 hours. The mixture was filtered and the filtrate was reduced on the rotary evaporator. The solution was then placed on an ice bath and it solidified. To drive off any remaining solvent the solid was placed in an oven overnight (40-50°C), a white solid was obtained [17].

Octakis(vinyldimethylsiloxy)octasilicate (109) and octakis(dimethylsiloxyloctasilicate(110)

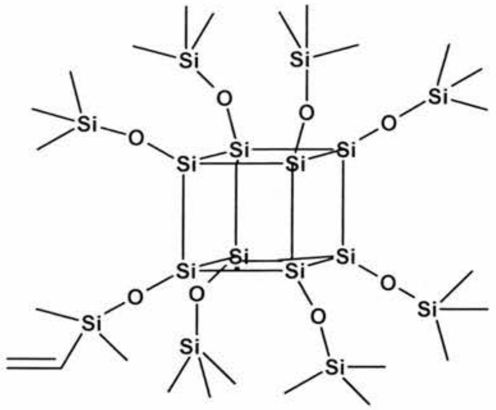




Tetramethylammoniumsilicate (0.47g, 0.413mmoles) was slowly added to a mixture of heptane (10ml), dimethylformamide (20ml, 18.9g, 258mmoles) and chlorodimethylvinylsilane (10ml, 8.7g, 72.4mmoles) previously stirred for 15 minutes at room temperature under argon. More chlorodimethylvinylsilane (2.4ml, 2.1g, 17.4mmoles) was added since the proportions were not correct initially. The reaction mixture was cooled to 0°C in an ice bath for 30 minutes after that it was hydrolysed with distilled water (1litre, added drop-wise). The mixture was removed from the ice bath and allowed to stir until it reached room temperature. The organic layer was separated from the mixture and washed with copious amounts of water before it was concentrated and placed in the freezer to complete crystallisation [12]. There was not a lot of product and not enough for analysis. The reaction was repeated with 5 times as much material and with the correct amount of water to hydrolyse the reaction and after some time had elapsed, produced crystals. ^{13}C {^{1}H} NMR (75MHz, $CDCl_3$, 25°C): δ 137.88, 132.38, -0.37. CHN analysis gave %C 30.06, %H 5.59 whereas the theoretical amounts were %C 31.34, %H 5.92. IR (KBr, cm^{-1}) 3045 (w), 3000 (vw), 2977 (m), 2886 (w), 1600 (m), 1400 (s), 1267 (s), 1178 (s, br), 1111 (vs, br), 1000 (s), 955 (m), 844 (vs), 800 (vs), 700 (m), 667 (m), 600 (m), 560 (s), 519 (s). Literature data ^{1}H NMR ($CDCl_3$): δ 0.208 (s, CH_3), 5.959 (m, CH), 1.63 (d, CH_2). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 0.219 (Si-CH_3), 132.7 (Si-CH), 138.2 (CH_2). ^{29}Si {^{1}H} NMR ($CDCl_3$): δ 0.531 (Si-CH_3), -109.1 (Si core). IR (KBr, cm-1): 2963, 1597, 1254, 1008, 559. CHN analysis gave %C 30.5 : %H 5.76 whereas the theoretical values were calculated at %C 31.3 : %H 5.87 [12]. A slightly different method was found whereby tetraethoxysilicate (22.5ml, 21.0g, 101mmoles) was added to a solution of tetramethylammoniumhydroxide (18.1g, 198mmoles), methanol (40ml) and water (9ml, 494mmoles). Additional methanol (27.5ml) was added to increase the volume of the solution and the resulting solution was stirred for 24 hours to form the cubic anion. Total volume of the solution was to be 100ml. This was added to a previously stirred solution of chlorodimethylvinylsilane (21ml, 18.4g, 152mmoles) in THF (150ml). The resulting solution was left to stir overnight. Water and hexane are added to the solution to allow easy separation of the organic layer that was then dried over magnesium sulfate. This was filtered and the volatile compounds were removed on the rotary evaporator. This oil was re-crystallised from acetone/ethanol and allowed to stand in air. Crystals were formed (0.61g, 0.497mmoles, 0.49%). Using less materials gave a better yield, i.e. using tetraethoxysilane (4.5ml, 4.2g, 20.2mmoles) yielded product (1.52g, 1.24mmoles, 6.1%). The yield is improved if the total volume of the cubic anion been added to the chlorodimethylvinylsilane is 100ml using silicate solution (20ml, 18.7g, 89.6mmoles), chlorodimethylvinylsilane (20ml, 17.5g, 145mmoles) and THF (60ml). ^{1}H NMR (300MHz, $CDCl_3$, 25^{o}C): δ 0.2 (s, 2H), 6.0 (s, 1H). CHN analysis yielded %C 30.33 : %H 6.06 and %C 30.43 : %H 6.22 compared to the theoretical values of %C 31.34 : %H 5.92.

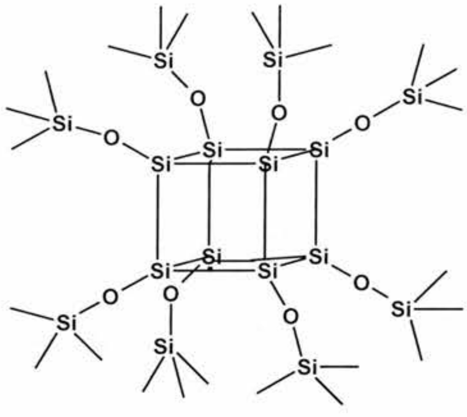
Tetraethoxysilane (22.5ml, 21g, 101mmoles) was added to a solution of tetramethylammonium hydroxide (18.1g, 198mmoles), methanol (41ml) and water (9ml, 494mmoles). Additional methanol (27.5ml) was added to increase the volume of the solution to 100ml, the resulting solution was stirred overnight. This solution was added to a previously stirred solution of chlorodimethylsilane (21ml, 17.9g, 189mmoles) in THF (150ml). The resulting solution was allowed to stir overnight. Water and hexane were added to aid separation of the organic layer, which is then dried over magnesium sulfate. This is filtered and the volatile compounds were removed on the rotary evaporator. The mixture was crystallised in acetone/ethanol. ^{1}H NMR (300MHz, $CDCl_3$, 25^{o}C): δ 0.25 (m, 9H), 4.75 (m, 1H) plus some other peaks. This was repeated using different amounts i.e. tetraethoxysilane (4.5ml, 4.2g, 20.2mmoles), water (1.8ml, 98.9mmoles), tetramethylammoniumhydroxide (3.66g, 40.2mmoles) and the rest of the volume is made up to 20ml with THF. This mixture is added to chlorodimethylsilane (20ml, 17.0g, 180mmoles) in THF (60ml). The final product from this reaction was a gel so concentration in these reactions is crucial otherwise a gel is produced. CHN analysis yielded %C 19.47 : %H 5.50 compared to the theoretical values %C 18.88 : %H 5.54.

Vinyldimethylheptakis(trimethylsiloxy)octasilicate (111)



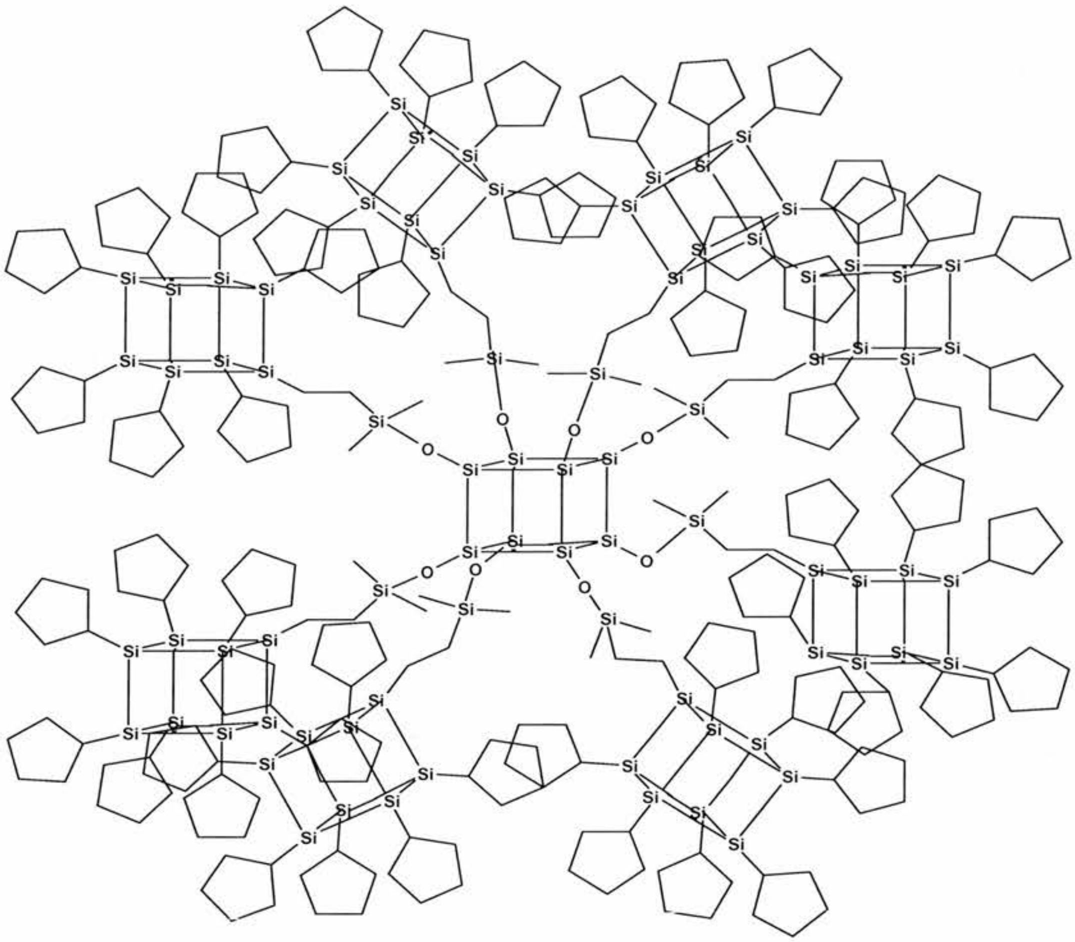
Tetramethylammoniumsilicate (2.38g, 2.09mmoles) was added to a previously stirred solution of dimethylformamide (100ml, 94.4g, 1.29moles), hexane (50ml), chlorodimethylvinylsilane (8ml, 7.0g, 58.0mmoles) and trimethylchlorosilane (48ml, 41.1g, 378mmoles). This mixture was allowed to stir for an hour. The mixture was cooled in an ice bath at 0°C for 50 minutes, after which it was hydrolysed with distilled water (500ml, 27.46moles) added drop-wise to complete the formation of the siloxane. The mixture was removed from the ice bath and filtered to remove any non-reacted tetramethylammoniumsilicate. The organic layer was separated from the mixture and washed with copious amounts of water. The organic layer was concentrated and placed in the freezer to complete crystallisation [12]. The crystals were filtered off and analysed by ^{13}C NMR. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ -0.32, 0.30, 1.15, 1.85, 131.36, 132.31, 137.88, 139.58 plus other smaller peaks. From the NMR it appears that there are 2 species present so the sample was dissolved in acetone and placed in the fridge to re-crystallise. The repeat reaction gave cleaner spectra. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ -0.33, 1.14, 132.31, 137.87. CHN analysis gave %C 27.00: %H 6.32 whereas the theoretical composition was calculated as %C 26.28: %H 6.35. IR (KBr, cm^{-1}) 2954 (m), 2932 (w), 1400 (w), 1255 (s), 1167 (s), 1100 (vs, br), 1000 (m), 967 (w), 866 (vs), 833 (vs), 778 (m), 744 (s), 689 (w), 644 (w), 588 (m), 554 (s), 530 (s), 461 (vw).

Octakis(triimethylsiloxy)octasilicate (112)



Tetramethylammoniumsilicate (2.39g, 2.10mmoles) was added to a previously stirred solution of trimethylchlorosilane (55ml, 47.1g, 433mmoles), hexane (65ml) and dimethylformamide (100ml, 94.4g, 1.29moles). The resulting solution was allowed to stir for 1 hour and was then cooled in an ice bath for 30 minutes, after which it was hydrolysed with distilled water (500ml, 27.46moles) added drop-wise to complete the formation of the siloxane. The mixture was removed from the ice bath and allowed to stir until room temperature was attained. The mixture was filtered and the organic layer was separated and washed with copious amounts of water. The organic layer was concentrated and placed in a freezer to complete crystallisation of the product. After some time, crystals were filtered off from the solution and the filtrate was placed back into the flask in case more product would crystallise out [12]. $^{13}C\ \{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 1.14. CHN analysis gave %C 25.63, %H 6.30 whereas the theoretical was %C 25.50, %H 6.42. IR (KBr, cm^{-1}) 2977 (w), 1255 (m), 1167 (br, m), 1100 (br, s), 889 (s), 844 (s), 755 (s), 722 (m), 678 (m), 611 (m), 565 (s), 542 (s), 461 (w).

Octakis{1,3,5,7,9,11,13,15-(2-[heptakis(cyclohexyl) dimethyl]ethyl)pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane}octasilicate (113)



ChlorodimethylethylheptacyclopentylPOSSsilane, DMF (40ml, 37.8g, 516mmoles) and hexane (60ml) were stirred together in an attempt to dissolve chlorodimethylethylheptacyclopentylPOSSsilane. Tetramethylammonium silicate (0.01g, 0.00879mmoles) was added and the mixture was left stirring. ChlorodimethylethylheptacyclopentylPOSSsilane wasn't very soluble in the hexane/DMF mixture and the mixture was left stirring over two nights. Water (1.2ml, 65.9mmoles) was added with the mixture in an ice bath at 0^{o}C, to complete the formation of the siloxane. The organic layer was separated from the mixture and washed with copious amounts of water. It was placed in the freezer to complete crystallisation of the product [12]. The solid that had formed was filtered off from the solution. The hydrogen NMR showed peaks from the vinyl boxes that hadn't reacted with the chlorodimethylsilane but the carbon NMR only showed peaks relating to the cyclopentyl groups on the boxes. ^{13}C NMR (75.4 MHz, $CDCl_3$, 25°C): δ 27.12, 26.83, 22.06. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ 6.0 (m, 1H), 1.8 (s, 14.5H), 1.55 (m, 47H), 1.0 (m, 8.5H), 0.6 (m, 3H), 0.1 (s, 2.5H). Since there were peaks in the vinyl region of the 1H NMR spectra this indicated that the starting material was not pure. There were some extra peaks around the main methyl peak that could be due to non-reacted chorodimethylethylheptacyclopentyl POSS molecules. This was repeated with a similar result to the previous reaction.

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Chapter 5
Titanasiloxane synthesis and other reactions

5.1 Aims and objectives

The aims of this chapter were to make cubic titanasiloxanes. Several ways of making these molecules were tried i.e. by corner capping T_7 incompletely condensed POSS molecules (see Chapter 4) with cyclopentadienyltitaniumtrichloride, and also using hetero- and homofunctional condensation reactions with titanium and silicon species.

Any cubic titanium species made would have been interesting as a mimic of titanium attached to silica surface or as possible catalysts in epoxidation reactions. Also mentioned are attempts to perform catalytic epoxidation reactions with some of the titanium species made and the attempted syntheses of tris(trimethylstannyl)amine and Karstedt's catalyst. Tris(trimethylstannyl)amine is used in reactions for making cubic titanasiloxanes from tert-butyltris(hydroxy)silane and cyclopentadienyltitaniumtrichloride.

5.2 Results and discussion

5.2.1 Titanasiloxane synthesis

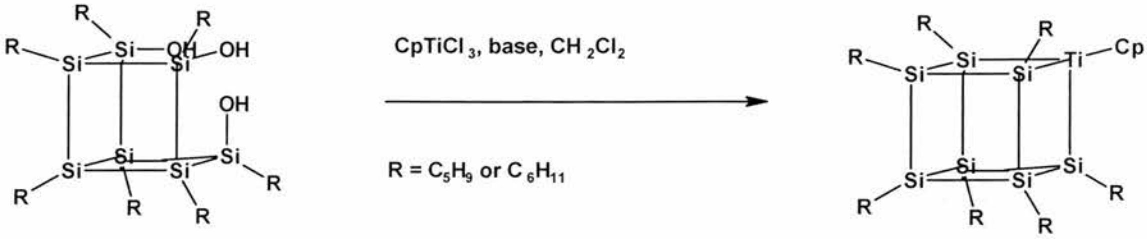
Three different methods were tried to make titanasiloxanes: corner capping of an incompletely condensed POSS molecule with cyclopentadienyltitaniumtrichlororide, hetero- as well as homofunctional condensation of silanes with titanium species.

5.2.1.1 Corner capping of incompletely condensed POSS molecules with cyclopentadienyltitaniumtrichloride

The reaction to form the corner capped product goes as follows: $CpTiCl_3$ in CH_2Cl_2 is added to a stirred CH_2Cl_2 solution of T_7 organotrisilanol which had been previously activated with excess Et_3N. The resultant colourless solution was stirred overnight, under argon. Volatile compounds were removed on the rotary evaporator, the solution was pale orange. It was extracted with petroleum ether (40 - 60) twice and the volatile compounds were again removed.

Corner capping T_7 cyclopentyl POSS molecule with cyclopentadienyltitaniumtrichloride **(114)** was successful according to the NMR results when compared to previous results (see Figure 5.1 and Scheme 5.1) [1]. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 6.45 (s, 1H), 0.85 (m, 7H), 1.55 (m, 70H). ^{13}C $\{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 115.75, 27.50, 27.43, 27.30, 26.92, 22.37, 22.27, 22.18. The main anomaly is the ratios of the protons. For the original reaction CHN analysis has proven interesting. For the CpTi - T_7 cyclopentyl POSS molecule, CHN gave %C 47.34 : %H 8.47 : %N 5.10. Recalculating the results, assuming that all the nitrogen comes from triethylamine gave %C 35.57 : %H 4.7. The reason the results do not fit with the theoretical data is due to the product being extracted with water and petrol ether. The repeat reaction gave %C 47.2 : %H 6.94 : %N 0.68. Calculated without triethylamine yielded %C 45.96 : %H 6.53. If we assume that the reaction yields a monomer then the CHN for that species is %C 48.7 : %H 6.96.

According to the source material [1], the product is a mixture of monomer and dimer species $[CpTi(cy_7Si_7O_{12})]$ and $[CpTi(cy_7Si_7O_{12})]_2$. The monomer can be extracted from the mixture by fractional crystallisation from chloroform. The dimer cannot be separated from the mixture in this manner.



Scheme 5.1 Corner capping reaction

The Si-Si bonds and the Si-Ti bonds, in this diagram, are actually Si-O-Si and Si-O-Ti bonds respectfully, the oxygens have been left out for clarity.

The CpTi - T7 cyclohexyl POSS molecule **(115)** yielded the following NMR results: ^{1}H NMR (300MHz, $CDCl_3$, 25^{o}C): δ 6.25 (s, 2H), 1.7 (s, 50H), 1.25 (m, 49H), 0.75 (m, 15H). ^{13}C {^{1}H} NMR (75MHz, $CDCl_3$, 25^{o}C): δ 115.89, 27.57, 27.48, 27.34, 27.19, 27.04, 26.92, 26.82, 26.73, 26.61, 26.38, 26.18, 26.04, 23.37, 23.15, 23.05, 22.90. The CHN analysis for the CpTi - T_7 cyclohexyl POSS gave %C 49.89 : %H 7.79 : %N 0.22. Again assuming that all nitrogen comes from triethylamine, the recalculated results give %C 49.55 : %H 7.67. Theoretical calculation for the monomer gives %C 52.09 : %H 7.63. A variety of dimeric species and the monomer structures have been reported in the literature as formed from reactions between titanium species and POSS molecules [2]. Pure monomer species tend to be formed when using POSS protected by -OSbMe$_4$ or –OTl [3].

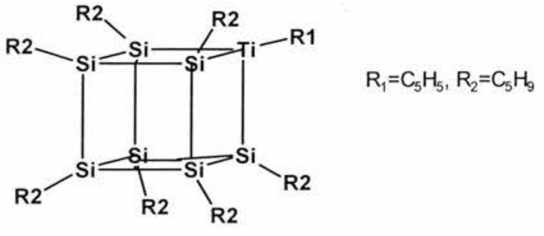
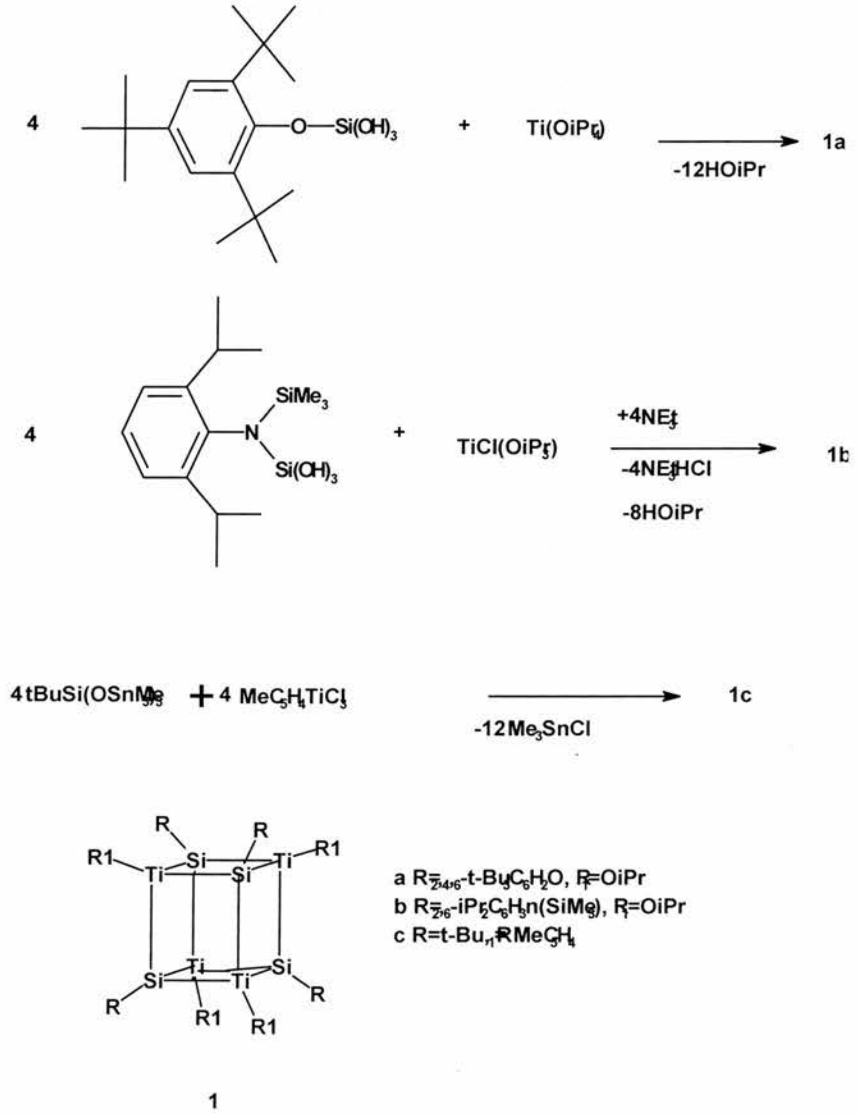


Figure 5.1 A POSS molecule that has been corner capped by $CpTiCl_3$

5.2.1.2 Heterofunctional condensation

Heterofunctional condensation uses two species with different functional groups i.e. $RSiX_3$ and $R'TiY_3$ to make a product that has alternating groups i.e. Si can hopefully only form an oxide linkage to Ti and vice versa.

There exists a few examples in the literature of mixed titanosiloxane species [4] (see Scheme 5.2).



Scheme 5.2 Titanosilsesquioxanes reported in the literature

5.2.1.2.1-5.2.1.2.2 Attempted synthesis of fully condensed titanosilsesquioxanes

The original reaction used in the attempt to make a fully condensed titanosilsesquioxane was as follows: to a suspension of $^{t-}$BuSi(OH)$_3$ in hexane, titanium (IV) isopropoxide was added. The reaction mixture was stirred for a period of 4 hours at room temperature, volatile compounds were removed on the rotary evaporator. There was a problem with solid sticking to the sides of the flask.

The reaction to form a titanasiloxane, using $^{t-}$BuSi(OH)$_3$ and titanium isoproxide **(116)**, has faced similar difficulties as the formation of the silsesquioxane using RSiCl$_3$ and $^{t-}$BuSi(OH)$_3$ (see Figure 5.2 and Chapter 4). These reactions have been repeated using dry solvents and carrying out the reaction under nitrogen. The titanium reaction appears to have produced a titanium polymer when tried in dry solvents, under nitrogen since the ^{29}Si NMR spectra contained no peaks. Higher dilution, slower addition of the titanium orthoester, with the reaction vessel in ice, might stop this from occurring again or it could be that the titanium orthoester was not pure enough (i.e. should have distilled the titanium orthoester before use). The titaniumsilsesquioxane recipe used for making the titanosiloxane was to make a titaniumsiloxane which had a large R group on the silicons, which would help form the cubic structure [5]. Also a reaction involving t-BuSi(OH)$_3$ in the literature had a protective/activating group i.e. SnMe$_3$ on it to make it more reactive.

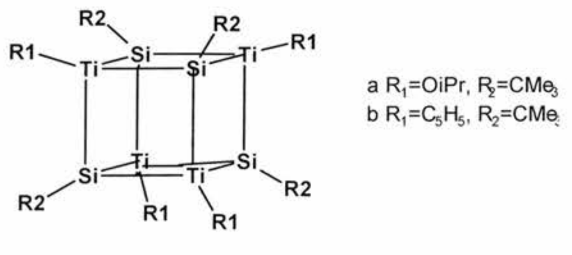


Figure 5.2 A fully condensed titanasiloxane

It appears that the titaniumsiloxane will not be formed using $^{t-}$BuSi(OH)3 and titanium isopropoxide. So a reaction using cyclopentadienyltitaniumtrichloride with $^{t-}$BuSi(OH)3 **(117)** was tried instead, using the titanium corner capping reaction conditions (see Figure 5.2b). ^{1}H NMR (300MHz, CDCl3, 25^{o}C): δ 0.95 (s, 2H), 6.3 (s, 1H). ^{13}C {^{1}H} NMR (75MHz, CDCl3, 25^{o}C): δ 7.95, 115.00 there are some extra peaks present. The ratio of 2H:1H ($^{t-}$Bu:Cp) is similar to the ratio which would be expected for this compound i.e. 9H:5H. The CHN analysis gave %C 42.79 : %H 8.58 : %N 5.28, calculated without triethylamine gave %C 25.25 : %H 4.66. The pale yellow needles gave CHN results %C 48.57 : %H 10.86 : %N 8.40, calculated without triethylamine gave %C 13.48 : %H 4.56. After the product had been extracted with hexane the CHN gave %C 46.98 : %H 7.66 : %N 1.43, calculated without triethylamine gave %C 44.19 : %H 6.82. The theoretical calculation for a 1:1 reaction to produce the Ti - POSS molecule gave %C 43.9 : %H 5.73. A similar molecule was made by Roesky et al using tris-OSnMe$_3$ as a protecting and activating group on $^{t-}$BuSi(OH)$_3$ (since ClSnMe$_3$ is a good leaving group) [5].

5.2.1.3 Homofunctional condensations

Homofunctional condensation involves condensing species which have the same functional groups attached to them i.e. RSiX$_3$ with R'TiX$_3$. This will probably not give an alternating species with Si only attached to Ti through oxide linkages but it was attempted anyway. Table 5.1 shows the mixtures tried.

	$C_5H_9SiCl_3$	$C_6H_{11}SiCl_3$	Me_3CSiCl_3	$C_3H_5SiCl_3$	$C_2H_3SiCl_3$
$CpTiCl_3$	**(118)**	**(119)**	**(120)**	**(121)**	**(122)**

Table 5.1 Mixed homofunctional condensations tried.

The powder diffraction pattern of species **(118)** (batch 2) appeared to have two peaks in it (which were sharp unlike the very broad peaks which appeared in the patterns for **(119)-(121)**). From the powder diffraction patterns of **(119)-(122)** it looks like these species were amorphous (having no discernible structure) and were not characterised any further. Although the results for species **(122)** were inconclusive, the fact that these species were made in the same fashion led me to believe that species **(122)** would also be amorphous.

There were several differences in the way that species **(118)** was synthesised and the way that species **(119)-(122)** were synthesised. Species **(118)** was refluxed and was purified using the synthetic methods used in the production of T_7 hepta(cyclopentyl)silanetriol. Whereas the synthesis used to produce species **(119)-(122)** involved placing the reactants in the same flask and letting them stand. A yellow solid appeared during the addition of the water to the mixtures used in species **(119)-(122)**. The final products from these reactions were not worked-up in the same fashion as for species **(118)** instead they were filtered off and analysed. These differences may determine why the powder diffraction pattern showed sharp peaks in the powder pattern for species **(118)** but only broad (and hence therefore an amorphous species) for species **(119)-(121)**. Although it is probable that species **(118)** is not completely crystalline.

5.2.2 Catalysis with titanium species

Four of the titanium species made where tested to see if they could catalyse the epoxidation of some alkenes. Due to the reaction conditions not being stringent enough (i.e. the temperature of the reaction was not necessarily at 50°C, the reactants were not always stored under argon as the reaction was being set up) and the titanium species not having been purified enough, no catalytic function was seen. It has been reported that one of the titanium species tested i.e. CpTi heptacyclohexyl POSS molecule **(115)** does exhibit catalytic properties in the reactions that were tried [6]. It could be that due to the aforementioned problems or the incompleteness of the characterisations that the compounds (used in the catalytic reactions) did not have the structure that was believed that they had and hence they were not catalytic.

5.2.3 Miscellaneous reactions

The synthesis of $(Me_3Sn)_3N$ **(123)** did not work probably due to not being stringent enough with the way that the experiment was carried out. This experiment was repeated with no success, the Li_3N is not reacting and the only way that has been thought of to fix this, would be to reflux the solution for longer [7]. Since the reaction had been unsuccessful a few times, it was abandoned.

The preparation of the Karstedt's catalyst **(124)** appears to have failed, since it did not catalyse the hydrosilation of vinylheptacyclopentyl POSS molecules with a SiH functionalised dendrimer. Since the Karstedt's catalyst has been purchased, it is unlikely to be repeated [8].

5.3 Conclusions

Reactions to form cubic titanasiloxanes (with one titanium atom in the structure **(114)** and **(115)**) are made using the corner capping reaction. Monomers and dimers are known to be formed in the corner capping reaction with cyclopentadienyltitaniumtrichloride and T_7 cyclohexylsilanetriol POSS **(115)** [1] and the monomer can be isolated through fractional crystallisation from chloroform.

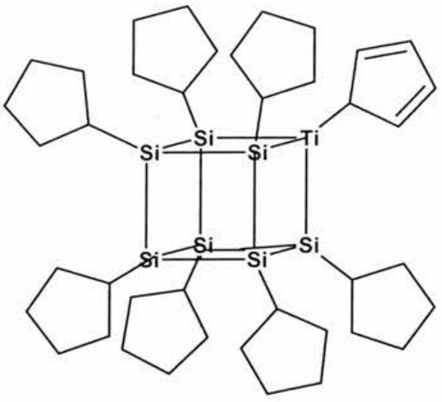
Reactions to form cubic titanasiloxanes (with more than 1 titanium atom in them **(116)**-**(122)**) would be best carried out using a heterofunctional (rather than a homofunctional) condensation reaction. Heterofunctional condensation of titanium and silicon species have given compounds with alternating Ti and Si atoms in the cage structure (separated by oxygen atoms) [4]. Heterofunctional condensation reactions should give greater control over the arrangement of atoms in the cubic structure (i.e. the titanium and silicon atoms should alternate in the structure (separated by oxygen atoms) than homofunctional condensation reactions. Therefore, any further study into the synthesis of cubic titanasiloxanes should look at heterofunctional condensation.

The catalytic epoxidation reactions and the other reactions, mentioned in this chapter, would probably work if more time had been devoted to them. The reaction to form Karstedt's catalyst **(124)** was abandoned because the Karstedt's catalyst that was purchased had arrived. Tris(trimethylstannyl)amine **(123)** would have been a useful compound to make since it could have been used to activate tert-butyl(trihydroxy)silane in some of the reactions using this compound to make other mixed cubic POSS molecules or in the production of cubic titanasiloxanes. The catalytic epoxidation reactions would be useful in gauging whether or not the titanium species formed would be useful as a catalyst.

5.4 Experimental

^{1}H (300MHz), ^{13}C (75MHz) and ^{29}Si (59.6MHz) NMR spectra were recorded on a Brucker AM 300. Some of the ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300. The ^{1}H and ^{13}C NMR solutions were placed in 5mm glass tubes whereas the ^{29}Si NMR solutions were placed in 10mm tubes. The spectra were recorded at room temperature in one of the following: d^{6} benzene, d^{4} methanol or $CDCl_3$ (Apollo Scientific/Aldrich) the ^{29}Si NMR samples were either in C_6D_6/C_6H_6 or $CDCl_3/CHCl_3$ solutions. The infra red spectra were recorded on a Perkin Elmer 1710. Liquid samples were placed between sodium chloride plates. Solid samples were made into potassium bromide (Aldrich) plates. Powder diffraction was carried out on a STOE Stadi/P uses copper radiation that has a wavelength of 1.54056 Å and has a motion sensitive detector. Single crystal diffraction was carried out on a Rigaku AFC7S diffractometer with graphite monochromated Mo-Kα radiation. All CHN measurements were made on a Carlo-Erba Modell 1106.

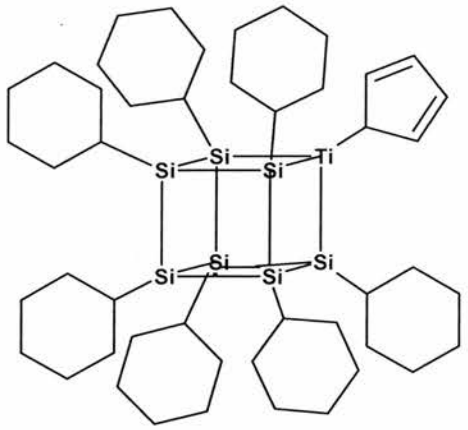
T_8 Cyclopentadienylhepta(cyclopentyl)titanasiloxane (114)



Cyclopentadienyltitaniumtrichloride (0.36g, 1.64mmoles) in dry dichloromethane (55ml) was added to a stirred dry dichloromethane (70ml) suspension of T7 silanetriol (1.4g, 1.55mmoles) that had been previously activated with excess triethylamine (3ml, 2.2g, 21.6mmoles). Dry pyridine (50ml) was added as a co-solvent to dissolve the T7 silanetriol. The reaction mixture was still orange so it was heated. The colour change was from orange to red to brown. Some of the volatile compounds were removed on the rotary evaporator and the rest were left to evaporate in air. The crystals were filtered off and analysed by NMR. The NMR results agreed with the values quoted in the thesis that the reaction was taken from [1]. ^{1}H NMR (300MHz, $CDCl_3$, 25°C): δ 6.45 (s, 1H), 0.85 (m, 7H), 1.55 (m, 70H). ^{13}C {^{1}H} NMR (75MHz, $CDCl_3$, 25°C): δ 115.75, 27.50, 27.43, 27.30, 26.92, 22.37, 22.27, 22.18. The sample was extracted twice with petroleum 40-60 (125ml, 75ml) which was meant to remove Et_3NHCl but also removed most of the pyridine present in the original spectra. CHN analysis gave %C 47.34 : %H 8.47 : %N 5.10, assuming that all the nitrogen comes from NEt_3 gave %C 33.42 : %H 4.7. The sample was dissolved in chloroform and put in the fridge to re-crystallise. The repeat reaction was extracted twice with hexane, filtered and the volatile compounds were removed on the rotary evaporator. The product was dissolved in hexane and the volatile compounds were allowed to evaporate off in air to allow crystals to form, when this did not work the sample was dissolved in hexane and placed in the freezer to re-crystallise. The CHN analysis of the repeat reaction gave %C 47.2 : %H 6.94 :

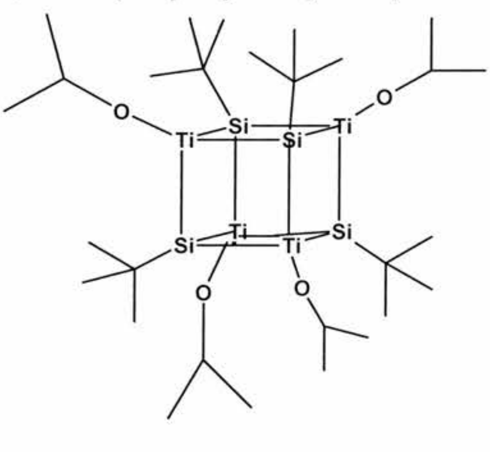
%N 0.68, calculated without NEt_3 and assuming that all the nitrogen comes from NEt_3 gives %C 45.96 : %H 6.53. A sample was dissolved in hexane and a tlc was run in hexane to see how pure the product was. The tlc plate had only one spot at the baseline.

T_8 Cyclopentadienylhepta(cyclohexyl)titanasiloxane (115)



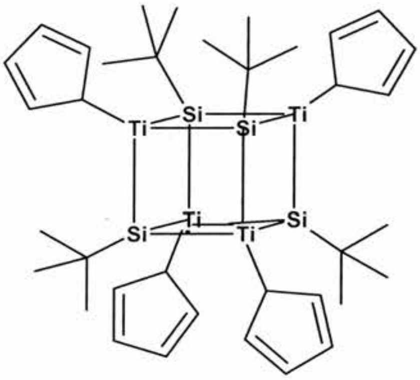
$CpTiCl_3$ (0.0144g, 0.0656mmoles) in CH_2Cl_2 (20ml) was added to a stirred CH_2Cl_2 (20ml) solution of T_7 cyclohexyltrisilanol (0.0556g, 0.0555mmoles) that had been previously activated with excess Et_3N (0.15ml, 0.11g, 1.082mmoles). The resultant colourless solution was stirred overnight, under argon. Volatile compounds were removed on the rotary evaporator, the solution was pale orange. It was extracted with petroleum ether (40 - 60) twice (5ml, 6ml) and the volatile compounds were again removed. The product was a yellow/orange powder. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 6.25 (s, 2H), 1.7 (s, 50H), 1.25 (m, 49H), 0.75 (m, 15H). $^{13}C\{^1H\}$ NMR (75MHz, $CDCl_3$, 25°C): δ 115.89, 27.57, 27.48, 27.34, 27.19, 27.04, 26.92, 26.82, 26.73, 26.61, 26.38, 26.18, 26.04, 23.37, 23.15, 23.05, 22.90. CHN analysis gave %C 49.89 : %H 7.79 : %N 0.22 assuming that all nitrogen comes from Et_3N, the results recalculated without Et_3N gave %C 49.55 : %H 7.67. A sample was dissolved in hexane and the volatile compounds were allowed to evaporate in air, so hopefully crystals would form. The sample was later again dissolved in hexane and placed in the freezer to re-crystallise. No product crystallised from the re-crystallisation. A sample was dissolved in hexane and a tlc was run in hexane to see how pure the reaction had been. The tlc plate had two spots one at the baseline and a weaker one further up the plate. The repeat reaction had fewer peaks associated with the POSS molecule in the NMR spectra. ^{13}C {^1H} NMR (75MHz, $CDCl_3$, 25°C): δ 27.57, 27.48, 27.20, 27.05, 26.92, 26.85, 26.73, 26.57, 23.37, 23.15 plus a few extra peaks. Literature data ^1H NMR (200.13MHz, $CDCl_3$, 25°C): δ 6.47 (s, 5H), 1.721 (br m, 35H), 1.236 (br m, 35H), 0.717 (br m, 7H). ^{13}C {^1H} NMR (50.03MHz, $CDCl_3$, 25°C): δ 116.00 (η^5-C_5H_5), 27.52, 27.49, 27.31, 26.87, 26.79 (all CH_2), 23.72, 23.39, 23.35 (3:3:1 all CH) by DEPT. CHN analysis gave %C 52.0 : %H 7.6 %Ti 4.2 whereas the calculated values were %C 52.1 : %H 7.6 : %Ti 4.4. Dimeric species analysed as a $[(\eta^5\text{-}C_5H_5)Ti(cy_7Si_7O_{12})]/[(\eta^5\text{-}C_5H_5)Ti(cy_7Si_7O_{12})]_2$ mixture: ^1H NMR (200.13MHz, $CDCl_3$, 25°C): δ 6.47 (s, 2H), 6.38 (m, 3H), 1.721 (br s, 35H), 1.236 (m, 35H), 0.717 (br m, 7H). ^{13}C {^1H} NMR (50.03MHz, $CDCl_3$, 25°C): δ 118.14, 116.00 (both η^5-C_5H_5), 27.66 (s), 27.56 (m), 27.52 (s), 27.505 (s), 27.14 (s), 27.02 (m), 26.93 (m), 26.83 (s), 26.67 (s), 26.55 (s) (all CH_2), 23.90, 23.57, 23.56 (3:3:1, CH), 23.47, 23.26, 23.25, 23.23, 23.13 (2:2:1:1:1 CH) by DEPT. CHN analysis yielded %C 52.0 : %H 7.6 : %Ti 4.1 whereas the calculated values were %C 52.1 : %H 7.6 : %Ti 4.4 [1].

T_8 Tetra(isopropxide)tetra(tert-butyl)titanasiloxane (116)



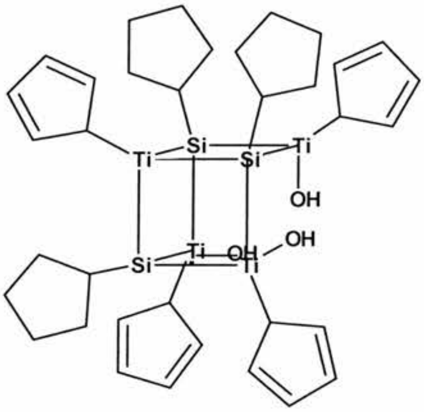
To a suspension of $^{t\text{-}}BuSi(OH)_3$ (0.41g, 3.01mmoles) in hexane (23ml) titanium (IV) isopropoxide (0.82ml, 0.78g, 2.76mmoles) was added. The reaction mixture was stirred for a period of 4 hours at room temperature. Extra solvent was added to try and stop the solid from sticking to the sides of the reaction vessel. The solvent was removed on the rotary evaporator and the resulting cream coloured solid was dried in a desiccator under vacuum overnight [5]. This reaction has been repeated in dry THF under a nitrogen atmosphere. The product from the original experiment had a powder diffraction pattern ran on it which showed no peaks which suggests that it was not crystalline. IR spectra of the product and $^{t-}BuSi(OH)_3$ showed no significant differences. IR (KBr, cm^{-1}) 3420 (brm), 2977 (s), 2954 (s), 2909 (s), 2864 (s), 1474 (s), 1457 (m), 1428 (m), 1383 (m), 1366 (m), 1348 (m), 1217 (m), 1177 (m), 1131 (brs), 1051 (brs), 863 (vbrvs), 743 (brs), 651 (brs), 519 (brm). The experiment run in dry solvents under nitrogen gave ^{29}Si NMR (59.6MHz, 50% v/v $CDCl_3/CHCl_3$, 25^{o}C): no peaks.

T_8 Tetra(cyclopentadienyl)tetra(tert-butyl)titanasiloxane (117)



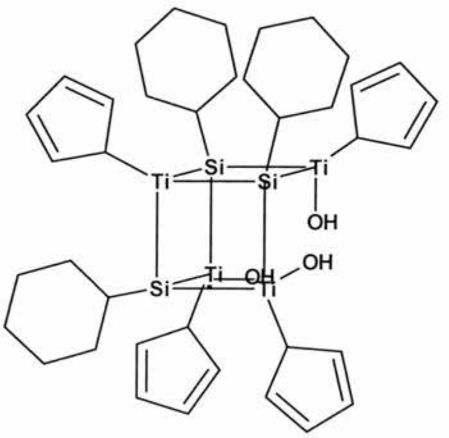
$^{t-}BuSi(OH)_3$ (0.21g, 1.54mmoles) and Et_3N (3ml, 2.2g, 21.6mmoles) in dry dichloromethane (50ml) had $CpTiCl_3$ (0.36g, 1.64mmoles) in dry dichloromethane (70ml) added to it under an argon atmosphere. The resulting solution was stirred overnight. The solution changed from red to orange-brown. To see if the reaction was complete, the solution was heated for a few hours. Volatile compounds were removed on the rotary evaporator. ^1H NMR (300MHz, $CDCl_3$, 25^{o}C): δ 0.95 (s, 2H), 6.3 (s, 1H). $^{13}C\{^1H\}$ NMR (75MHz, $CDCl_3$, 25^{o}C): δ 7.95, 115.00 there are some extra peaks present. The ratio of 2H:1H (^{t-}Bu:Cp) is not far off the ratio which would be expected for this compound i.e. 9H:5H. CHN analysis gave %C 42.79 : %H 8.58 : %N 5.28, calculated without NEt_3 gave %C 25.25 : %H 4.66. The re-crystallisation from acetone was filtered and it removed not only the non-dissolved product but also small pale yellow needles. CHN analysis gave %C 48.57 : %H 10.86 : %N 8.40, calculated without NEt_3 gave %C 13.48 : %H 4.56 The product was extracted twice with hexane (130ml, 80ml), filtered and the volatile compounds were removed on the rotary evaporator. CHN analysis gave %C 46.98 : %H 7.66 : %N 1.43, calculated without NEt_3 gave %C 44.19 : %H 6.82. Theoretical calculations for 1:1 stoichemometry gave %C 43.9 : %H 5.73. Hexane was added to the product in an effort to dissolve it, and allow the hexane to evaporate in air to hopefully leave some crystals but the product was not totally soluble in hexane [1]. This reaction was repeated. ^1H NMR (300MHz, $CDCl_3$, 25°C): δ 0.05 (m, 86H), 6.3 (m, 1H). There were some extra peaks present at 1 and 1.5 – 1.6. A similar compound has been made by another group whereby they activated the silanol groups with $SnMe_3$. They used $C_5H_4MeTiCl_3$. Literature data for similar compound ^1H NMR (250MHz, C_6D_6, 25°C): δ 1.20 (s, 9H, $C(CH_3)_3$), 2.23 (s, 3H, CH_3), 6.11 (m, 2H, C_5H_4), 6.25 (m, 2H, C_5H_4). ^{29}Si {^1H} NMR (79MHz, C_6D_6, 25°C): δ -68.6 (s) [4].

T_7 Terta(cyclopentadienyl)tris(cyclopentyl)titanasiloxanetriol (118)



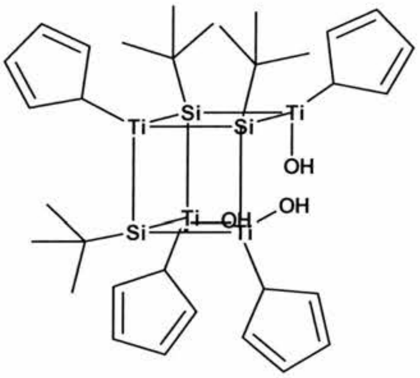
Cyclopentadienyltitanium trichloride (3.34g, 15.2mmoles), cyclopentyltrichlorosilane (2.33g, 11.4mmoles) and acetone (110ml) were placed into a 250ml round bottomed flask under a nitrogen atmosphere. Distilled water (30ml, 1.65moles) was added drop-wise and the resulting mixture was refluxed over the weekend. The reaction mixture was filtered and a yellow brown solid was collected. This was suspended in acetone (25ml) and stirred for 2 hours. The mixture was filtered and placed in an oven overnight. The crude powder (0.56g) was dissolved in pyridine (12ml) and stirred overnight. The mixture was filtered through a medium sintered glass funnel using pyridine (20ml). The filtrate was poured into HCl (32ml) mixed with ice. A brown solid formed that was collected on a medium sintered glass funnel and washed with copious amounts of water. The solid was dried in an oven overnight. This sample had an IR and NMR spectra run on it. The IR spectra showed a peak near 960cm^{-1} that is believed to be due to the Si-O-Ti bond stretch. The sample was also dissolved in pyridine in an attempt to re-crystallize it, another attempt was made later in chloroform. The filtrate that was taken after the solution had been refluxed and was transferred to a conical flask to see if any more solid would form. After some time had elapsed more solid was filtered off from the flask and the filtrate was returned to the flask. This sample had a powder diffraction pattern run on it and it showed peaks that suggested that the sample might be crystalline [9]. ^{13}C {^{1}H} NMR (75MHz, $CDCl_3$, 25^{o}C): δ 115.84, 115.04, 27.51, 27.29, 27.15, 26.88, 22.56, 22.28, 22.19.. ^{1}H NMR (300MHz, $CDCl_3$, 25^{o}C): δ 0.925 (m, 3H), 1.6 (m, 24H), 6.45 (s, 2H). IR (KBr, cm^{-1}) 3500 (m), 3454 (m), 3386 (m), 3318 (m), 2954 (s), 2875 (s), 1131 (vs), 1108 (vs), 1074 (s), 1063 (s), 1051 (s), 1028 (m), 931 (m), 908 (m). The second batch had a different FT-IR trace. IR (KBr, cm^{-1}) 3114 (vbrs), 1628 (s), 1463 (m), 1263 (m), 1108 (brs), 1029 (s), 703 (vbrvs).

T_7 Tetra(cyclopentadienyl)tris(cyclohexyl)titanasiloxanetriol (119)



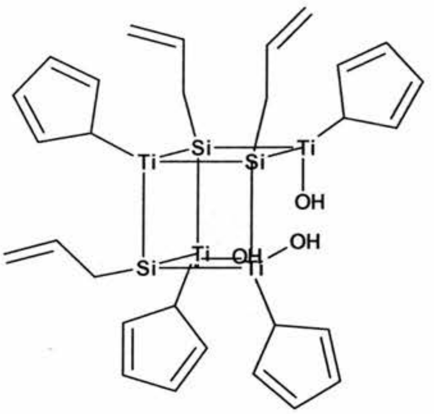
$CpTiCl_3$ (1.11g, 5.06mmoles), cyclohexyltrichlorosilane (0.831g, 3.82mmoles) were dissolved in acetone (35ml) and had distilled water (10ml, 549mmoles) added drop-wise, with stirring. The resulting mixture was allowed to stand. Yellow solid appeared during the addition of the water. The solid was filtered off and an IR was run on the sample, but the region where the Si-O-Ti stretch appears was obscured. A powder pattern was also run [9]. The powder pattern showed two very broad, undefined peaks, this implies that the sample had no real structure i.e. the sample is amorphous. IR (KBr, cm^{-1}) 3454 (brm), 3114 (m), 2932 (vs), 2864 (s), 1817 (brm), 1451 (s), 1166 (m), 1131 (s), 1097 (s), 1063 (s), 1017 (vs), 943 (brs), 886 (s), 840 (s), 811 (vs), 731 (brs), 663 (brs), 628 (brs), 583 (brs), 502 (m).

T_7 Tetra(cyclopentadienyl)tris(tert-butyl)titanasiloxanetriol (120)



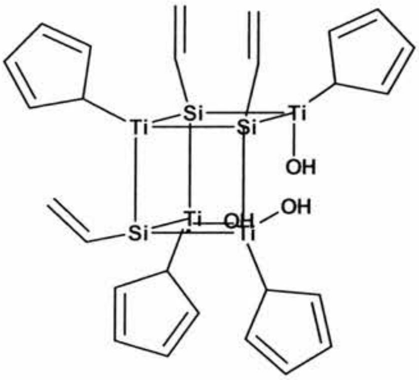
$CpTiCl_3$ (0.557g, 2.54mmoles), $^{t-}$butyltrichlorosilane (0.36g, 1.88mmoles) were dissolved in acetone (17ml) and had distilled water (5ml, 275mmoles) added drop-wise, with stirring. The resulting mixture was allowed to stand. Yellow solid appeared during the addition of the water. The solid was filtered off and an IR was run on the sample, but the region where the Si-O-Ti stretch appears was obscured. A powder pattern was also run [9]. The powder pattern showed two very broad, undefined peaks, this implies that the sample had no real structure i.e. the sample is amorphous. IR (KBr, cm^{-1}) 3954 (m), 3420 (brs), 3239 (s), 2966 (s), 2932 (s), 2886 (s), 2864 (s), 1720 (m), 1617 (brm), 1474 (m), 1463 (m), 1440 (m), 1377 (m), 1354 (m), 1229 (m), 1108 (m), 1023 (vs), 800 (brvs), 646 (brvs), 577 (brvs), 479 (s).

T_7 Tetra(cyclopentadienyl)tris(allyl)titanasiloxanetriol (121)



$CpTiCl_3$ (0.556g, 2.54mmoles), allyltrichlorosilane (0.306g, 1.74mmoles) were dissolved in acetone (17ml) and had distilled water (5ml, 275mmoles) added drop-wise, with stirring. The resulting mixture was allowed to stand. Yellow solid appeared during the addition of the water. The solid was filtered off and an IR was run on the sample, but the region where the Si-O-Ti stretch appears was obscured. A powder pattern was also run [9]. The powder pattern showed two very broad, undefined peaks, this implies that the sample had no real structure i.e. that the sample is amorphous. IR (KBr, cm^{-1}) 3954 (s), 3307 (vbrvs), 1714 (s), 1640 (vs), 1451 (s), 1428 (m), 1400 (m), 1371 (m), 1314 (m), 1183 (s), 800 (vbrvs).

T_7 Tetra(cyclopentadienyl)tris(vinyl)titanasiloxanetriol (122)



$CpTiCl_3$ (0.57g, 2.60mmoles), vinyltrichlorosilane (0.376g, 2.33mmoles) were dissolved in acetone (18ml) and had distilled water (5ml, 275mmoles) added drop-wise, with stirring. The resulting mixture was allowed to stand. Yellow solid appeared during the addition of the water. The solid was filtered off and an IR was run on the sample, but the region where the Si-O-Ti stretch appears was obscured. A powder pattern was also run on the sample but it wasn't helpful since the powder fell out of the disc during the experiment [9]. IR (KBr, cm^{-1}) 3954 (s), 3318 (vbrvs), 2386 (m), 2295 (m), 2091 (m), 1943 (brm), 1840 (brm), 1731 (s), 1646 (s), 1600 (s), 1451 (s), 1411 (s), 1377 (m), 1286 (m), 1229 (m), 800 (vbrvs).

5.2.2.1 Catalysing the epoxidation of cis cyclooctene using T_8 cyclopentadienylheptacyclopentyltitansiloxane(114)

Cis cyclooctene (0.15ml, 0.13g, 1.15mmoles), $^{t-}$BuOOH (1ml of a 0.00165 moles solution), titanium species (25mg) and hexane (1ml) were stirred at 50°C for 3 hours under argon. The catalyst did not dissolve into the reaction mixture also the temperature at which the reaction was carried out was too high (i.e. it reached 110°C) and that probably caused the loss of most of the reactants. All the reactions were tested with hydrogen NMR to see if any reaction had taken place. The only peaks that appeared in the hydrogen NMR were peaks for hexane and cis cyclooctene [6].

5.2.2.2 Catalysing the epoxidation of cis cyclooctene using T_7 tetra(cyclopentadienyl)tris(cyclopentyl)titansiloxanetriol (118)

Cis cyclooctene (0.15ml, 0.13g, 1.15mmoles), $^{t-}$BuOOH (1ml of a 0.00165 moles solution), titanium species (25mg) and hexane (1ml) were stirred at 50°C for 3 hours under argon. The catalyst did not dissolve into the reaction mixture and also the temperature of the reaction was a bit too low i.e. 48°C. Same results as before [6].

5.2.2.3 Catalysing the epoxidation of octene using T_8 cyclopentadienylheptacyclopentyltitansiloxane (114)

Octene (0.15ml, 0.11g, 0.956mmoles), $^{t-}$BuOOH (1ml of a 0.00165 moles solution), titanium species (25mg) and hexane (1ml) were stirred at 50°C for 24 hours under argon. The catalyst did not dissolve into the reaction mixture, the temperature of the mixture was at 48°C and the mixture was not stirred effectively. The hydrogen NMR showed peaks only for octene and hexane [6].

5.2.2.4 Catalysing the epoxidation of octene using T_7 tetra(cyclopentadienyl)tris(cyclopentyl)titansiloxanetriol (118)

Octene (0.15ml, 0.11g, 0.956mmoles), $^{t-}$BuOOH (1ml of a 0.00165 moles solution), titanium species (25mg) and hexane (1ml) were stirred at 50°C for 24 hours under argon. The catalyst did not dissolve into the reaction mixture, the temperature of the mixture was at 48°C and the mixture was not stirred effectively. Same results as before [6].

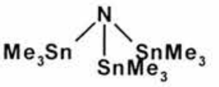
5.2.2.5 Catalysing the epoxidation of cis cyclooctene using T_8 tetra(cyclopentadienyl)tetra(tert-butyl)titansiloxane (117)

Cis cyclooctene (0.15ml, 0.13g, 1.15mmoles), $^{t-}$BuOOH (1ml of a 0.00165 moles solution), titanium species (25mg) and hexane (1ml) were stirred at 50°C for 3 hours under argon. The titanium species did not dissolve into the reaction mixture. The hydrogen spectra only showed peaks for cis cyclooctene and hexane [6].

5.2.2.6 Catalysing the epoxidation of cis octene using T_8 cyclopentadienylheptacyclohexyltitansiloxane (115)

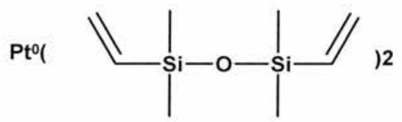
Cis octene (0.15ml, 0.13g, 1.15mmoles), $^{t-}$BuOOH (1ml of a 0.00165 moles solution), titanium species (25mg) and hexane (1ml) were stirred at 50°C for 3 hours under argon. This was the only reaction tried where the titanium species dissolved into the reaction mixture but the reaction still did not occur possibly due to the reaction conditions not being stringent enough i.e. the reaction vessel was not under argon when the reactants were first added. The results are the same as before [6].

Tris(trimethylstannyl)amine (123)



To a slurry of Li_3N (1.74g, 50.0mmoles) in dry THF (50ml), maintained under an atmosphere of nitrogen with stirring, a solution of Me_3SnCl (7.5ml, 7.50mmoles) in THF (42.5ml) was added drop-wise over a period of an hour. After the addition was completed the reaction mixture was refluxed for 2 hours. The major portion of the THF was removed on the rotary evaporator. Petroleum ether (40/60) (150ml) was added to the concentrate and the mixture was filtered to remove insoluble LiCl. The filtrate was reduced on the rotary evaporator [7]. A red oil was produced which when filtered produced a yellow liquid. ^{13}C NMR (75MHz, $CDCl_3$, 25°C): plenty of peaks, not one corresponding to the literature value for $(Me_3Sn)_3N$. The reaction was repeated but the Li_3N did not appear to have reacted at all.

Karstedt's catalyst(124)



Hexachloroplatinic acid (0.35g, 0.854mmoles), tetramethyl-1,3-divinyldisiloxane (0.32g, 1.72mmoles) and $NaHCO_3$ (0.91g) in ethanol (50ml) were refluxed for 30 minutes with stirring and left to stand for 15 hours. The reaction mixture was filtered and the solvent was removed on the rotary evaporator [8]. This catalyst was tested in the hydrosilation reaction between vinyl-T_7cyclopentylPOSS and $Si(CH_2CH_2SiH_3)_4$, it did not work.

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Chapter 6

Polymers

6.1 Aims and objectives

POSS species have received considerable attention as building blocks for polymers. In particular, the US airforce have developed a whole new range of polymers based on POSS technology, which they claim is the most important large-scale production of brand new polymer feedstock in the last forty years [1]. The chemical nature of POSS species makes them very easy to incorporate into common plastics by copolymerisation and blending, and results in some remarkable property enhancements. These include (amongst many others) enhanced fire retardation, higher thermal stability and use temperatures, improved mechanical properties (increase of modulus and hardness) and enhanced oxidation resistance, all while retaining the excellent processability necessary for polymer applications [1].

One striking feature of POSS molecules is their similarity to the secondary building units of zeolites. For example, the $R_8Si_8O_{12}$ unit (see Figure 1) can be regarded as structurally equivalent to the 4,4' (Double four ring) unit found in zeolites LTA and ACO. This opens up the possibility of producing zeolite-like species by linking POSS molecules together. Independently, Harrison [2] and Laine [3] have shown that it is possible to prepare porous polymers using POSS species. This author's research group have used similar, but not identical, methods to produce porous, thermally–stable POSS polymers [4].

Zeolites and other related porous inorganic solids such as the mesoporous MCM family of silicas are immensely important in industry with high volume applications in catalysis, ion exchange and adsorption, and they are becoming increasingly important in fine chemical synthesis and membrane applications [5]. However, if POSS-based polymers are to rival these inorganic porous solids in applications such as catalysis they must first be imbued with chemical reactivity that the purely silsesquioxane materials do not possess. Other members of the research group have functionalised POSS-based porous polymers using a recently discovered reaction of POSS species that will allow selective derivatisation of the POSS subunits in a polymer with an active species such as a transition metal cation [6].

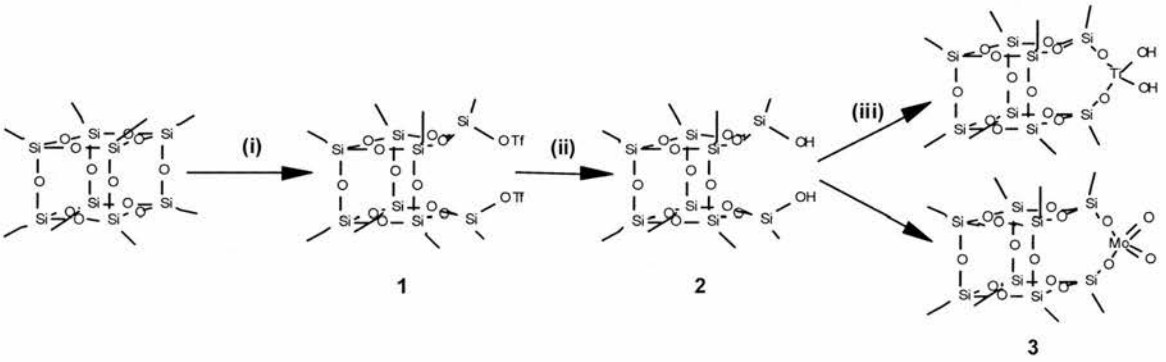


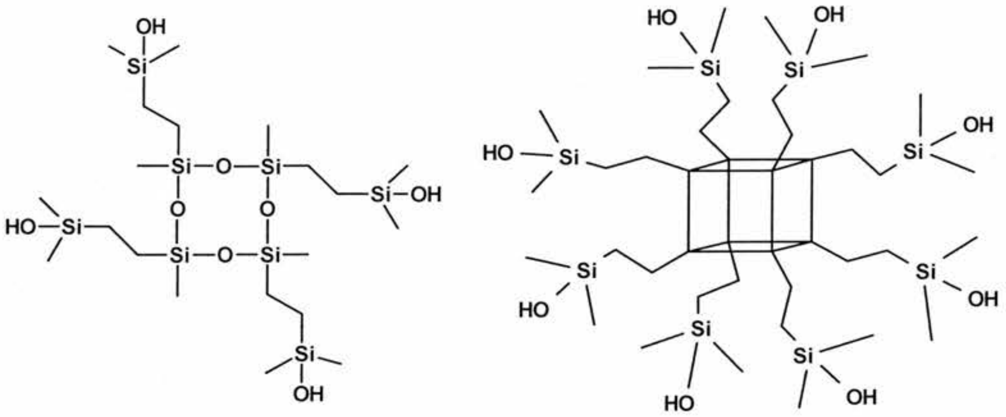
Figure 6.1 The remarkable reaction of octaalkyl-POSS molecules with triflic acid [6] [step (i), xs (5 equiv) triflic acid, toluene, 25°C, 30 min], produces the ditriflate 1 in quantitative yield. This is followed by hydrolysis [(ii) H_2O, 25°C] to form 2, and reaction with metallocene species [(iii) Cp_2MCl_2 (M=Ti, Mo, but other metals could also be used e.g. V, Nb, Zr etc), Et_3N, 40°C, followed by calcination in flowing O_2] to form the metallo-POSS species 3.

The reaction of octaalkyl POSS species with triflic acid, which produces the ditriflate **1** in 100% yield, is shown schematically in Figure 6.1. This is a remarkable reaction in that the ditriflate **1** is completely stable and does not react further [6]. Hydrolysis using water produces the disilanol **2**, which can be reacted with a transition metal complex (such as a metallocene dichloride) to produce a metal functionalised POSS species **3**. This last reaction (iii) is exactly analogous to the well known derivatisation of MCM 41 mesoporous materials that has been used with great success during the last few years [7,8]. The reaction of the POSS-based polymers, which are in effect octa-alkyl POSS species in the solid state, with triflic acid (as shown in Figure 6.1) will allow one to selectively engineer one reactive site per POSS subunit. Because of these features, polymers made from these types of molecular monomer may well prove to be interest in a number of fields.

In this chapter, the author has worked to extend the POSS work to see if the square cyclosiloxane material can be incorporated into porous polymers. The square siloxane is analogous to the single four ring building unit found in zeolites.

6.2 Results and discussion

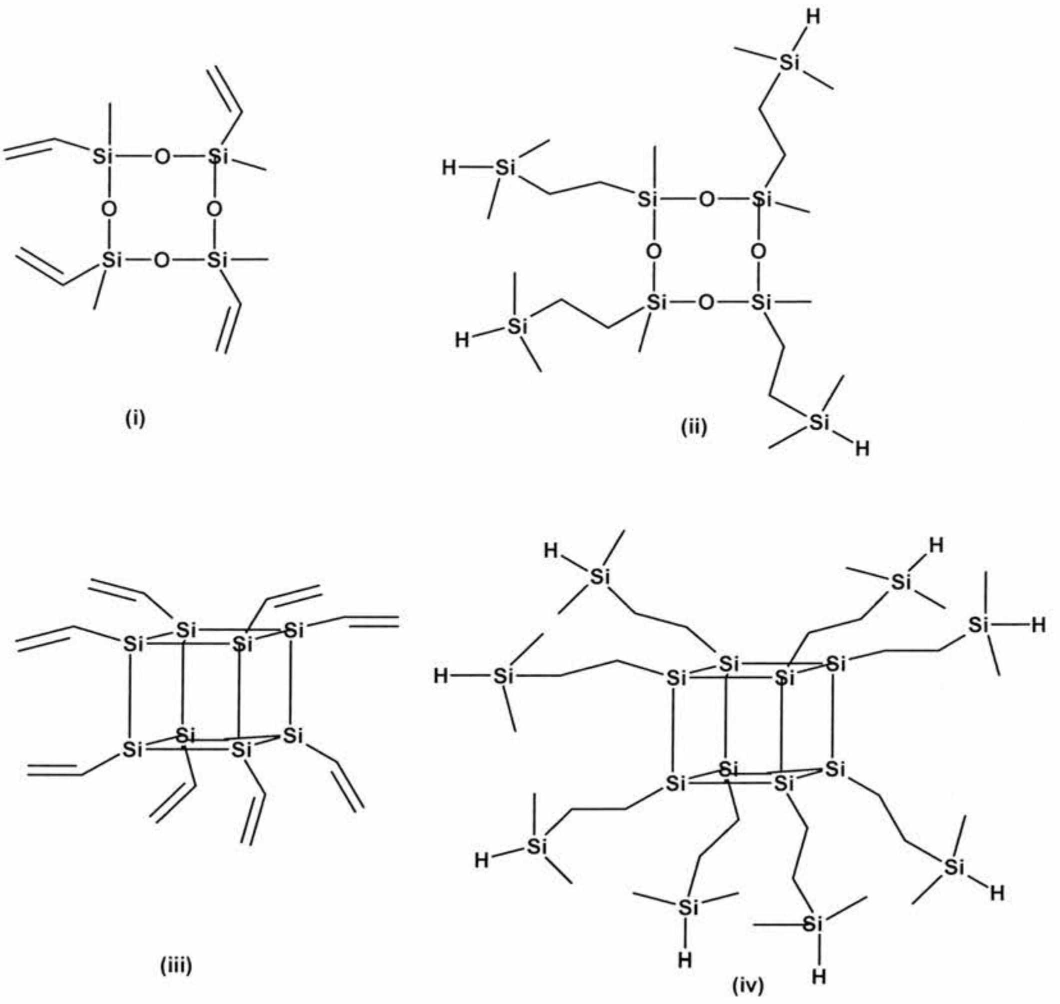
The reactions of acid hydrolysis and hydrosilation were used in an attempt to synthesize porous polymers from POSS and siloxane dendrimer cores. Hydrolysis was performed on two silanol functionalised cores (see Figure 6.2) using an acid catalyst. In the initial plan hydrolysis of triethoxy functionalised dendrimers was also meant to occur but there were problems in the synthesis of these molecules so this was not attempted. It is quite likely that these molecules would have been made if there had been more time. There was not enough of the cubic silanol polymer to run any analysis on, so this was scrapped. The square silanol polymer (polymer A) had multi-point BET analysis run on it but this only proved that the polymer produced was not porous (see Table 6.1) [].



(i) (ii)

Figure 6.2 Silanols used for hydrolysis reaction. (i) 1,3,5,7-tetrakis{2-[dimethylhydroxysilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane (75) and (ii) 1,3,5,7,9,11,13,15-octakis{2-[dimethylhydroxysilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane [10]

Hydrosilation was also used to make polymers. These reactions were tried on 1,3,5,7-tetra{2-[dimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane with 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane (polymer B) and with T_8 octavinyl POSS (polymer C). octakis{2-[dimethylsilyl]ethyl} POSS and 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane were hydrosilated (polymer D) to see if there was any difference caused by having the functional groups on the different molecules (see Figure 6.3). Multi-point BET analysis was carried out on these polymers (see Table 6.1) but as before the polymers were found to be non-porous.



(i) (ii)

(iii) (iv)

Figure 6.3 This figure depicts the various cores used in the hydrosilation reaction to produce the polymers. Core (i) is 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane (4), core (ii) is 1,3,5,7-tetrakis{2-[dimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane (48), core (iii) is 1,3,5,7,9,11,13,15-octavinylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (91) and core (iv) is 1,3,5,7,9,11,13,15-octakis{2-[dimethylsilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane [11]

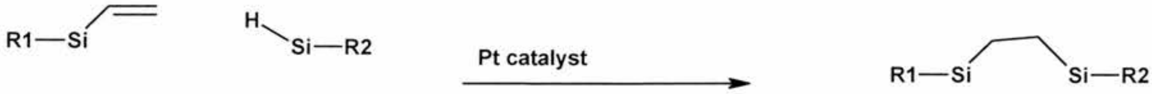
6.2.1 Polymerisation by hydrolysis

The reaction to polymerise the silanols is described as follows (see Scheme 1 for a diagram of acid hydrolysis): the silanol was added to THF (25ml) and HCl (1M, 2ml). The resulting solution was to be stirred until it gelled but, as explained in the experimental section, after 6 days neither of the solutions had gelled. In an attempt to make the solutions gel the resulting solutions were heated. Again the solutions did not gel and after the volatile compounds had been removed from the solutions one of the solutions was analysed whereas the other solution was discarded (due to there not being enough sample to analyse).

Scheme 1 Hydrolysis reaction

6.2.2 Polymerisation by hydrosilation

The basic hydrosilation reaction was as follows (see Scheme 6.2): the two cores (one functionalised with vinyl groups and the other with silane groups) were placed in toluene (10ml), under argon, in ice and had Karstedt's catalyst (1.2ml of a 0.2mmole solution) added to it. The resulting mixture was stirred overnight. Only polymer C gelled overnight, the other two polymers required some heat before they gelled. The polymers were dried on the Kugelrohr before they were sent for multi-point BET analysis (see Table 6.1).



Scheme 6.2 Hydrosilation reaction

Polymer	Multi-Point BET surface area (m^2/g)
Polymer A*	< 0.1
Polymer B**	< 0.1
Polymer C***	< 0.1
Polymer D****	< 0.1

Table 6.1 Results from multi-point BET analysis

All samples proved to be below the accuracy of the instrument, <0.1 m^2/g.

* Polymer A was formed from the hydrolysis of 1,3,5,7-tetrakis{2-[dimethylhydroxysilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane **(75)** (see Figure 6.2i).

** Polymer B was formed from the hydrosilation of 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane **(4)** and 1,3,5,7-tetrakis{2-[dimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane **(48)** (see Figure 6.3i and ii).

*** Polymer C was formed from the hydrosilation of 1,3,5,7-tetrakis{2-[dimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane **(48)** and 1,3,5,7,9,11,13,15-octavinylpentacyclo[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]octasiloxane **(91)** (see Figure 6.3 ii and iii).

**** Polymer D was formed from the hydrosilation of 1,3,5,7-tetravinyl-1,3,5,7-tetramethyltetracyclosiloxane **(4)** and 1,3,5,7,9,11,13,15-octakis{2-[dimethylsilyl]ethyl}pentacyclo[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]octasiloxane (see Figure 6.3 i and iv).

It is possible that porous polymers could be made using these methods and that all that is required is the optimisation of the reaction conditions. Changing the porosity of POSS based polymers, formed by hydrosilation reaction, has been accomplished by varying the temperature at which the reaction is carried out at [12].

6.3 Conclusions

The hydrolysis reaction might have worked better with either a higher dilution of the acid in solution or a weaker concentration of the reactant. This might have caused any polymers produced to be porous.

The hydrosilation reactions might have given porous polymers if either a weaker solution of Karstedt's catalyst was used or a weaker concentration of the reactants was used.

6.4 Experimental

The multi-point BET analysis was carried out on a Gemini 2360 instrument from Micromeritics using N_2 at 77K. Samples were pre-treated in flowing N_2 at 368K (1hr) and for a further hour at 398K. Nitrogen adsorption was measured between p/p_0 values of 0.05 and 0.2. All surface area measurements were made with glass inserts in the vessels. These ensured small dead space volumes thus increasing the accuracy of the results, especially for low surface areas but increased the analysis time. The instrument was checked prior to use with a standard. The reference sample, silica - alumina, has a reported surface area of 214 ± 6 m^2/g, the measured surface area in this instance with all the same variables was 211 m^2/g (R=1.0000). ^1H (300MHz) NMR spectra were recorded on a Varian Gemini 300. The ^1H solutions were placed in 5mm glass tubes. The spectra were recorded at room temperature in d^4 methanol (Apollo Scientific/Aldrich).

Hydrolysis of 1,3,5,7,9,11,13,15-octakis{2-[dimethylhydroxysilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane

1,3,5,7,9,11,13,15-octakis{2-[dimethylhydroxysilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (0.07g, 0.0584mmoles) had THF (25ml) and HCl (1M, 2ml) added to it. The resulting solution was stirred over six days [13]. The silanol dissolved into the THF well but it hadn't gelled after 6 days and so it was heated for 7 hours. It still didn't gel so the volatile compounds were removed then methanol was added to see if the solid would dissolve. It was then dissolved in d^4-methanol to be examined by ^1H NMR. Very little material was present since no extra peaks showed up on the NMR. Since there was not enough material present to carry out an analysis on, this experiment was scrapped.

Polymer A

1,3,5,7-tetrakis{2-[dimethylhydroxysilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane

(0.136g, 0.204mmoles) had THF (25ml) and HCl (1M, 2ml) added to it. The resulting solution was stirred over 6 days at room temperature [13]. The starting material didn't dissolve very well into the solvent. Since it hadn't gelled after the stirring it was refluxed for 7 hours. It still didn't gel so the volatile compounds were removed on the rotary evaporator and methanol was added to see if it would dissolve. An NMR was run on the sample but there was not enough material present to analyse in this fashion. This was filtered and placed on top of the oven to dry overnight. This was dried on the Kugelrohr for 4 hours at 150°C. It was then sent for multi-point BET measurements.

Polymer B

1,3,5,7-tetra{2-[dimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane (0.727g, 1.24mmoles), 1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane (0.435g, slight excess, 1.26mmoles), toluene (10ml) under argon, in ice had Karstedt's catalyst (2.4ml of a 0.2mmole solution) added to it, the resulting mixture was stirred overnight. Way to much catalyst had been added and there is the possibility that water might be present also in the sample. Since it had not gelled overnight the sample was heated at over 80°C for three-quarters of an hour during which time it did gel [3]. This was filtered and placed on top of the oven to dry overnight. There was difficulty experienced in filtering this product so it hadn't filtered properly before drying on top of the oven. This was dried on the Kugelrohr for 4 hours at 150°C. An attempt was made to crush and ground the product but it didn't work. It was sent for multi-point BET analysis in an uncrushed state. ^{29}Si CP MAS NMR (59.59MHz, 25°C): δ 7.81, 5.91, -2.21, -3.99, -20.22, -33.56. ^{13}C CP MAS NMR (75.43MHz, 25°C): δ 137.14, 133.20, 9.64, 6.62, -0.81, -3.72.

Polymer C

1,3,5,7-tetra{2-[dimethylsilyl]ethyl}-1,3,5,7-tetramethyltetracyclosiloxane (0.71g, 1.21mmoles), 1,3,5,7,9,11,13,15-octavinylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (0.384g, 0.607mmoles), toluene (10ml), under argon, in ice had Karstedt's catalyst (1.2ml of a 0.2mmole solution) added to it, the resulting mixture was stirred overnight during which time it gelled [3]. This was filtered and placed on top of the oven to dry overnight. This was dried on the Kugelrohr for 4 hours at 150°C. The product was crushed and ground in a mortar and pestel before being sent for multi-point BET analysis. ^{29}Si CP MAS NMR (59.59MHz, 25°C): δ 5.85, -10.20, -19.97, -65.84, -80.47. ^{13}C CP MAS NMR (75.43MHz, 25°C): δ 135.87, 130.38, 9.59, 5.94, -0.95, -3.67.

Polymer D

1,3,5,7-tetramethyl-1,3,5,7-tetravinyltetracyclosiloxane (0.346g, 1.00mmoles), 1,3,5,7,9,11,13,15-octakis{2-[dimethylsilyl]ethyl}pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (0.558g, 0.501mmoles) in toluene (10ml), under argon, in ice had Karstedt's catalyst (1.2ml of a 0.2mmole solution) added to it, the resulting mixture was stirred overnight. Since it had not gelled overnight the mixture was heated above 80°C for about three-quarters of an hour during which time it did gel [3]. This was filtered and placed on top of the oven to dry overnight. There was difficulty experienced in filtering this product so it hadn't filtered properly before drying on top of the oven. This was dried on the Kugelrohr for 4 hours at 150°C. The product was crushed and ground in a mortar and pestel before being sent for multi-point BET analysis. ^{29}Si CP MAS NMR (59.59MHz, 25°C): δ 15.62, 5.85, -3.99, -9.89, -19.54, -33.74, -66.14. ^{13}C CP MAS NMR (75.43MHz, 25°C): δ 137.18, 133.01, 9.20, 5.80, -3.58.

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Chapter 7
Experimental

7.1 General

7.1.1 Gases

Reactions were carried out under an inert atmosphere of nitrogen (BOC gases), argon (BOC gases) or syngas (BOC gases), unless it does not state that they were, then they were carried out in air. Gases were used as received.

7.1.2 Solvents

Where it is stated, dry solvents were used. Solvents which were used as received were: propan-2-ol (Fischer Scientific), petroleum ether 40-60 (Fischer Scientific), xylene, acetone, heptane (M and B laboratory chemicals), toluene (Rectapur tm), N,N'-dimethylformamide (Lancaster), hexane (Ultrafine Ltd), dioxane (Avocado), dichloromethane (Cannon), methanol (Cannon), xylene (Fischer Scientific), acetone (Fischer Scientific), chloroform (Aldrich) and diisopropylether (Fluka). Dichloromethane was distilled from calcium hydride. Tetrahydrofuran (Fischer Scientific) and diethyl ether (Rectapur tm) were distilled from sodium benzophenone. Toluene was distilled from sodium. Hexane was distilled onto 4Å/5Å molecular sieves. Methanol and ethanol were refluxed with magnesium turnings and iodine before being distilled onto 3Å molecular sieve beads.

7.1.3 Reagents

Aniline (Fluka), triethylamine (Avocado), lithium nitride (Aldrich), hydrochloric acid (Fischer Scientific), vinylmagnesiumbromide (Aldrich), trimethylchlorosilane (Avocado), tetravinylsilane (Aldrich), trichlorosilane (Aldrich), vinyltrichlorosilane (Flurochem), cyclopentyltrichlorosilane (Flurochem/Apollo Scientific), silicic acid (BDH chemicals), titanium isopropoxide (Lancaster), tetramethylammoniumhydroxide pentahydrate (Aldrich), cyclopentadienyltitaniumtrichloride (Aldrich), chlorodimethylvinylsilane (Aldrich), dichloromethylsilane (Aldrich), cyclohexyltrichlorosilane (Flurochem), 1,3-divinyltetramethyldisiloxane (Aldrich), chlorodimethylsilane (Aldrich), tert-butyltrichlorosilane (Aldrich), trivinylmethylsilane (Apollo Scientific), 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (Apollo Scientific), tetraallyloxysilane (Apollo Scientific), tetraallylsilane (Apollo Scientific), platinium-divinyltetramethylsiloxane complex in xylene - Karstedt's catalyst (ABCR), trimethyltinchloride (Aldrich), hydrogen hexachloroplatinate(IV)hydrate - Speier's catalyst (Aldrich), lithium cyclopentadienylide (Aldrich), quinuclidine (Aldrich), benzoyl peroxide (BDH laboratory reagents), tetrahydronaphthalene (M & B laboratory chemicals), magnesium sulfate (Fischer Scientific), allyltrichlorosilane (Aldrich), ammonium chloride (Fischer Scientific), sodium chloride (Fisons), sand (Aldrich), potassium carbonate (Aldrich), silica (Fischer Scientific), lithium aluminium hydride (Lancaster), sodium sulfate (Fisons), palladium on charcoal (Aldrich), sulfuric acid (Prolabo), butyllithium (Aldrich), cis-cyclooctene (Aldrich), t-butylperoxide (Fluka), octene (Aldrich), sodium hydrogen carbonate (Fisons), molecular sieves (Prolabo/Avocado), calcium hydride (Aldrich), iodine (Fisons), magnesium turnings (Fisons), sodium hydroxide (Fischer Scientific), calcium chloride (Fischer Scientific), sodium thiosulfate (Fischer Scientific), bromine

(Aldrich), p-bromoanisole (BDH Chemicals Ltd), 4-bromobenzaldehyde (Lancaster), pyridinium p-toluenesulfonate (Lancaster), ethylene glycol (Avocado), 3-bromobenzaldehyde (Lancaster), p-toluene sulfonic acid (Lancaster), borontribromide (Aldrich), acetic acid (Fisons), trimethoxyvinylsilane (Lancaster), sodiumdihydrogen orthophosphate (BDH), rhodium acetate (Aldrich), triphenyl phosphine (Lancaster), potassium permangante (Aldrich), tetraethylorthosilicate (Lancaster), ferric chloride (Fisons) and triethoxysilane (Lancaster) were all used as received. Where stated dry pyridine was used. Pyridine (Fischer Scientific) was distilled from calciumhydride onto 4 Å /5 Å molecular sieves. Where stated dry triethylamine was used. Triethylamine was dried over $MgSO_4$, under argon and then transferred to a flask containing CaH_2 from which it was distilled onto 4 Å molecular sieves and stored under argon.

Chapter 8
Conclusions and Future Work

This chapter recounts the main conclusions from the thesis and suggests some possible future work that could be carried out.

This project was interested in the synthesis of dendrimers, silsesquioxanes and titanasiloxanes. Over the last few years there has been a lot of interest in these materials. Dendrimers have already found uses in the fields of catalysis [1-5], biology [5-9] and as viscosity modifiers [10]. Dendrimers being used as catalytic supports is due to the fact that once a homogeneous catalyst is attached to a large enough dendrimer it can be ultrafiltered out of the reaction mixture. Silsesquioxanes have found uses as models of catalysts [11-30], in comparison to zeolites [19,21,23,28,31,32], for thermal stability in polymers [28,33,34], as hard blocks in polymers [33] and as dentist filling material [35]. Titanasiloxanes have uses as models of titanium on silica surfaces and can have catalytic activity.

8.1 Conclusions

Chapter 2 was concerned with dendrimer synthesis and characterisation. It described two methods of addition across a double bond i.e. hydrosilation and hydrobromination. It also described three different ways to functionalise Si-Cl bonds i.e. by reducing the bonds with LAH, and reactions with organometallic species i.e. Grignard reagents and organolithium reagents. Other reactions carried out on Si-Cl bonds involved the corner capping reaction that was used in an attempt to make dendrimers with POSS molecules at the end of their branches. There were other attempts to make dendrimers which had POSS molecules at the end of their branches and these syntheses involved hydrosilation reaction between a reduced dendrimer (a dendrimer functionalised with Si-H branch ends) and mono alkenyl functionalised POSS. When these reactions were not successful, tests were tried of the hydrosilation reaction between mono alkenyl functionalised POSS with mono hydrido functionalised silanes and eventually between mono alkenyl functionalised silanes and mono hydrido functionalised silanes.

Conclusions drawn from work carried out on dendrimer synthesis and characterisation were:

- Hydrosilation is better than hydrobromination for adding groups across a double bond due to the greater scope for functionalising the product.
- Grignard reagents worked better than organolithium reagents on Si-Cl bonds but this could be due to more work being carried out with Grignard reagents than with organolithium reagents.
- Hydrosilation of POSS molecules and allyltrichlorosilane onto dendrimers functionalised with Si-H branch ends was unsuccessful.
- Corner capping reactions of incompletely condensed POSS molecules onto dendrimers with Si-Cl branch ends was unsuccessful.

Chapter 3 was concerned with how to functionalise dendrimers to produce silanols and aldehydes. Three methods were found for making silanols: two methods involved high dilution, the other method involved a catalytic process. All the methods worked on different kinds of groups attached to the silicon. The first method tried involved high dilution with a base on Si-Cl bonds. The second method covered in the chapter involved high dilution with acid on Si-OMe bonds. The final method involved Pd/C on Si-H bonds. The syntheses of two different kinds of aldehyde were reported in this chapter: the synthesis of aromatic aldehydes and the synthesis of aliphatic aldehydes. The synthesis of aromatic aldehydes involved making a protected bromobenzaldehyde then transforming it into a silane via a Grignard reaction, hydrosilating it onto a core material followed by de-protection of the aldehyde functionality. The production of an aliphatic aldehyde was via the hydroformylation reaction using high temperature and pressure and a rhodium catalyst. The final section of the chapter dealt with the attempted synthesis of carboxylic acid from the aldehydes.

Conclusions drawn from work carried out on silanols and aldehydes were:

- Catalytic method (Pd/C) to make silanols was more successful than either of the high dilution methods.
- Production of dendritic aromatic aldehydes via hydrosilation is successful but suffers from the same drawbacks as other hydrosilation reactions (i.e. α/β mixtures).
- Hydroformylation reaction was successful but a mixture of n/i products was obtained.
- Reaction to form carboxylic acids from the aldehydes using potassium permanganate went too far.

Chapter 4 dealt with the synthesis of cubic silsesquioxanes and silicates. This consisted of the production of incompletely condensed POSS molecules and the corner capping reaction, two different strategies to synthesising mixed POSS molecules (POSS molecules that had alternating R groups) and the synthesis of silicate molecules. The two different strategies for synthesising mixed POSS molecules were the homofunctional copolymerisation and heterofunctional condensation reactions.

Conclusions drawn from work carried out on silsesquioxanes were:

- Reactions to produce incompletely condensed POSS molecules with cyclopentyl and cyclohexyl groups were successful. Reactions to produce other incompletely condensed POSS molecules, whether they were mixed species or pure species, were unsuccessful.
- Corner capping incompletely condensed POSS molecules with vinyl- and allyltrichlorosilane was successful.
- Synthesis of mixed T_8 POSS species was unsuccessful.
- Synthesis of cubic silicates with all the same organic groups were successful, synthesis with mixed organic groups was unsuccessful.

Chapter 5 dealt with the synthesis of cubic titanasiloxanes and other reactions that had been unsuccessful were recounted in this chapter. The various ways of synthesizing titanasiloxanes were: corner capping the incompletely condensed POSS molecules with cyclopentadienyltitaniumtrichloride, homofunctional condensation reactions and heterofunctional condensation reactions. Other reactions mentioned in this chapter include attempts to use some of the titanium species formed in a catalysis reaction, the synthesis of tris(trimethylstannyl)amine and the synthesis of the Karstedt's catalyst.

Conclusions drawn from work carried out on titanasiloxanes and other reactions were:

- Corner capping incompletely condensed POSS molecules with cyclopentadienyltitaniumtrichloride was partially successful since both monomers and dimers were formed.
- Reactions to produce cubic titanasiloxanes using either homo- or heterofunctional means was unsuccessful.
- Catalytic epoxidation reactions and the other reactions mentioned in this chapter were unsuccessful.

Chapter 6 dealt with the synthesis of polymers from organosilicon dendrimers. Two different reactions were tried to synthesize the polymers: one involved the hydrolysis of Si-OH bonds [36], the other involved hydrosilation between Si-H bonds and Si-C=C bonds [37].

Conclusions drawn from work carried out on synthesising polymers were:

- Neither method made porous polymers

8.2 Future Work

Any future work would involve the hydrosilation reaction. It would be a good idea to check the syntheses of carbosilane dendrimers to see if any of the reaction conditions reported could be used to make dendrimers without β isomer and H-Si/ vinyl-Si swapping. Failing that, it would probably be advantageous to look into other species with vinyl groups that are not attached to silicon atoms and have bulky γ substituents to make future dendrimers by attaching them to Si-H functionalised cores (i.e. cores like T_8 hydridooctasilsesquioxane e.t.c.).

Such reactions would have a bearing on the future production of dendrimers which were made using the hydrosilation method (i.e. the dendrimers functionalised with aromatic aldehyde groups and silanol groups).

It may also be advantageous to look at different protective groups for phenol groups since anisole proved difficult to revert to phenol in the anisole functionalised dendrimer (see Chapter 2).

A dendrimer with Si-OH branch ends could be reacted with $CpTiCl_3$ to produce a possible catalyst. Basically the preparation of various titanium containing POSS molecules, dendrimers, dendrimers with POSS arms and mirco- and/or meso- porous molecules is important so that their catalytic ability can be measured and compared to each other. A possible reaction that could be used for testing the catalytic abilities of the titanium species is the epoxidation of cis-cyclooctene and octene with tert-butylhydroperoxide.

The attempts to make a dendrimer with POSS arms should be kept up since such a molecule would make either a viscosity modifier or (if a metal was either attached through a corner capping reaction or by opening up the side of the molecule) a possible catalyst could be made.

The attempts to make mixed POSS species and titanasiloxanes products should be continued. Attempts using the protective group/activator $(Me_3Sn)_3N$ or Li (Li would only be used to try to synthesise mixed POSS species since it has been known to produce other products than cubic titanasiloxane when tried during its synthesis) to activate $^tBuSi(OH)_3$ or other groups with OH groups. Another possibility would be to try to synthesise mixed POSS species using vinyl$Si(OMe)_3$ and cy$SiCl_3$ in a reaction carried out in the same way to make T_7 cyclopentylsilsesquioxane with the same work up. A similar attempt could be made using $HSi(OEt)_3$ and cy$SiCl_3$. A similar reaction could be tried with $CpTiCl_3$ depending on any success gained from the reaction to make the mixed POSS species. Any such product made could be made into a polymer using the hydrosilation reaction.

Making titanasiloxanes with OEt group on the titanium could then be polymerised. Such species could be reacted with Si-Cl branch ended dendrimers to form polymers.

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Appendix

X-ray Structure Report

Monday April 13 1998

Experimental

Data Collection

A colourless block crystal of $C_{25}H_{40}Si_{16}O_{20}$ having approximate dimensions of 0.25 x 0.20 x 0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 20 carefully centred reflections in the range $6.50 < 2\theta < 12.62°$ corresponded to a primitive triclinic cell with dimensions:

a = 10.964(6) Å	$\alpha = 98.98(3)°$
b = 13.528(3) Å	$\beta = 95.94(5)°$
c = 10.916(6) Å	$\gamma = 77.42(3)°$
V = 1556(1) Å^3	

For Z = 1 and F.W. = 1109.95, the calculated density is 1.18 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

P1 (#1)

The data were collected at a temperature of 200 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 49.9°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.29° with a take-off angle of 6.0°. Scans of $(1.21 + 0.35\tan\theta)°$ were made at a speed of 16.0°/min (in omega). The weak reflections ($I < 15.0\sigma(I)$) were rescanned (maximum of 4 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm and the crystal to detector distance was 235 mm. The computer controlled slits were set to 9.0 mm (horizontal) and 13.0 (vertical).

Data Reduction

Of the 4457 reflections which were collected, 4148 were unique (R_{int} = 0.033). The intensities of three representative reflection were measured after every 150 reflections. No decay correction was applied.

The linear absorption coefficient, μ, for Mo-Kα radiation is 3.8 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods [1] and expanded using Fourier techniques [2]. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement [3] was based on 2786 observed reflections ($I > 3.00\sigma(I)$) and 541 variable parameters and converged (largest parameter shift was (7.49 times its end) with unweighted and weighted agreement factors of:

$$R = \Sigma||Fo| - |Fc|| / E|Fo| = 0.081$$

$$Rw = [\Sigma w(|Fo| - |Fc|)^2/\Sigma wFo^2]^{0.5}$$

The standard deviation of an observation of unit weight [4] was 4.66. The weighting scheme was based on counting statistics and included a factor (p = 0.005) to downweight the intense reflections. Plots of $E(|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.64 and –0.83 $e^-/ Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber [5]. Anomalous dispersion effects were included in Fcalc [6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and M^{c}Auley [7]. The values for the mass attenuation coefficients are those of Creagh and Hubbel [8]. All calculations were performed using the teXsan [9] crystallographic software package of Molecular Structure Corporation.

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[3] Least-squares:

Function minimised: $\Sigma w(|Fo| - |Fc|)^2$

where $w = 1/[\sigma^2(Fo)] = 4Fo^2/[\sigma^2(Fo^2)$

$\sigma^2(Fo2) = S^2(C + R^2B) + (pFo^2)^2/Lp^2$

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

B = Total background count

Lp = Lorentz-polarisation factor

P = p-factor

[4] Standard deviation of an observation of unit weight:

$$[\Sigma w(|Fo| - |Fc|)^2/(No - Nv)]^{0.5}$$

where: No = number of observations

Nv = number of variables

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[8] Creagh, D.C. & Hubbell, J.H.; "International Tables for Crystallograhy", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

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Experimental Details

A. Crystal Data

Empirical Formula	$C_{25}H_{40}Si_{16}O_{20}$
Formula Weight	1109.95
Crystal Colour, Habit	colourless, block
Crystal Dimensions	0.25 X 0.20 X 0.20 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	20 (6.5 – 12.6°)

Omega Scan Peak Width At Half-Height	0.29°
Lattice Parameters	a = 10.964(6) Å
	b = 13.528(3) Å
	c = 10.916(6) Å
	α = 98.98(3)°
	β = 95.94(5)°
	γ = 77.42°
	V = 1556(1) Å^3
Space Group	P1 (#1)
Z value	1
D_{calc}	1.184 g/cm^3
F_{000}	574.00
μ(MoKα)	3.80 cm^{-1}

B. *Intensity Measurements*

Diffractometer	Rigaku AFC7S
Radiation	MoKα (l = 0.71069 Å)
	graphite monochromated
Attenuator	Zr foil (factor = 8.53)
Take-off Angle	6.0°
Detector Aperture	9.0 mm horizontal
	13.0 mm vertical
Crystal to Detector Distance	235 mm
Temperature	200.0°C
Scan Type	ω-2θ
Scan Rate	16.0°/min (in ω) (up to 4 scans)
Scan Width	(1.21 + 0.35tanθ)°
2θmax	49.9°
No. of Reflections Measured	Total: 4457

	Unique: 4148 (R_{int} = 0.033)
Corrections	Lorentz-polarisation

C. *Structure Solution and Refinement*

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least- squares
Function Minimised	$\Sigma w(\lvert Fo \rvert - \lvert Fc \rvert)^2$
Least Squares Weights	$1/[\sigma^2(Fo)] = 4Fo^2/[\sigma^2(Fo)^2]$
p-factor	0.0050
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>3.00\sigma(I)$)	2786
No. Variables	541
Reflection/Parameter Ratio	5.15
Residuals: R; Rw	0.081 ; 0.081
Goodness to Fit Indicator	4.66
Max Shift/Error in Final Cycle	7.49
Maximum peak in Final Diff. Map	0.64 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.83 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Si(1)	1.341(2)	-0.023(2)	1.244(2)	3.88(9)
Si(2)	1.063(2)	0.062(2)	1.291(2)	3.82(9)
Si(3)	1.249(2)	-0.290(2)	1.016(2)	5.1(1)
Si(4)	1.316(2)	-0.236(2)	1.290(2)	4.27(10)
Si(5)	1.271(2)	-0.078(2)	0.964(2)	4.15(9)
Si(6)	1.035(2)	-0.154(2)	1.337(2)	4.50(9)
Si(7)	0.990(2)	0.005(2)	1.009(2)	4.6(1)
Si(8)	0.965(2)	-0.209(2)	1.059(2)	4.59(10)
Si(9)	1.293(2)	-0.515(2)	0.886(2)	8.2(1)

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
Si(11)	0.861(2)	0.173(2)	0.847(2)	17.7(3)
Si(12)	0.762(2)	-0.339(2)	1.000(2)	9.1(2)
Si(13)	1.443(2)	-0.405(2)	1.432(2)	14.1(3)
Si(14)	1.547(2)	0.105(2)	1.294(2)	7.9(2)
Si(15)	0.997(2)	0.285(2)	1.393(2)	11.2(2)
Si(16)	1.372(2)	0.004(2)	0.754(2)	14.1(2)
Si(17)	0.910(2)	-0.224(2)	1.538(2)	12.9(2)
O(1)	0.975(2)	-0.193(2)	1.201(2)	4.3(2)
O(2)	1.283(2)	-0.195(2)	0.958(2)	6.7(3)
O(3)	1.342(2)	-0.035(2)	1.091(2)	5.3(2)
O(4)	1.304(2)	-0.294(2)	1.148(2)	5.1(2)
O(5)	1.098(2)	-0.273(2)	1.005(2)	5.3(2)
O(6)	1.339(2)	-0.055(2)	0.852(2)	6.3(2)
O(7)	1.409(2)	-0.306(2)	1.368(2)	6.0(2)
O(8)	0.942(2)	-0.098(2)	1.011(2)	6.5(2)
O(9)	1.123(2)	-0.020(2)	0.959(2)	5.1(2)
O(10)	1.027(2)	-0.027(2)	1.350(2)	4.3(2)
O(11)	1.002(2)	0.163(2)	1.365(2)	4.8(2)
O(12)	0.998(2)	0.064(2)	1.145(2)	6.1(2)
O(13)	1.297(2)	-0.398(2)	0.920(2)	6.5(3)
O(14)	1.448(2)	0.035(2)	1.294(2)	6.6(3)
O(15)	0.891(2)	0.077(2)	0.918(2)	7.0(2)
O(16)	1.366(2)	-0.312(2)	1.288(2)	5.2(2)
O(17)	0.851(2)	-0.261(2)	0.992(2)	6.5(2)
O(18)	1.210(2)	0.047(2)	1.282(2)	4.9(2)
O(19)	1.178(2)	-0.207(2)	1.349(2)	5.3(2)
O(20)	0.970(2)	-0.173(2)	1.445(2)	7.6(3)
C(1)	1.316(2)	-0.472(2)	1.413(2)	7.9(4)
C(2)	1.432(2)	-0.568(2)	0.812(3)	15.0(7)

Table 1. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B_{eq}
C(3)	1.138(2)	-0.512(2)	0.772(2)	11.0(4)
C(4)	1.369(3)	0.143(2)	0.825(2)	9.1(5)
C(5)	1.451(2)	0.212(2)	1.208(2)	8.3(4)
C(6)	0.911(3)	0.354(2)	1.522(2)	9.8(5)
C(7)	1.572(2)	-0.441(2)	1.534(3)	20.7(8)
C(8)	0.979(2)	0.271(2)	0.911(3)	12.4(6)
C(9)	1.223(3)	-0.563(2)	0.993(2)	13.7(7)
C(10)	1.055(3)	0.341(2)	1.266(2)	10.6(8)
C(11)	1.573(2)	-0.495(2)	1.269(2)	12.8(5)
C(12)	0.749(3)	0.193(3)	0.760(3)	13.2(10)
C(13)	0.815(3)	-0.426(2)	1.134(3)	17(1)
C(14)	0.936(3)	0.083(2)	0.665(2)	16.6(7)
C(15)	1.527(2)	0.200(2)	1.455(2)	11.0(5)
C(17)	1.662(2)	0.038(2)	1.161(2)	15.7(7)
C(19)	0.618(2)	-0.264(2)	1.044(3)	18.9(8)
C(21)	0.838(2)	-0.328(2)	1.262(2)	17.6(8)
C(28)	0.646(3)	-0.319(3)	0.888(2)	30(1)
C(31)	1.216(3)	0.015(2)	0.626(2)	21.5(7)
C(32)	0.899(4)	-0.139(4)	1.685(3)	44(2)
C(33)	0.716(2)	-0.183(2)	1.473(3)	21.6(7)
C(34)	1.430(3)	-0.037(2)	0.629(2)	17.0(7)
C(35)	0.960(3)	-0.367(2)	1.491(3)	19(1)

$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$

Table 2. Anisotropic Displacement Parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)	0.041(2)	0.047(2)	0.064(2)	-0.016(2)	0.008(2)	0.012(2)
Si(2)	0.055(2)	0.044(2)	0.046(2)	-0.013(2)	0.015(2)	- 0.005(2)
Si(3)	0.061(2)	0.040(2)	0.093(3)	-0.014(2)	0.006(2)	0.007(2)
Si(4)	0.047(2)	0.050(2)	0.068(2)	-0.011(2)	0.000(2)	0.019(2)
Si(5)	0.066(2)	0.038(2)	0.063(2)	-0.014(2)	0.031(2)	0.012(2)
Si(6)	0.049(2)	0.058(2)	0.068(2)	-0.025(2)	-0.011(2)	0.012(2)
Si(7)	0.055(2)	0.049(3)	0.075(3)	-0.019(2)	-0.001(2)	0.019(2)
Si(8)	0.057(2)	0.055(3)	0.071(2)	-0.036(2)	-0.010(2)	0.010(2)
Si(9)	0.167(4)	0.046(3)	0.095(3)	-0.020(3)	0.024(3)	-0.007(2)
Si(11)	0.192(7)	0.202(7)	0.344(9)	-0.130(6)	-0.167(6)	0.235(7)
Si(12)	0.076(4)	0.111(5)	0.182(6)	-0.065(3)	-0.003(3)	0.037(4)
Si(13)	0.133(6)	0.141(7)	0.30(1)	-0.081(5)	-0.139(7)	0.183(8)
Si(14)	0.087(4)	0.101(4)	0.132(4)	-0.068(3)	-0.029(3)	0.032(3)
Si(15)	0.232(7)	0.037(3)	0.179(5)	-0.032(4)	0.140(5)	-0.012(3)
Si(16)	0.397(10)	0.063(3)	0.112(4)	-0.085(4)	0.156(5)	-0.023(2)
Si(17)	0.220(6)	0.138(5)	0.176(6)	-0.061(5)	0.142(5)	0.039(4)
O(1)	0.053(5)	0.042(5)	0.070(2)	-0.025(4)	0.019(3)	-0.019(4)
O(2)	0.107(8)	0.034(3)	0.122(8)	-0.023(5)	0.064(6)	-0.010(4)
O(3)	0.071(6)	0.086(6)	0.068(2)	-0.044(5)	-0.008(4)	0.048(4)
O(4)	0.049(6)	0.031(5)	0.091(3)	0.018(4)	0.004(4)	-0.027(3)
O(5)	0.062(3)	0.067(6)	0.076(6)	-0.026(4)	-0.003(4)	0.004(4)
O(6)	0.078(6)	0.080(6)	0.107(6)	-0.062(5)	0.074(5)	-0.018(4)
O(7)	0.054(5)	0.135(7)	0.050(5)	-0.033(5)	-0.023(4)	0.046(5)
O(8)	0.065(6)	0.037(4)	0.148(8)	0.001(3)	0.044(5)	0.007(4)
O(9)	0.061(3)	0.052(6)	0.094(7)	-0.020(4)	0.007(4)	0.038(5)
O(10)	0.047(5)	0.056(3)	0.063(5)	-0.018(4)	-0.009(4)	0.018(3)
O(11)	0.082(6)	0.039(3)	0.058(6)	-0.016(4)	0.014(4)	-0.009(4)
O(12)	0.107(8)	0.093(6)	0.056(3)	-0.057(6)	-0.018(4)	0.048(3)
O(13)	0.076(8)	0.049(4)	0.122(8)	-0.122(6)	0.042(6)	-0.012(4)

Table 2. Anisotropic Displacement Parameters (continued)

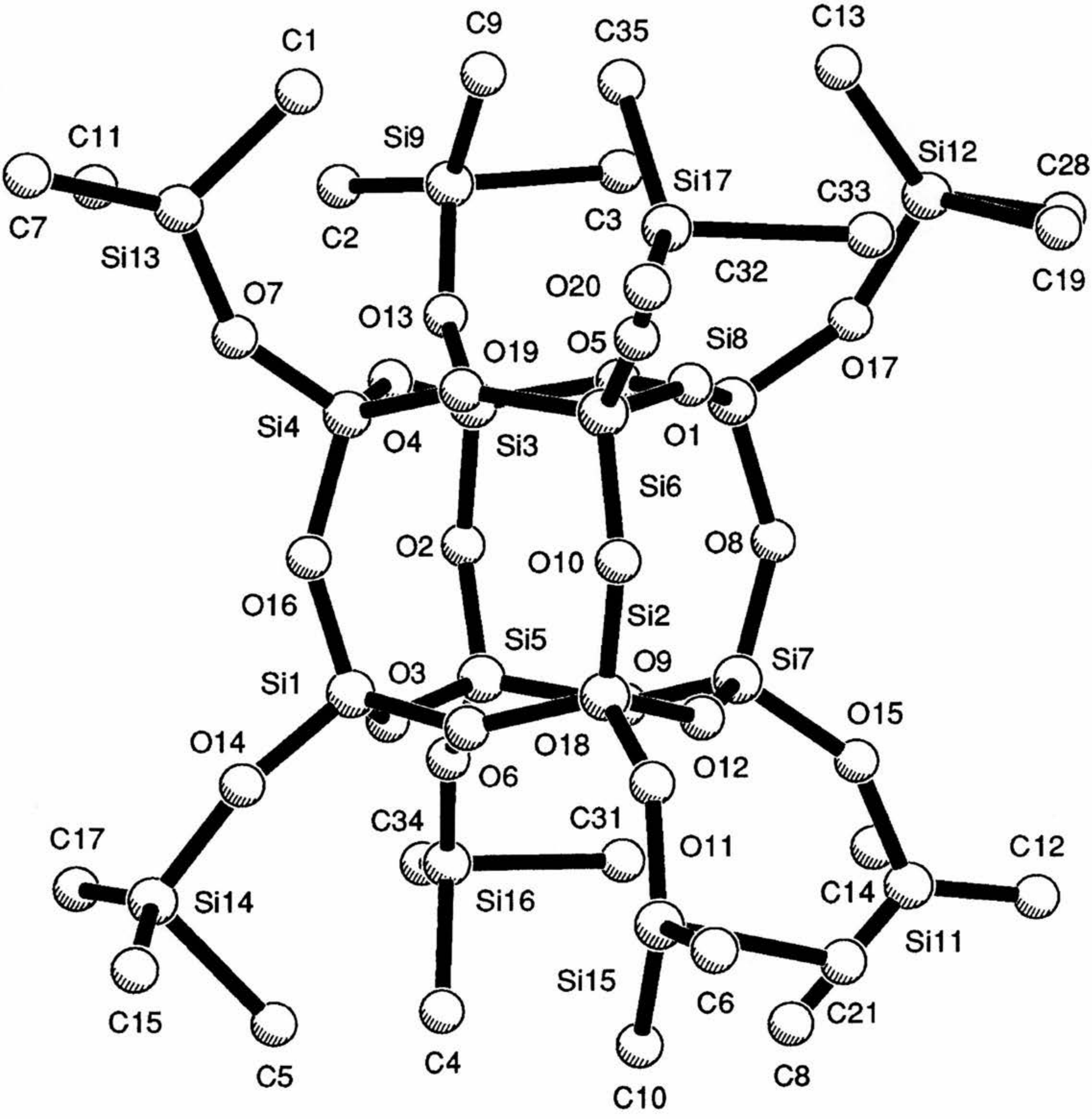
atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(14)	0.060(5)	0.046(6)	0.130(9)	-0.016(4)	-0.015(5)	-0.018(5)
O(15)	0.039(5)	0.071(5)	0.134(8)	0.006(4)	-0.033(4)	0.000(4)
O(16)	0.074(6)	0.064(5)	0.077(6)	-0.049(4)	-0.056(5)	0.051(4)
O(17)	0.078(6)	0.128(7)	0.074(6)	-0.084(5)	-0.041(4)	0.051(5)
O(18)	0.055(3)	0.040(6)	0.090(6)	-0.006(3)	0.019(4)	0.007(5)
O(19)	0.051(3)	0.069(6)	0.080(7)	-0.004(4)	0.012(4)	0.011(5)
O(20)	0.111(7)	0.124(8)	0.040(5)	0.016(6)	-0.013(4)	0.032(5)
C(1)	0.16(1)	0.064(8)	0.088(9)	-0.016(9)	0.003(9)	0.016(7)
C(2)	0.18(2)	0.070(9)	0.32(3)	-0.027(10)	0.16(2)	-0.06(1)
C(3)	0.20(1)	0.119(9)	0.10(1)	-0.098(9)	-0.046(9)	-0.018(8)
C(4)	0.15(2)	0.042(7)	0.17(1)	-0.03(1)	0.06(1)	0.009(8)
C(5)	0.13(1)	0.069(8)	0.14(1)	-0.021(7)	0.052(8)	0.031(7)
C(6)	0.14(2)	0.067(10)	0.15(1)	-0.02(1)	0.017(9)	-0.039(8)
C(7)	0.15(1)	0.27(2)	0.41(3)	-0.11(1)	-0.17(2)	0.19(2)
C(8)	0.14(1)	0.10(1)	0.25(2)	-0.012(8)	0.10(1)	0.04(1)
C(9)	0.28(2)	0.11(1)	0.18(2)	-0.08(1)	0.14(2)	0.04(1)
C(10)	0.18(3)	0.12(2)	0.13(1)	-0.06(2)	-0.02(1)	0.06(1)
C(11)	0.092(9)	0.12(1)	0.27(2)	0.025(8)	0.06(1)	0.06(1)
C(12)	0.18(2)	0.16(3)	0.16(2)	0.01(2)	-0.06(2)	0.13(2)
C(13)	0.34(4)	0.21(2)	0.15(2)	-0.10(2)	-0.01(2)	0.10(2)
C(14)	0.49(3)	0.12(1)	0.034(10)	-0.11(2)	0.00(1)	0.004(9)
C(15)	0.18(2)	0.12(1)	0.130(10)	-0.11(1)	-0.05(1)	0.002(7)
C(17)	0.16(2)	0.17(2)	0.28(2)	0.00(1)	0.15(1)	0.03(1)
C(19)	0.061(9)	0.34(3)	0.34(2)	-0.008(10)	0.07(1)	0.13(2)
C(21)	0.29(2)	0.14(2)	0.20(2)	0.03(2)	-0.02(1)	0.06(2)
C(28)	0.23(3)	0.85(7)	0.22(1)	-0.40(4)	-0.15(1)	0.19(2)
C(31)	0.58(3)	0.14(2)	0.047(8)	-0.01(2)	-0.06(2)	0.014(9)
C(32)	0.49(5)	0.9(1)	0.18(4)	-0.10(6)	0.12(3)	-0.38(5)
C(33)	0.124(6)	0.13(1)	0.61(3)	-0.011(9)	0.21(1)	0.06(2)

Table 2. Anisotropic Displacement Parameters (continued)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(34)	0.43(3)	0.12(1)	0.14(1)	-0.05(2)	0.20(2)	0.019(9)
C(35)	0.33(3)	0.113(7)	0.31(4)	-0.08(2)	0.01(2)	0.07(2)

The general temperature factor expression:

$$\mathrm{Exp}(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$


C1
C9
C35
C13
C11
Si9
Si12
C28
Si17
C7
Si13
C2
C3
C33
C32
C19
O7
O20
O13
O19
O5
Si8
O17
Si4
O4
Si3
O1
Si6
O2
O10
O8
O16
Si2
Si5
Si1
O3
O9
Si7
O15
O14
O18
O6
O12
C34
C31
O11
C17
C12
C14
Si14
Si16
Si11
Si15
C6
C21
C15
C5
C4
C8
C10

X-ray Structure Report

Monday June 23 1997

Experimental

Data Collection

A ColourlessBlock Block crystal of $Si_8O_{12}C_{37}H_{80}$ having approximate dimensions of 0.40 x 0.35 x 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 14 carefully centred reflections in the range $7.61 < 2\theta < 13.09^{\circ}$ corresponded to a trigonal hexagonal cell (laue class: $\bar{3}$) with dimensions:

$$a = 15.964(9)\ \text{Å}$$
$$c = 16.946(7)\ \text{Å}$$
$$V = 3740(1)\ \text{Å}^3$$

For Z = 3 and F.W. = 941.72, the calculated density is 1.25 g/cm^3. Based on the systematic absences of:

hkil: -h + k + l != 3n

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$$R\bar{3}\ (\#148)$$

The data were collected at a temperature of $20 \pm 1^{\circ}$C using ω-2θ scan technique to a maximum 2θ value of 40.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.49° with a take-off angle of 6.0°. Scans of $(1.89 + 0.35 \tan\theta)^{\circ}$ were made at a speed of 16.0°/min (in omega). The weak reflections ($I < 15.0\sigma(I)$) were rescanned (maximum of 4 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm and the crystal to detector distance was 235 mm. The computer controlled slits were set to 9.0 mm (horizontal) and 13.0 mm (vertical).

Data Reduction

Of the 2436 reflections which were collected, 780 were unique ($R_{int} = 0.044$). The intensities of three representative reflection were measured after every 150 reflections. No decay correction was applied.

The linear absorption coefficient, μ, for Mo-Kα radiation is 2.7 cm^{-1}. Azimuthal scans of several reflections indicate no need for an absorption correction. The data were corrected for Lorentz and polarisation effects.

Structure Solution and Refinement

The structure was solved by direct methods [1] and expanded using Fourier techniques [2]. The non-hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement [3] was based on 780 observed reflections ($I > 0.00\sigma(I)$) and 49 variable parameters and converged (largest parameter shift was 3.16 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma||Fo| - |Fc|| / E|Fo| = 0.174$$

$$Rw = [\Sigma w(|Fo| - |Fc|)^2/\Sigma wFo^2]^{0.5} = 0.183$$

The standard deviation of an observation of unit weight [4] was 7.12. The weighting scheme was based on counting statistics and included a factor ($p = 0.002$) to downweight the intense reflections. Plots of $\Sigma w(|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.35 and -0.55 $e^-/$ Å ^{3}, respectively.

Neutral atom scattering factors were taken from Cromer and Waber [5]. Anomalous dispersion effects were included in Fcalc [6]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [7]. The values for mass attenuation coefficients are those of Creagh and Hubbel [8]. All calculations were performed using the teXsan [9] crystallographic software package of Molecular Structure Corporation.

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[1] SIR92: Altomare, A., Burla, M.C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A., Polidori, G. (1994). J. Appl. Cryst., in preparation.

[2] DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegan, The Netherlands.

[3] Least-squares:

Function minimised: $\Sigma w(|Fo| - |Fc|)^2$

where $w = 1/[\sigma^2(Fo)] = 4Fo^2/[\sigma^2(Fo^2)$

$\sigma^2(Fo2) = S^2(C + R^2B) + (pFo^2)^2/Lp^2$

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

B = Total background count

Lp = Lorentz-polarisation factor

P = p-factor

[4] Standard deviation of an observation of unit weight:

$$[\Sigma w(|Fo| - |Fc|)^2/(No - Nv)]^{0.5}$$

where: No = number of observations
Nv = number of variables

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Experimental Details

A. Crystal Data

Empirical Formula	$Si_8O_{12}C_{37}H_{80}$
Formula Weight	941.72
Crystal Colour, Habit	ColourlessBlock, Block
Crystal Dimensions	0.40 X 0.35 X 0.30 mm
Crystal System	trigonal

Lattice Type	R-centred
No. of Reflections Used for Unit Cell Determination (2q range)	14 (7.6 – 13.1°)
Omega Scan Peak Width At Half-height	0.49°
Lattice Parameters	a = 15.964(9) Å
	c = 16.946(7) Å
	V = 3740(1) Å^3
Space Group	R$\bar{3}$ (#148)
Z value	3
D_{calc}	1.254 g/cm^3
F_{000}	1530.00
μ(MoKα)	2.68 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC7S
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated