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Novel materials based on functionalised silsesquioxanes

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NOVEL MATERIALS BASED ON FUNCTIONALISED SILSESQUIOXANES

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STATEMENT

The work included in this thesis was carried out by the author during the period October 1996 to September 2000, in the chemistry department at the Open University, under the supervision of Professor Alan Bassindale and Dr Peter Taylor.

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ABSTRACT

The functionalisation of silsesquioxanes results in materials with novel physical properties. A series of compounds has been coupled with silsesquioxanes $[HSiO_{3/2}]_8$ and $[SiO_{3/2}]_8[OSi(CH_3)_2H]_8$ and the properties of the products investigated. Typically, coupling reactions involved hydrosilylation with H_2PtCl_6 or $[Pt\{(\eta-ViMe_2Si)_2O\}(P^tBu_3)]$.

Mesogenic compounds have been shown to undergo a change in the liquid crystalline phase produced, once attached to the silsesquioxane core. A more ordered phase was observed due to the tethering of the mesogen to the cage. The silsesquioxanes core was considered to have been deformed in the production of this phase.

Silsesquioxanes capable of complexing metal atoms have also been studied. Polyether derivatised cages were prepared and preliminary studies indicate potential for potassium complexation. Vinyl functionalised silsesquioxanes have also been shown to complex platinum, in an exchange reaction with $[Pt\{(\eta-ViMe_2Si)_2O\}(P^tBu_3)]$.

Investigations into the hydrosilylation reaction have involved coupling triethylsilane, triethoxysilane and the silsesquioxanes with a variety of vinyl, allyl and alkenic compounds. The proportions of α and β adducts were considered. Particular substituents were found to encourage α addition, with species having an oxygen or phenyl group at the allylic position producing the α-regioisomer as well as the typical β product. It is suggested that such substitution affects the mode of *cis* ligand insertion in the Chalk

Harrod mechanism. A preference for the α-regioisomer was also observed for the hydrosilylations of vinyl silsesquioxane compounds.

ABBREVIATIONS

COSY	Correlated Spectroscopy
DEPT	Distortionless enhancement by polarization tranfser
DIPEA	Diisopropylethylamine
DHB	2,5-Dihydroxybenzene
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DSC	Differential Scanning Calorimetry
D_3	Hexamethylcyclotrisiloxane
D_4	Octamethylcyclotetrasiloxane
D_5	Decamethylcyclopentasiloxane
FTIR	Fourier Transform Infra Red
GPC	Gel Permeation Chromatography
HOBt	1-hydroxybenzotriazole
D-HyV	D-α-Hydroxyvaleric Acid
Iso	Isotropic Liquid
K	Crystalline Solid
L-Lac	L-Lactic Acid
MEK	Methylethylketone
MAS NMR	Magic Angle Spinning Nuclear Magnetic Resonance
N	Nematic
NMR	Nuclear Magnetic Resonance
OMM	Organolithic Macromolecular Material

ppm	Parts per million
Pyr	Pyridine
S	Smectic
S_A	Smectic A
S_B	Smectic B
S_C	Smectic C
T_8	Octa(hydrido)silsesquioxane
TBTU	O-(7-benzotriol-1-yl)-1,1,3,3-tetramethyluronium
TEOS	Triethoxysilane
TES	Triethylsilane
THF	Tetrshydrofuran
Tg	Glass Transition Temperature
T_h	Tetrahedral
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMAS	Tetramethylammoniumsilicate
TMDS	Tetramethyldisiloxane
D-Val	D-Valine
L-Val	L-Valine
UV	Ultra Violet Visible spectroscopy

For Mum

"...when I see you in my dreams does it mean anything, are you trying to talk to me..."

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CHAPTER ONE

An Introduction to Silsesquioxanes

1.0 GENERAL INTRODUCTION

Silsesquioxanes[1] are a unique class of three dimensional polyhedral silicon oligomers that have recently attracted a great deal of interest from the polymer industry. The desire for materials with specific molecular formulae and controlled physical properties has increased dramatically in recent years. Silsesquioxanes had previously seen limited use, generally because of their time-consuming syntheses. Recent developments have led to the consistent and simple production of sizeable quantities of such materials. With the general formula $(RSiO_{3/2})_n$, where n is an even number, they are composed of a silicon-oxygen framework where R can be an organic or inorganic substituent. R is typically a methyl, halogen, vinyl or phenyl group, with each silicon atom bound to three oxygens. Also referred to as spherosiloxanes, the polyhedral organisation of these frameworks can be random, ladder-like, or cage, (complete or partial). Silsesquioxanes have immense potential for the preparation of highly functionalised compounds. The nature of the R group enables the synthesis of numerous species with pre-defined structures. A number of hydrogen silsesquioxanes are known ranging from n = 6 to 16^2. Silsesquioxanes are commonly synthesised by a condensation route involving complete hydrolytic condensation of trifunctional monomers such as $HSiCl_3$.

n=8   n=12
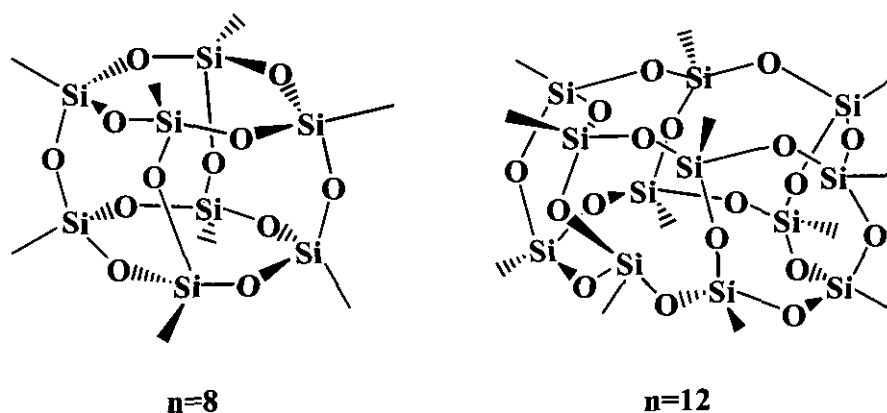
Figure 1: Polyhedral representation of silsesquioxanes with general formula $[RSiO_{3/2}]_n$

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The most common and therefore most widely studied silsesquioxane is the octamer where n=8. The hydrogen silsesquioxane, which has eight hydrogen atoms bonded to the silicon atoms at the corners of the silicon-oxygen core, $(HSiO_{3/2})_n$ is called T_8H_8[3]. The crystal structure of the compound has been shown to have a T_h symmetry for the Si_8O_{12} framework, and S_6 symmetry for the hydrogen atoms[4].

Throughout this thesis, the central core of the octameric compound T_8 will be represented as a cube, as shown in Figure 1b.

n = 8
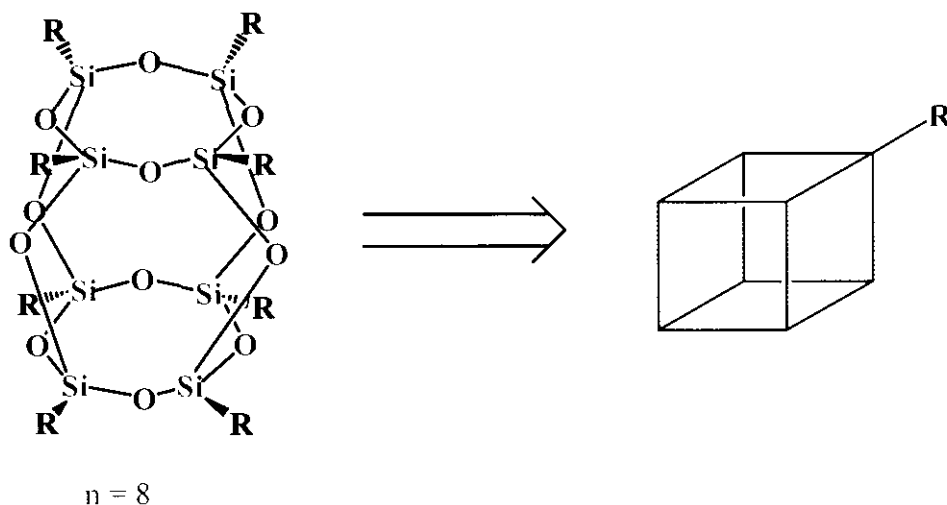
Figure 1b. Schematic representation of T_8

Silsesquioxanes date back to the 19th century when simple octameric compounds were first synthesised by hydrolysis of $RSiCl_3$ [5,6]. The intention was to produce analogues of carboxylic acids in the form of $RSiO_2H$, with the resulting products being inaccurately thought to be the anhydrides, $(RSiO)_2O$[7]. In the 1930's cyclohexylsilsesquioxanes $(C_6H_{11}SiO_{3/2})_n$[8] were prepared and patented for use as a thermoplastic material[9]. Methylsilsesquioxane $(CH_3SiO_{3/2})_n$[10] was also successfully prepared from methyltrichlorosilane in 1946 and identified as the octameric compound[11].

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These crucial syntheses led the way in raising the profile of silsesquioxane chemistry. Interest has escalated as new synthetic pathways have been devised. This growth is highlighted by the increase in patent applications for silsesquioxane materials.

1.1 NOMENCLATURE

Compounds with the general formula $(RSiO_{3/2})_n$ are named using a systematic nomenclature based on the polycyclosiloxane framework. The syllables 'sil', 'sesqui' and 'oxane' refer to the ratio of silicon atom to 3/2 oxygen atoms. The substituents attached to the silicon atoms are named in accordance with IUPAC terminology[12]. In cases were the number of similar substituents in the molecule is equal to the number of siloxane links i.e. $(RSiO_{3/2})$, no figures are used to denote the position of these substituents. An example of this trivial nomenclature is $(HSiO_{3/2})_8$ which is known as octasilsesquioxane or octa(hydridosilsesquioxane)[3].

For ease of reference, when discussing a number of silsesquioxane species, a further trivial system has been devised. Here the symbol refers to the number of oxygen atoms surrounding the silicon atom. This can be between 1 and 4 oxygen atoms, the prefix given relates to that number. For example, a mono-substituted silicon compound would be given the prefix M, D for a di-substituted species, T for tri-substituted and Q for a quaternary silicon atom, as indicated in Table 1.

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Structure	Composition	Functionality	Symbol
R | R—Si—R | R	R_4Si		N
R | R—Si—O | R	$R_3SiO_{1/2}$	Monofunctional	M
O | R—Si—O | R	R_2SiO	Difunctional	D
O | R—Si—O | O	$RSiO_{3/2}$	Trifunctional	T
O | O—Si—O | O	SiO_2	Tetrafunctional	Q

Table 1 :Nomenclature for siloxanes

1.2 APPLICATIONS AND USE OF SILSESQUIOXANES

Recently these novel compounds have been used as well defined models for silica surfaces[13] and as ligands for main group and transition metal catalysts on silica surfaces[14-17]. Silsesquioxanes have also found widespread use in sol-gel polymerisation[18], as liquid crystalline polymers[19], alternatives for SiO_2 thin films[20] and as models for zeolite activity[21]. The framework of the cage of the spherosilicate is considered to be analogous to the double 4-ring of a zeolite[21].

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1.3 GENERAL PREPARATION OF SILSESQUIOXANES

In 1991 Bürgy, Calzaferri, Herren and Zhdanov[22] identified three methodologies for preparing both spherosiloxanes and spherometallosiloxanes as;

a)   Hydrolytic condensation of trifunctional monomers, as utilised by Frye and Collins[3] and shown in Figure 2.

Figure 2 :Hydrolytic condensation of trifunctional monomers

This strategy employs reactions that form new Si-O-Si bonds, with continued build up of the Si-O lattice. These reactions are complex, multi-step processes that allow the synthesis of silsesquioxanes from silanes and linear, cyclic or polycyclic siloxanes. The first hydrolytic condensation of silsesquioxanes was carried out by Andrianov et al..[23] who reacted 1,3,5,7 tetramethylcyclotetrasiloxane with 1,3,5,7 tetraphenylcyclotetra-1,3,5,7 siloxanol, to give the corresponding phenyl-methyl silsesquioxane. This early work led the way to a range of oligosilsesquioxane chemistry. A review was published in 1982[2] documenting oligosilsesquioxane condensation chemistry.

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a)   Hydrolytic condensation of trifunctional monomers, as utilised by Frye and Collins[3] and shown in Figure 2.

ASiX$_3$

DSiX$_3$ $\xrightarrow{\text{H}_2\text{O}}$

RSiX$_3$

Figure 2 :Hydrolytic condensation of trifunctional monomers

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b) Chemical modifications of substituents already present on the silsesquioxane, as utilised by Feher and Budzichowski in the hydrogenation of aryl-substituted silsesquioxanes[24]. This is represented in Figure 3.
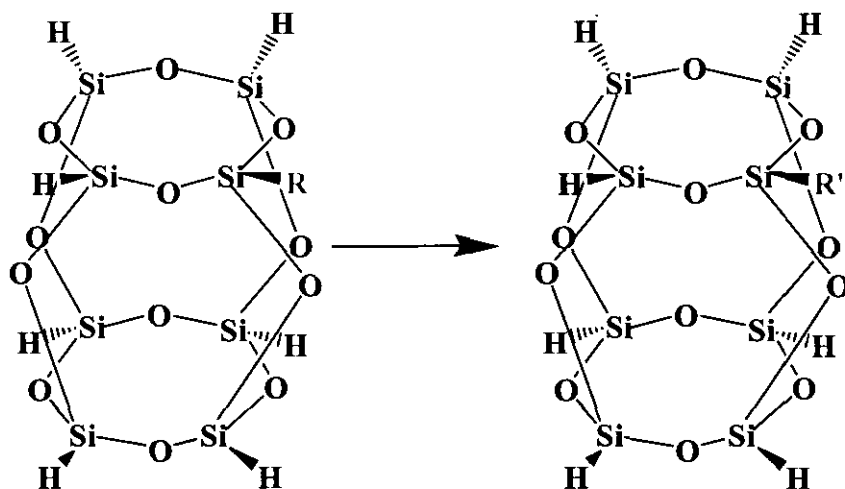
Figure 3: Substituent modifications of a silsesquioxane

Examples of this methodology include the preparation of $[SiO_{3/2}]_8\{C_6H_5Cl\}_8$, in order to synthesise new silsesquioxanes by replacement of the chlorine atoms, as shown in Reaction Scheme 1.

Compound 1

Compound 2
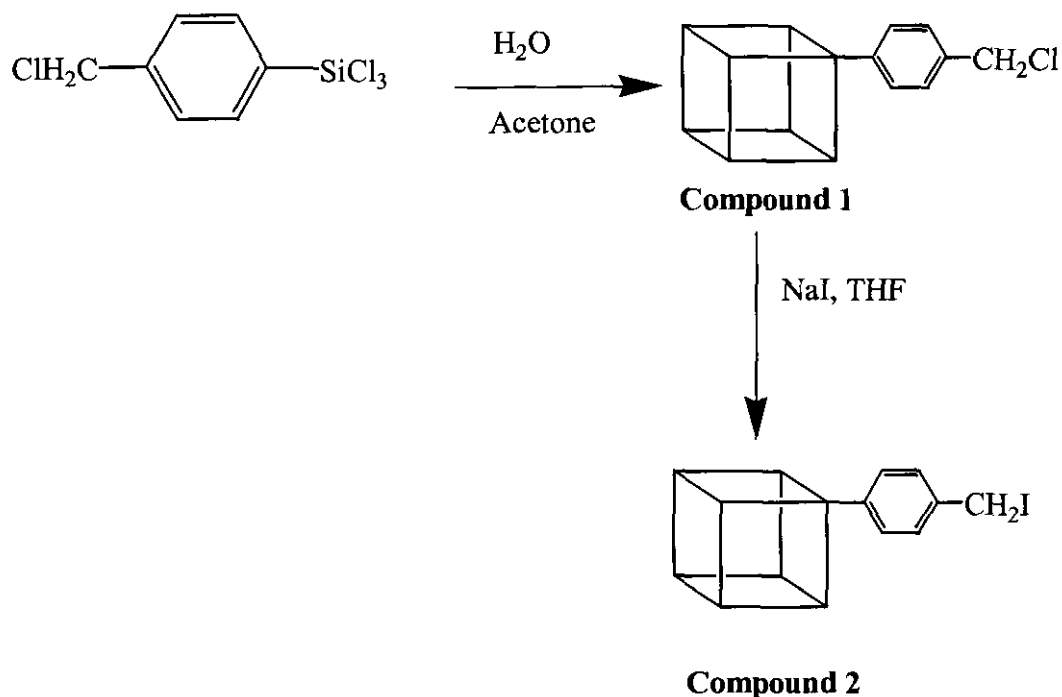
Reaction Scheme 1: Preparation of Functionalised silsesquioxanes by Feher[24]

c) Reaction at the atom directly attached to the silicon of the cage framework, as
    represented in Figure 4.
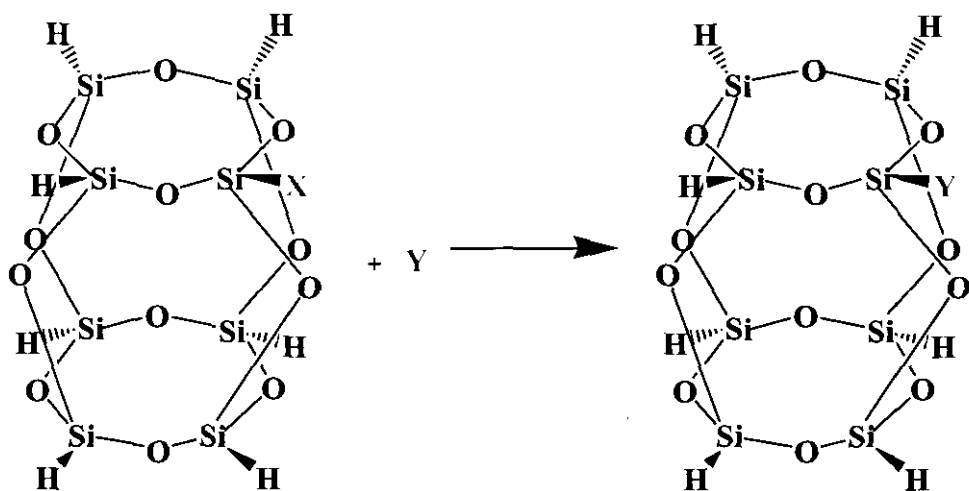
Figure 4: Reactions of silsesquioxanes.

Until recently only three examples of this reaction had been published. Firstly the

photochlorination of $(HSiO_{3/2})_8$, to produce $(ClSiO_{3/2})_8$, was reported by Klemperer in

1985[18]. Similarly the methoxylation of $(ClSiO_{3/2})_8$ by CH_3ONO resulting in $(CH_3OSiO_{3/2})_8$ is reported in the same paper. This methodology has been further developed by Agaskar to successfully synthesise organolithic macromolecular materials (OMM's)[25,26]. OMM's are substances containing both silicate and organic compounds. Other examples of the use of this methodology include the deuterium exchange of $(HSiO_{3/2})_8$ to give $(DSiO_{3/2})_8$ catalysed by Pd as described by Bürgy and Calzaferri[27] . This process was assumed to be a radical mechanism.

In the first part of this literature review, the preparation of silsesquioxanes based on hydrolytic condensations will be discussed.

1.4 HYDRIDO-SILSESQUIOXANE PREPARATION.

The earliest work on silicon-oxygen compounds focused on the production of silicon oxyhydride, $HSiO_{3/2}$. This highly crosslinked polymer was first called silicoformic anhydride by analogy with the carbon compounds of similar molecular formulae. Buff and Wohler first prepared this compound in 1857[5] by the hydrolysis of trichlorosilane in water. Since then variations in the synthesis have resulted in improved yields. Schwarz[28] prepared the compound by passing trichlorosilane vapour in dry air through water at O°c, this produced a sample of 80% purity. In 1920 Schwarz and Sourard used the same procedure, but using CO_2 as the carrier gas, and improved yields to 92%[29]. Müller found triethoxysilane afforded the same compound in good yield[30].

At this stage, chemists were not aware of the structure of the products obtained. With improvements in characterisation techniques, analysis was possible to identify the exact

nature of the mixtures. This resulted in more direct syntheses to give species such as linear, ring and cubic siloxanes[30,31,32,33,34].

The earliest reported synthesis of hydrogen silsesquioxane involved the vapour and solution hydrolysis of trichlorosilanes and trialkoxysiloxanes[30,31]. The products were completely insoluble, non-volatile, cross-linked gels, which were shown to be amorphous using X-ray crystallography. Wiberg and Simmler described the initial synthesis of soluble hydrogen silsesquioxane in 1956[32]. The hydrolysis of $HSiCl_3$ in ether was carried out with stoichiometric quantities of water at -40°C. Although said to be soluble, the product was found to be an insoluble gel upon evaporation of the reaction solvent.

The first reported fully condensed, completely soluble, oligomeric silsesquioxane was prepared unintentionally by Müller et al.. in 1959 whilst studying the preparation of compound 3[33]. The octa(hydrido)silsesquioxane was made by the hydrolysis of trichlorosilane with 80% sulfuric acid in the presence of $Me_3SiOSiMe_3$.

$$Me_3SiO \underset{}{\overline{}} [Si(OSiMe_3)O]_{\overline{x}} OSiMe_3$$

Compound 3

With yields of just 0.2%, the cubic structure of T_8 was confirmed by single crystal X-ray crystallography[4]. The octameric compound was found to be sparingly soluble in benzene and hexane.

Some ten years later, Frye and Collins reported a major improvement in the method of silsesquioxane preparation. The slow addition of a solution of $HSiCl_3$ in benzene, to a

stirring solution of benzene and sulfuric acid, afforded the octa(hydrido)silsesquioxane, T_8H_8, along with higher homologues[3], as shown in Reaction Scheme 2.

$$HSiCl_3 \xrightarrow[C_6H_6]{H_2SO_4} (HSiO_{3/2})_{8-12} + (HSiO_{3/2})_{>16}$$

Volatile   Non-Volatile
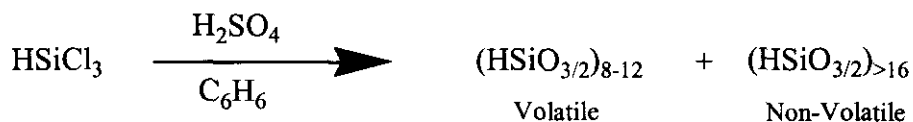
Reaction Scheme 2: Scarce water hydrolysis of (hydrido)silsesquioxane.

Yields of up to 99% were achieved for the mixture of hydrogen silsesquioxanes. However, analysis of the resultant resin revealed that 92% of this comprised volatile components such as T_{10}, T_{12}, T_{14}, and T_{16}. T_8H_8 was present in only trace amounts. Frye and Collins went on to develop a dilute solution hydrolysis of $HSi(OMe)_3$ using concentrated HCl, in a cyclohexane-acetic acid medium[3]. Yields of the octomer were increased to 13%.

Research in silsesquioxane chemistry has been limited by the poor yields of T_8H_8 that could be obtained. Agaskar et al. were influential in developing a more efficient procedure[34]. In 1987, they published a modification to the Frye and Collins procedure which gave mixtures of the spherosilicate compounds in yields as great as 30%. Utilising 'scarce water hydrolysis', followed by gel permeation chromatography, a mixture of cages $(HSiO_{3/2})_n$, n=8, 10, 12, 14 and 16 was obtained. $[Si_{12}O_{18}]H_{12}$, compound **4**, and two isomers of $[Si_{14}O_{21}]H_{14}$, compound **5** were subsequently isolated. The structures of these compounds were characterised by X-ray crystallography and NMR spectroscopy. Compound **4** was found to have a D_{2d} framework, whilst one isomer of compound **5** had D_{3h} and the second isomer was less symmetrical with a C_{2v} framework[34]. The addition of $Me_3NOSiMe_3Cl$ to these purified siloxanes enabled trimethylsilylated derivatives to be prepared. Agaskar developed his synthetic procedure further in 1991[35], enabling the

isolation of reasonable quantities of T_8H_8. To this point, yields of individual species had been low, procedures elaborate and purification difficult. This new preparation of T_8H_8 involved addition of trichlorosilane to a biphasic mixture of iron chloride in toluene, hexane, HCl and methanol. Stirring the mixture for 9 h, followed by drying and reducing the organic layer, yielded a mixture of T_8 and T_{10} (3.5:1) in approximately 27.5% yield. Recrystallisation in hexane resulted in a 17.5% yield of pure T_8H_8. The symmetrical structure of the pure compounds was confirmed by ^{29}Si NMR spectroscopy.

The thermal reactivity of hydrogensilsesquioxanes prepared from trichloro and trialkoxysilanes was reported by Corriu in 1991[36]. Under argon at temperatures greater than 400°C cleavage of the Si-H bonds led to redistribution of the cage, producing SiH_4. When ammonia was added thermal decomposition of the silsesquioxanes produced a silicon oxynitride ceramic. This application involved rapid thermal processing at 400°C. Thus hydrogensilsesquioxane could be used to form silica coatings for environmental protection and dielectric circuits.

Throughout the development of siloxane chemistry functionalised silsesquioxanes have been a major goal. Initially, condensation reactions were attempted in a direct adaptation of the cage formation procedure. However, these preparations were fraught with poor yields and impurities. Hydrosilylation reactions were found to be one way of achieving octameric silsesquioxanes in high yields[37].

1.5 FUNCTIONALISED SILSESQUIOXANES.

1.5.1 Preparation through condensation routes

A series of crystalline organosilsesquioxanes were prepared using alkali-catalysed silicone cracking. Barry et al.[38] carried out siloxane re-arrangement of organotrichlorosilane hydrolyzates. This salt catalysed both condensation and rearrangement of siloxanes. The lower molecular weight silsesquioxanes produced were distilled and crystallised. Methyl, ethyl, *n*-propyl, *n*-butyl and cyclohexyl derivatives were prepared in this way. The octaphenylsilsesquioxane was produced by means of a KOH solution. Although these techniques provided reasonable yields, 80-90%, the process was slow and complex.

Olsson described the development of a single, high yielding route to octafunctionalised silsesquioxanes[39,40]. Sprung and Guenther[41] obtained methylsilsesquioxane in 10%, but the ethyl compound in only 1.1% yield. Olsson investigated the hydrolysis of ethyltrialkoxysilane with methanol and HCl. Sublimation was used to obtain the pure product in optimum yield. As with the work of Barry et al., the *n*-propyl, n-butyl, *iso*-propyl, phenyl and methyl derivatives were prepared. Rates of the hydrolysis of the trialkoxysilanes were studied, with the expected trend, ethyl>*iso*-propyl>*tert*-butyl, as a result of steric hindrance.

Of these functionalised silsesquioxanes the octa(phenylsilsesquioxane)[42] has received the most attention. This compound is characterised by its high thermal stability. It was reported that the compound crystallises in several forms, monoclinic, triclinic[43] and rhombohedral[44]. A number of methods of preparation have been studied including the

mixing of phenyltrichlorosilane, acetone and water[45]. The molecular structure was analysed by Hossain et al. in 1979[46]. The eight phenyl rings were combined to form a cage with silicons at the corners bridged by oxygens. An acetone molecule was found to be trapped in the cavities formed by six silsesquioxanes, without having specific intermolecular interactions.

Day, Klemperer, Mainz and Millar prepared functionalised silsesquioxanes in 1985[18]. A two step reaction sequence was used to prepare $[SiO_{3/2}]_8[OCH_3]_8$. Initial attempts via an alkylation of $[Si_8O_{20}]^{8-}$ were unsuccessful due to insoluble intermediates. Using T_8 prepared via 'scarce water hydrolysis', the functionalised silsesquioxane was produced by a photochemical chlorination, followed by sublimation of the product. The chlorinated octomer $(ClSiO_{3/2})_8$, was then reacted with methyl nitrite in a sealed tube, as shown in Reaction Scheme 3. Structural parameters were determined by single X-ray crystallography.

STEP 1

$$[HSiO_{3/2}]_8 \ + \ Cl_2 \ \xrightarrow{\textit{hv, CCl}_4} \ [ClSiO_{3/2}]_8 \ + \ 8HCl\uparrow$$

STEP 2

$$[ClSiO_{3/2}]_8 \ + \ CH_3ONO \ \longrightarrow \ [SiO_{3/2}]_8[OCH_3]_8 \ + \ 8NOCl\uparrow$$
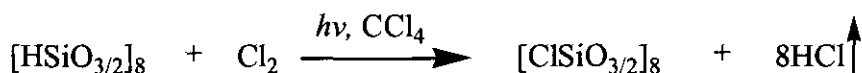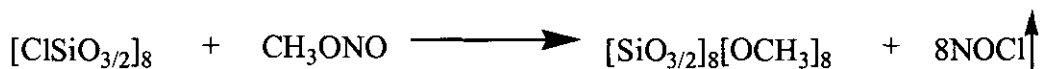
Reaction Scheme 3: A Route to Methoxy Functionalised Silsesquioxane

Sublimation and crystallisation from toluene gave the methoxysiloxane in 45% yield. Analysis by ^{29}Si NMR confirmed the polysilicate framework remained intact throughout the reaction process.

As mentioned earlier, Feher and Budzichowski reported a hydrolytic condensation of a substituted chlorosilane (Reaction Scheme 1)[24]. Compound **1** was prepared from *p*-$ClCH_2C_6H_4SiCl_3$ in relatively low yields (6-15%) by condensation in aqueous acetone. The octamer was found to provide an excellent entry into a variety of octafunctionalised silsesquioxanes through replacement of the peripheral chlorine atoms. The benzyl chloride groups in compound **1** were found to be remarkably inert towards substitution and hydrolysis. For example, no reaction was observed in the presence of $AgNO_3$ or $AgClO_4$ in aqueous acetone. This prompted an investigation into the electron withdrawing nature of the Si_8O_{12} framework. Studies indicated an equivalence to that of the trifluoromethyl group, CF_3. The overall inertness prevents compound **1** from being used to synthesise a range of functionalised silsesquoixane molecules. The iodide derivative, compound **2**, prepared by refluxing compound **1** with NaI in THF in the dark, was far more reactive towards substitution. From the octa(iodobenzyl)silsesquioxane Feher et al. prepared a variety of further functionalised compounds including esters and phenols, as shown in Figure 5.

R =

$-CH_2OH$

$-CH_2ONO_2$

$-CH_2O$—C(=O)—OCH_3

$-CH_2O$—C(=O)—O—(p-C$_6$H$_4$)—NO_2

$-CH_2O$—C(=O)—O—(p-C$_6$H$_4$)—C(=O)—OCH_3
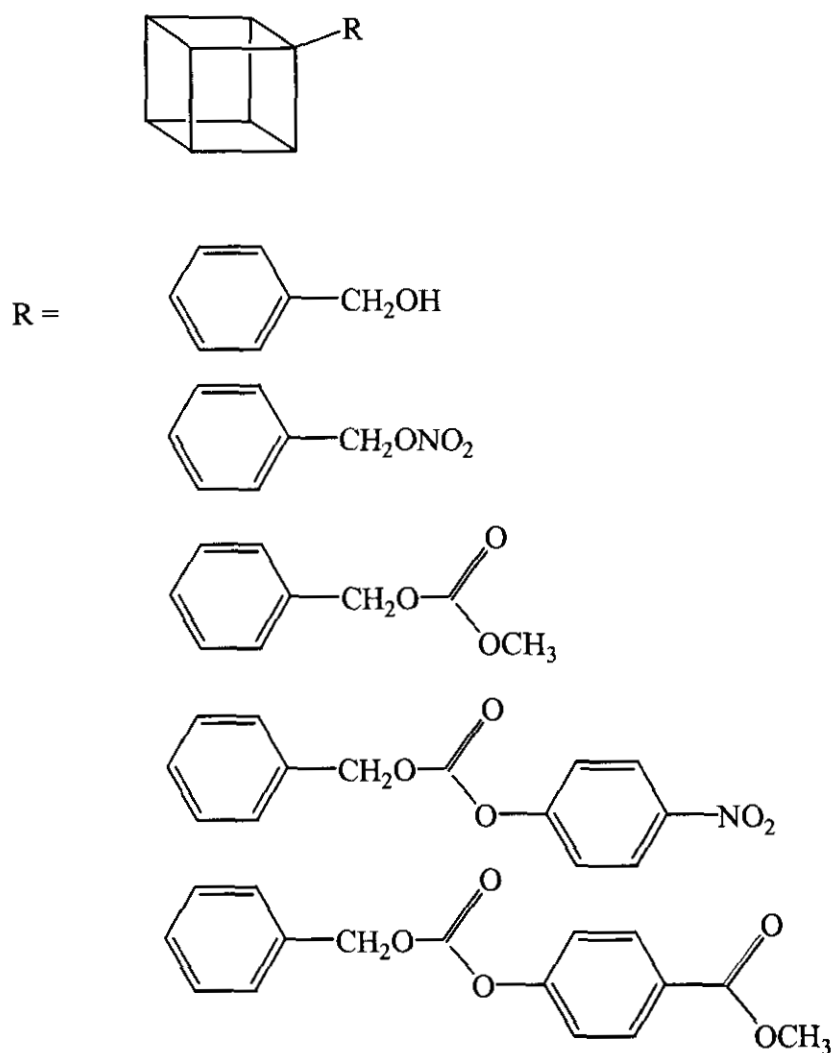
Figure 5: Silsesquioxanes prepared by Feher from Compound 2

Compound **2** was later used to prepare a series of organometallic gels[47] via the phosphorous substituted silsesquioxanes synthesised as shown in Reaction Scheme 4.

$$[p\text{ICH}_2\text{C}_6\text{H}_4\text{SiO}_{3/2}]_8 \xrightarrow{\text{Ph}_2\text{POEt}} [\text{Ph}_2\text{P(O)CH}_2\text{C}_6\text{H}_4\text{SiO}_{3/2}]_8$$

Compound 2

$$\downarrow \begin{array}{l} \text{AlH}_3 \\ \text{Trifluoroacetic acid} \end{array}$$

$$[(\text{Ph}_2\text{PCH}_2\text{C}_6\text{H}_4)_{8-n}(\text{CH}_3\text{C}_6\text{H}_4)_n\text{Si}_8\text{O}_{12}]$$
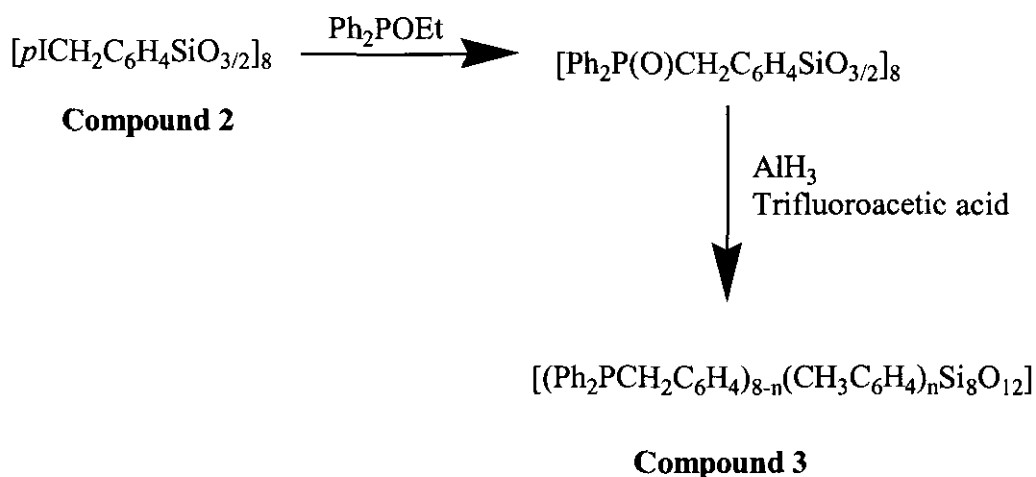
Compound 3

Reaction Scheme 4: Phosphorous silsesquioxanes prepared using compound 2

A number of difficulties in the preparation of compound **3** were encountered, particularly the reduction of $[\text{Ph}_2\text{P(O)CH}_2\text{C}_6\text{H}_4\text{SiO}_{3/2}]_8$. A number of reducing agents were tried, but this was limited by its relative insolubility. AlH_3 in trifluoroacetic acid was the most successful. The final product was a mixture of many different silsesquioxanes with a statistical distribution of $\text{C}_6\text{H}_4\text{CH}_3$ and $\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2$ groups. Compound **3** was further reacted with $[(\text{CO})_2\text{RhCl}]_2$ to produce an organometallic gel. It was observed that the majority of the ruthenium from the metallic reagent had been incorporated into the final product.

Such organometallic gels were expected to exhibit catalytic activity. However, attempts by the authors to effect olefin isomerisation, hydroformylation and hydrogenation were disappointing. The dissociation of the phosphine from the Rh, which was required to achieve catalytic activity, proved to be difficult in such a silsesquioxane network.

In an attempt to prepare new and potentially useful silsesquioxanes, the hydrogenation of a number of octameric species such as, $[\text{PhSiO}_{3/2}]_8$, $[\text{PhSiO}_{3/2}]_{12}$ and $[p\text{-tolSiO}_{3/2}]_8$ was also examined[48]. The starting compounds were prepared in a condensation process from the

corresponding aryltrichlorosilane and analysed by ^{1}H, ^{13}C, ^{29}Si NMR, mass spectrometry and infrared spectroscopy. Hydrogenation of these species using 10% Pd/C yielded the expected products, as shown in Figure 6. Hydrogenation of compound **4** and **5** afforded little selectivity, producing a mixture of both the *cis* and *trans* isomers. The hydrogenated compounds were found to exhibit similar air and thermal stabilities to the compounds from which they were derived; however their solubilities were greatly improved.

YIELDS

70% cis
30% trans

Compound 4

76% cis
26% trans

Compound 5
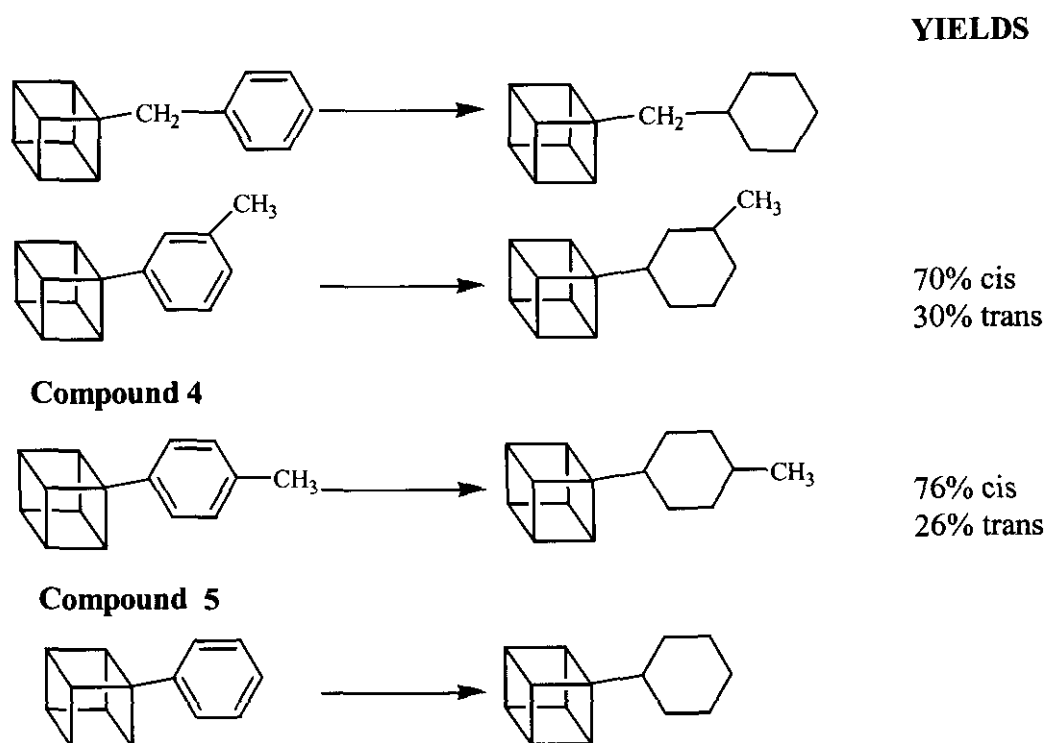
Figure 6: Hydrogenated side arms of silsesquioxanes. *Cis/trans* refers to the configuration of the methyl substituents relative to the siloxane framework on the cyclohexyl rings.

Dendrimer molecules have also been prepared using oligosilsesquioxanes[49,50] prepared via a condensation process. Several new compounds including the amine compound **6**[51] and the ester compound **7**[52], were produced in anticipation of their use in dendrimer synthesis.

Compound 6

Compound 7
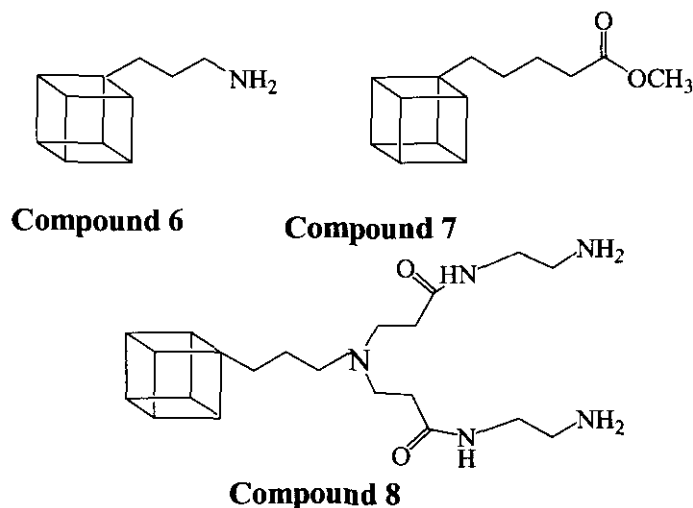
Compound 8

The octaamine was synthesised as the hydrochloride salt in a one step process from $H_2N(CH_2)_3Si(OEt)_3$, whereas compound **7** was prepared by hydrosilylation of methyl 3,3-dimethylpent-4-enoate with T_8H_8[52]. The preparation of dendrimer species involved a standard synthesis via the progressive reactions of compound **6** with methyl acrylate and ethylenediamine to produce compound **8**[51].

Compound **8** has the potential to produce more generations of the starburst dendrimer; however, such a divergent process would ultimately result in low yields as a result of steric crowding. Making use of the potential for 16-fold functionalisation, Feher, also investigated replacing both amine protons of compound **6** with 16 Ph_2PCH_2- groups. Using an adaptation of the methodology for attaching phosphine pendant groups to amine terminated PAMAM[53] dendrimers, he reacted compound **6** with CH_2O/Ph_2PH to give $\{[CH_2P(C_6H_5)_2]_2N(CH_2)_3\}_8Si_8O_{12}$.

Feher went on to report the preparation of N-protected amino acid functionalised silsesquioxanes[54] from compound **6** and $[p\text{-HO-CH}_2C_6H_4]_8Si_8O_{12}]$. This latter octaalcohol was synthesised from $p\text{-Cl-CH}_2C_6H_4SiCl_3$[48]. Standard coupling conditions were employed to react the octaamine with N-protected amino acids and N-protected di- and tri- peptides, as shown in Reaction Scheme 5. Yields for all couplings were in excess of 85%. The

octaalcohol reactions used similar coupling processes, however yields were far lower. This was thought to be due to the poorer nucleophilicity of the benzylic hydroxyl group.

$$[H_2N(CH_2)_3]_8Si_8O_{12} \; HCl \xrightarrow[\substack{TBTU,\\ HOBt \; H_2O,\\ DIPEA, \; DMF}]{Z\text{-Pro-OH}} [Z\text{-Pro-NH}(CH_2)_3]_8Si_8O_{12}$$

$$\downarrow \substack{H_2, \; 10\% \; Pd/C,\\ 1M \; HCl\text{-MeOH}\\ 8H, \; 25^{\circ}C}$$

$$[Z\text{-Ala-Pro-NH}(CH_2)_3]_8Si_8O_{12} \xleftarrow[\substack{TBTU,\\ HOBt \; H_2O,\\ DIPEA, \; DMF}]{Z\text{-Ala-OH}} [H\text{-Pro-NH}(CH_2)_3]_8Si_8O_{12}.8HCl$$

$$\downarrow \substack{H_2, \; 10\% \; Pd/C,\\ 1M \; HCl\text{-MeOH}\\ 8H, \; 25^{0}C}$$

$$[H\text{-Ala-Pro-NH}(CH_2)_3]_8Si_8O_{12} \, . \, 8HCl$$
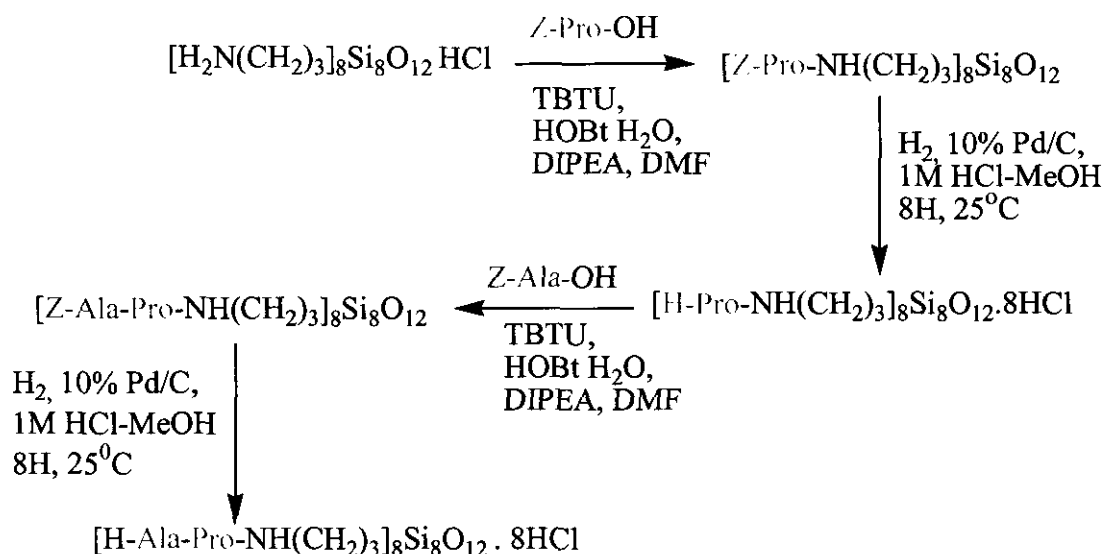
Reaction Scheme 5: Preparation of Amino Acid functionalised silsesquioxanes

Carbohydrate functionalised silsesquioxanes have been prepared by reacting compound **6** with δ-lactonolactone and δ-maltonolactone, as shown in Figure 7[54]. These reactions were carried out in DMSO, at room temperature, with a 15-fold excess of the carbohydrate. The yields were 53% and 26% for the lactonolactone and maltonolactone respectively.

19

$R_8Si_8O_{12}$

R = CH₂CH₂CH₂NH ... (structure) 53%

R = CH₂CH₂CH₂NH ... (structure) 26%
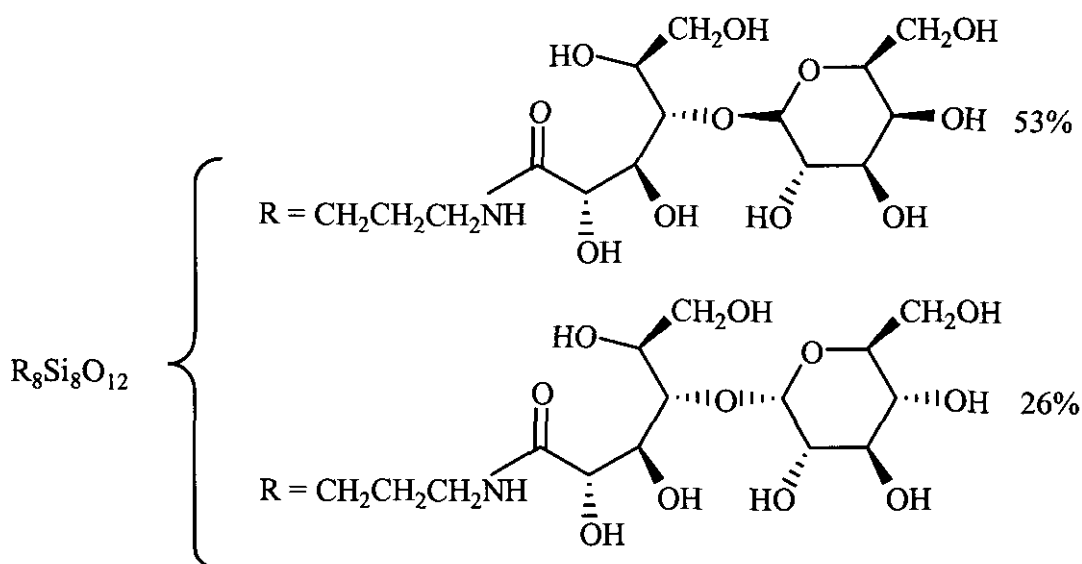
Figure 7: Carbohydrate Silsesquioxanes

The compounds discussed above are just a few examples of the diverse range of functionality which have been attached to silsesquioxanes. Many more have been reported including caprolactone and gluconolactone functionalised T_8's[55].

1.5.2 Preparation through Hydrosilylation

An important reaction in silicon chemistry, leading to the formation of Si-C bonds, is the hydrosilylation reaction[56]. Early examples were thought to proceed via a radical mechanism. More recently a platinum catalysed process has been favoured[57] where the active species is determined by platinum colloid formation[58]. The exact nature of these mechanisms is discussed in Chapter 3.

Hydrosilylation of vinyl groups by octahydridosilsesquioxane cages has been shown to proceed with retention of the cage[59-61]. Herren et al. reported the successful hydrosilylation

of hex-1-ene and of methylenecyclohexane with T_8H_8 to produce octa(hexylsilsesquioxane) and octa(cyclohexylmethylsilsesquioxane) in yields greater than 90%[59]. These reactions were catalysed by H_2PtCl_6, known as Speier's catalyst[62].

A range of alkyl-substituted octasilsesquioxanes was prepared using hydrosilylation by Frey et al.[60]. The homologous series, synthesised using H_2PtCl_6, was prepared in order to study their thermal properties. The same catalyst was used by Bassindale et al. to prepare a series of novel eight-fold hydrocarbon functionalised silsesquioxanes. Model compounds were prepared by hydrosilylating T_8 with hex-1-ene, dec-1-ene, tetradec-1-ene and octadec-1-ene using Speier's catalyst[61]. GPC and NMR confirmed the formation of the expected products and the monodispersity of the reaction. Octopus molecules with siloxane arms were also prepared using $Bu[Si(CH_3)_2O]_3Si(CH_3)_2CH=CH_2$ and $Bu[Si(CH_3)_2O]Si(CH_3)_2CH_2CH=CH_2$. ^{29}Si NMR indicated several 'T' environments. ^{13}C NMR spectroscopy confirmed that α and β addition had taken place. Evidence of a further by-product and non-mono-dispersity was provided by GPC, which indicated that a H/vinyl exchange had occurred to produce a dimeric species. Such a compound would possess 2 silsesquioxane cores joined by an ethylene linkage, the remaining 14 arms would be the expected hydrocarbon chains. Reactions were also carried out using the allyl siloxane which again gave multiple peaks in the ^{29}Si NMR spectroscopy indicating that allyl/H exchange was occurring. This was the first reported allyl/H exchange in a hydrosilylation reaction. Work was also carried out to assess the effect of catalyst activity on the α/β regioselectivity and H/vinyl exchange at silicon[63]. Homogeneous and heterogeneous catalysts were used, with Pt/C, sulfided Pt/C and Rh/C requiring higher reaction temperatures and longer reaction times, than the traditional Speier's and Karstedt's catalysts[64]. The increased proportion of α adducts and H/vinyl exchange at silicon found

when using these heterogeneous catalysts was thought to be a result of the increased temperature and reaction times.

Morán et al. prepared a series of compounds starting with octakis(hydrodimethylsiloxy)octasilsesquioxane, $[H(CH_3)_2SiO]_8Si_8O_{12}$[65]. Using activated Karstedt's catalyst[63], eightfold hydrosilylation was found to be complete by IR spectroscopy, affording $[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4CH_2CH_2Si(CH_3)_2O)]_8Si_8O_{12}$. Both α and β addition were observed by ^1H NMR, in line with the observations made by Bassindale et al.[61]. ^{29}Si NMR confirmed total substitution of the cage, with resonances present in the Q and M silicon regions. Reaction with one equivalent of vinylferrocene under the same conditions achieved mono-substitution, as may be expected affording $[(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4CH_2CH_2Si(CH_3)_2O)]-[H(CH_3)_2SiO]_7Si_8O_{12}$.

Over the last five years Jutzi et al. have continued their work on the eight-fold functionalisation of T_8H_8 via hydrosilylation[66]. Functionalities incorporated into the cage compounds included dodecarboranyl, methylcymantrenyl and ferrocenylsilyl species. The latter of these was prepared using a vinyldimethylsilyl derivative of the silsesquioxane. 16 and 24 fold-substituted silsesquioxanes were also produced as useful substrates for the introduction of further functionalities based on dendrimer methodology. Such compounds were prepared by hydrosilylating vinyldimethylsilylsilsesquioxane with dichloromethylsilane and triethoxysilane. The silsesquioxane cage was found to remain intact throughout the reaction. Only β addition was observed in all of these cases, in contrast to the results Morán[64] and Bassindale[61].

Examples of more diverse functionalities attached to the silsesquioxane cage include liquid crystal arms[67,68], peptides[53] and carbohydrates[54]. Liquid crystalline arms, attached by

hydrosilylation, have been seen to undergo a change in liquid crystalline properties when attached to the cages.

It can be seen from this summary of the silsesquioxane literature that a wide range of functionalities has been incorporated into the silsesquioxane structure, both by condensation routes and hydrosilylation techniques. This diverse range of compounds has found uses in many applications, with silsesquioxane chemistry recently diversifying into preparation and functionalisation of the less well known structures such as T_6[69].

CHAPTER TWO

Liquid Crystalline Silsesquioxanes

2.0 INTRODUCTION

2.0.1 What is a liquid crystal?

The liquid crystalline state exists between the rigidly ordered solid state and molecularly disordered liquid state[70]. In crystalline materials the molecules possess both positional and orientational order. The molecules are held in a certain lattice position due to strong intermolecular interactions. In liquids the molecules have less order, usually diffusing at random. In the liquid crystalline state the molecules maintain some degree of orientational order along with some positional order. In general they share the properties usually associated with both liquids and solids. Within the liquid crystalline state several distinct transitions exist. There are also a number of different classes of liquid crystal.
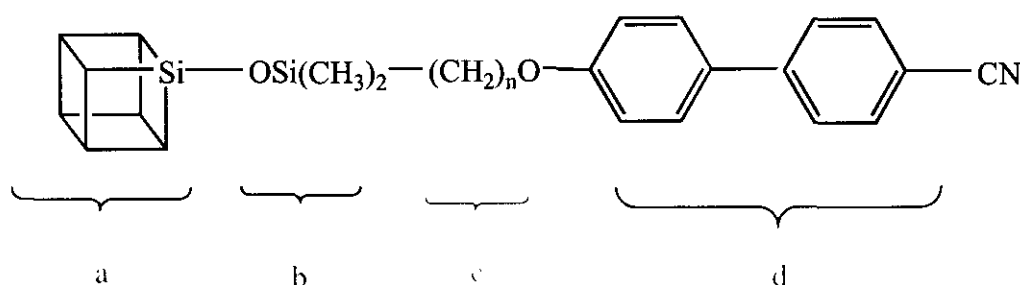
Figure 8: General structure of a liquid crystalline silsesquioxane.

A liquid crystalline silsesquioxane consists of a mesogen attached to a siloxane structure as shown in Figure 8. The silsesquioxane core is the central body of the structure (a) from which the mesogens (d) radiate. A hydrocarbon spacer is the link between the mesogen and the polyhedral cage (c). This linkage can contain an organosilicon spacer unit (b). All polyhedral silsesquioxanes to date have been prepared by a convergent route, whereby the

cage and liquid crystal are synthesised separately. The coupling of these is the final step in the procedure[71-77].

2.1 TYPES OF LIQUID CRYSTAL.

There are two main groups of liquid crystalline material, thermotropic and lyotropic[78]. With thermotropic species the phase is only stable across a specific temperature range. However, with lyotropic species the phase will only form when the compound is mixed with a particular solvent. In this latter case the concentration of the solution is critical for liquid crystalline phase stability.

Thermotropic liquid crystals can be further divided into two classes, calamitic and discotic compounds[70]. The most common of these is the calamitic, which is formed by rod-shaped molecules and can have a number of phases. Calamitic liquid crystals must have at least one part of the molecule that is rigid, so that its elongated shape can be maintained throughout the phase transitions. Such species typically have a series of rings linked together by rigid spacer groups such as carbonyls. Compound **9** is an example of a calamitic liquid crystal[79].
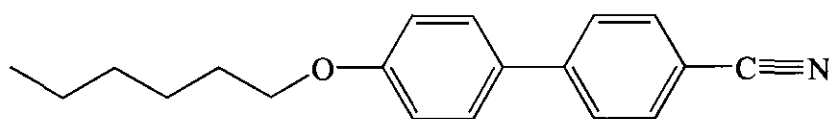
Compound 9: Typical calamitic liquid crystal.

Discotic liquid crystals are typically formed from disc-like molecules. Here the central core of the compound is rigid and usually based upon a derivatised benzene or triphenylene[80]. The derivatisation will include a number of arms that are themselves calamitic liquid crystalline molecules, as shown in Figure 9.
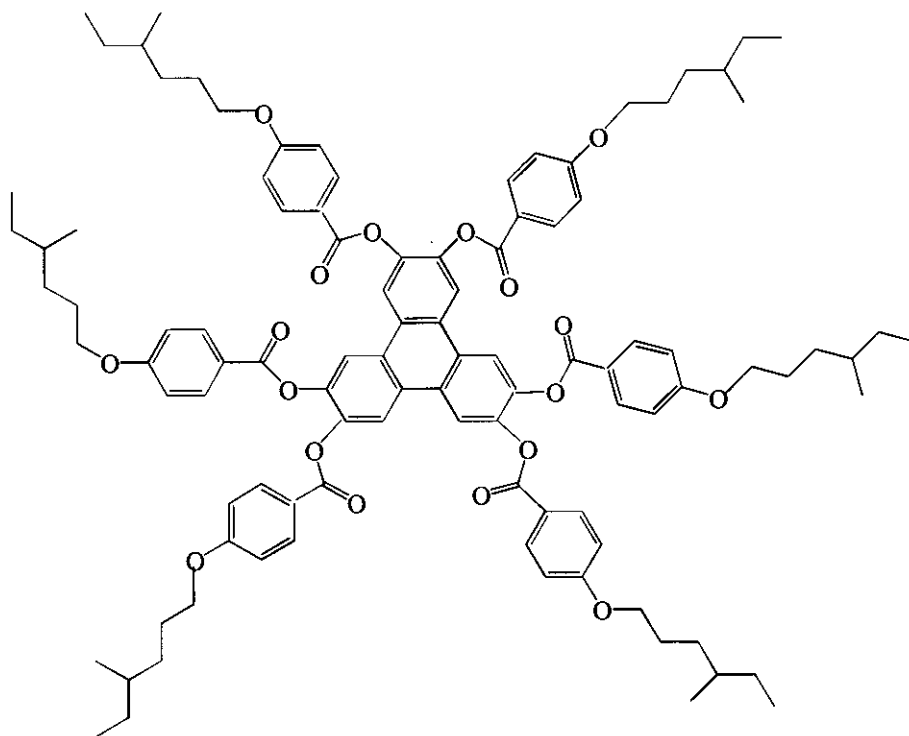
Figure 9: Typical discotic liquid crystal.

The simplest and, therefore, most widely studied liquid crystals are the calamitic liquid crystals.

2.2 CALAMITIC LIQUID CRYSTALS.

A number of phase transitions exist for calamitic liquid crystals. These phases can often be predicted based on the molecular geometry of the compounds in question and can be identified using a number of well established techniques. The most common phases are the nematic and smectic phases [81]. More complex phases do exist, these being variations based upon the simplest transitions.

Liquid crystalline phases are identified by means of optical analysis and differential scanning calorimetry (DSC). Specific phases produce different patterns known as textures. The texture produced by a phase has been shown to be dependent upon the previous phases. Textures of different phases are often found to merge into each other. This phenomenon is called paramorphoticy and can result in incorrect phase analysis[78]. For this reason experimental classification of phases is usually carried out by cooling from the isotropic liquid. If the material is first heated and then cooled the first mesophase formed is a natural one and hence any further paramorphotic phases will be derived from the natural texture of this transition.

The properties of liquid crystals arise due to defects within the phase at the molecular level[70]. There are many types of defects possible, our understanding of which lies in solid state chemistry. The most common defects are point defects, grain boundaries and dislocations. The presence of a defect increases the internal energy of the crystal. A large number of defects in the crystalline solid will lead to its destabilisation. In turn this results in a greater probability of a liquid crystalline phase being produced.

# 2.3 MOLECULAR SHAPE AND STRUCTURE OF LIQUID CRYSTALS.

The type of liquid crystalline phase formed is dependent on the molecular properties of the compound. A primary factor is the shape of the species[82]. Three unique shapes can be identified as giving rise to specific crystalline phases. Spheroidal, ellipsoidal and discoidal compounds are the main molecular shapes producing liquid crystal phases. The most common of these is the ellipsoidal giving rise to calamitic liquid crystals. Some compounds contain combinations of these shapes; these are known as mesomorphic compounds, displaying more than one phase transition.

It is not only the molecular shape that causes a species to exhibit such transitions. Generally mesogens consist of two distinct regions with chemically unique properties. This is achieved by preparing a mesogen by combining compounds with specific properties - for example, combining aliphatic and aromatic moieties, dipolar and non-polar species, hydrocarbon and fluorocarbons as well as coupling rigid and flexible materials. The two components of the final material provide a 'dual personality'. In this way both parts of the molecule can interact with the corresponding section of a neighbouring molecule, causing internal phase separation. This results in a phase structure comprising areas of strong and weak interactions.

2.3.1 The Nematic Phase.

The most straightforward calamitic phase is known as the nematic phase (N)[81]. In this phase molecules maintain an orientational order, however any degree of positional order is lost. The transition from crystalline solid to nematic phase involves a loss of 'in plane' and 'out of plane' molecular interactions, resulting in a statistically parallel arrangement of molecules. The loss of order from the crystalline solid to the nematic phase is reasonably large such that many strong intermolecular forces of attraction must be broken. In contrast the degree of order lost when the compound is heated to isotropy from this phase is relatively small, i.e. most of the intermolecular attractions have been lost prior to this stage. This can be seen clearly in Figure 10.

Crystalline Solid   Nematic phase   Isotropic Liquid

Orientational Order
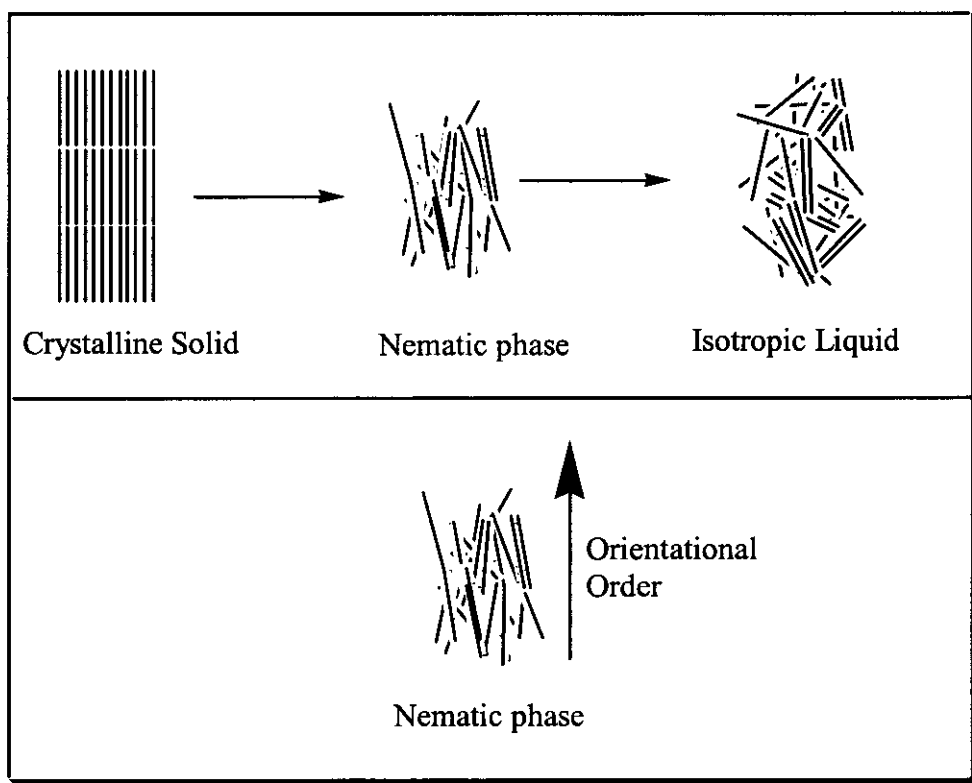
Nematic phase

Figure 10: Schematic representation of molecular arrangement for nematic phase formation.

It should be noted that this particular phase can be formed by calamitic and some discotic molecules; however, it is most commonly seen with rod-shaped calamitic molecules, such as Compound **9**.

The nematic phase is the most disordered phase and hence it is usually observed as the last transition prior to isotropy. Phases that involve more molecular order will be experienced first, as a gradual transition occurs from the crystalline solid to the isotropic liquid. A typical example of a phase that occurs before the nematic phase is the smectic phase

2.3.2 The Smectic Phase

The smectic phase is more ordered than the nematic phase and it exists in a number of different types[81]. It arises when only some of the intermolecular forces of attraction are broken down with heating. In this case the 'in plane' transitional order is lost, however, positional and orientational order is maintained. The result is a lamellar arrangement whereby the layers are not perfectly defined. Interlayer attractions are weak compared to the lateral forces between the molecules, hence the layers can slide over each other.

It is because of the lack of layer definition that more than one smectic phase is possible. Heating the smectic phase can either result in the loss of 'out of plane' ordering to produce the nematic phase, or if this is combined with loss of orientational order an isotropic liquid is produced, as depicted in Figure 11.
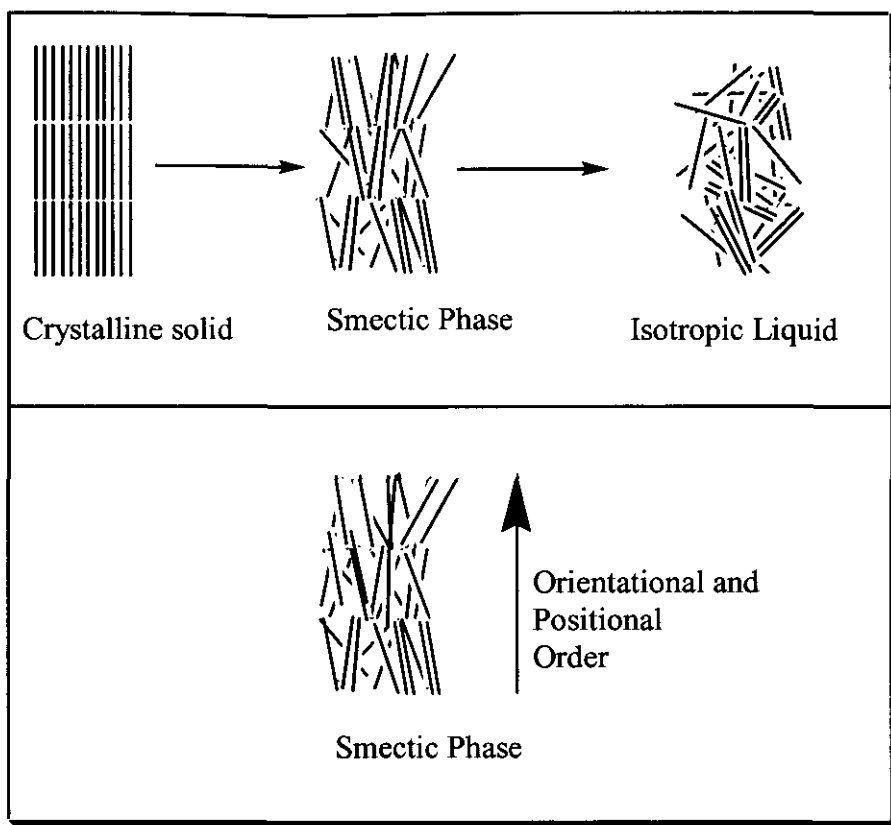
Figure 11: Schematic representation of molecular arrangement for smectic phase formation.

There have been eleven smectic phases identified differing only by the tilt angle of the layers and the presence of hexagonal ordering[78]. Until recently the most well characterised phases were the basic smectic phases, S_A, S_B and S_C. A brief explanation of these phases will identify the crucial molecular requirements and indicate their differences.

2.3.3 Smectic A, B and C Phases.

Smectic A (S_A) phases are the least ordered of all the smectic phases. Molecules in S_A phases are arranged into layers, within each layer the molecules have no positional

ordering as shown in Figure 12. The layers are not tilted and the lack of molecular organisation results in the layers being flexible.
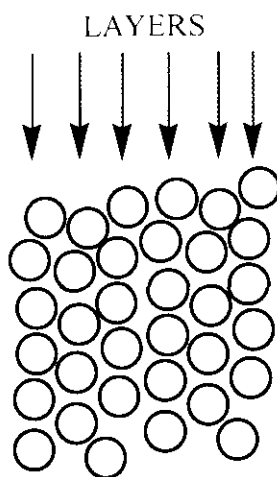
LAYERS

Figure 12: Molecular organisation in the Smectic A phase.

The Smectic C phase is a tilted analogue of the Smectic A phase. The molecules are disordered within the layers and the layers are free to slide across each other. Smectic B phases differ from both of the aforementioned phases in that they have an ordered arrangement of molecules within the layers. Hexagonal packing is thought to be a result of molecules rotating about their long axis, creating close packed cylindrical units. This degree of order makes the phase much more rigid than the S_A and S_C. The degree of order and tilt present in the smectic phases results in different appearances under a polarising light microscope.

There are a number of other smectic phases arising out of the above descriptions. The effect of tilting the layers and the evidence of hexagonal packing of the molecules results in the formation of new subdivisions of smectic phases. There is not time within the constraints of this thesis to discuss every possible smectic phase.

2.4 ANALYTICAL TECHNIQUES USED IN IDENTIFICATION OF LIQUID CRYSTAL PHASES.

2.4.1 Hot stage polarising microscopy.

The most widely used technique of liquid crystal phase identification is optical polarising microscopy. This reveals that each different liquid crystal phase has a distinct optical texture. Phase identification usually involves viewing a section of the sample with a microscope. The sample is placed in a hot stage apparatus that is temperature controlled. The temperature range is usually between -20°C and 300°C. The sample is viewed between polarising filters crossed at 90° to each other as shown in Figure 13. The top graphic shows two polarisers so that their optical axes are parallel. Light can pass through them. However when the polarisers are crossed as in the bottom graphic, light passed through the first is extinguished by the second.
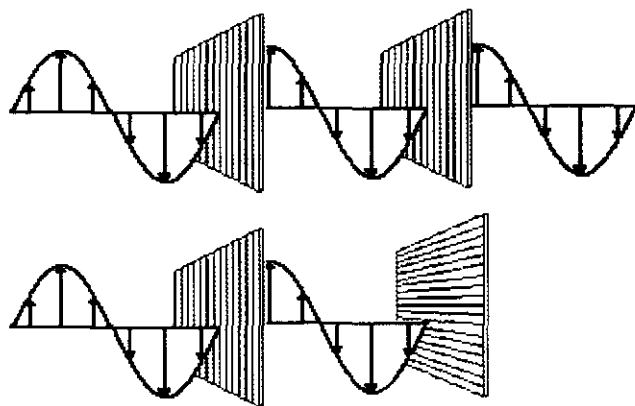

Figure 13: Schematic representation of the effect crossed polarisers have on light.
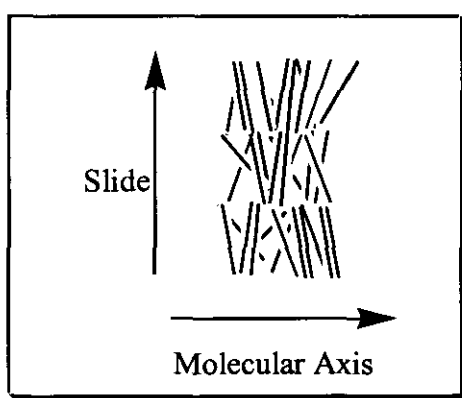
The effect of a liquid crystalline sample placed between the two polarisers is to twist the plane of plane polarised light such that the light can pass through the second polariser. The

molecular alignment in the sample results in the light being carried down the optical axis, and as a result is twisted by a certain angle, if this is 90° then light will be passed through.

The molecular arrangement can be assessed by analysis of the texture produced across a temperature range. With the polarising lenses crossed at 90° to each other, no light is visible when there is no molecular alignment. An isotropic liquid will have little effect on the polarised light and this will appear dark. However, the onset of an anisotropic medium results in some light being visible and the presence of a birefringent texture. The optical texture provides information regarding the molecular alignment within the samples. The two basic types of alignment are homeotropic and homogeneous. Homeotropic alignment involves molecules being orientated such that their long axis is perpendicular with the slide as shown in Figure 14.
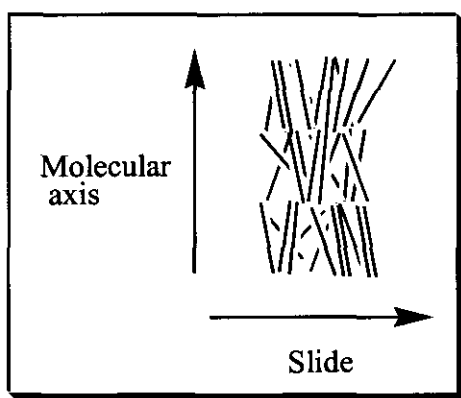
Figure 14: Homeotropic alignment.　　　　　　**Figure 15: Homogeneous alignment.**

In this case molecules within the sample will not affect the polarised light and hence will be observed as complete blackness. Homogeneous alignment involves the molecules being parallel to the slide as shown in Figure 15. With homogeneous ordering, a thin film of the liquid crystal phase exhibits birefringence, producing a coloured texture. All samples will produce the two forms of alignment, with both occurring throughout a sample. It has been

observed that the thickness of the sample can effect the alignment of the molecules. Thin samples tend to favour homeotropic alignment, while thicker samples contain areas of homogeneous ordering.

2.4.2 Differential Scanning Calorimetry.

Other analytical techniques are also used in conjunction with polarising light microscopy. One of the most important of these methods is differential scanning calorimetry. When a compound melts a change of state occurs. The process is endothermic. The reverse procedure, crystallisation, is exothermic. DSC calculates the enthalpy change of the transitions generated by measuring the heat either released or absorbed by the system. Whilst this process cannot identify the phase directly, the magnitude of the enthalpy change can provide an indication of the phase change involved. The enthalpy change involved when a solid melts to become an isotropic liquid, for example, is far greater than when an intermediate liquid crystalline phase is generated.
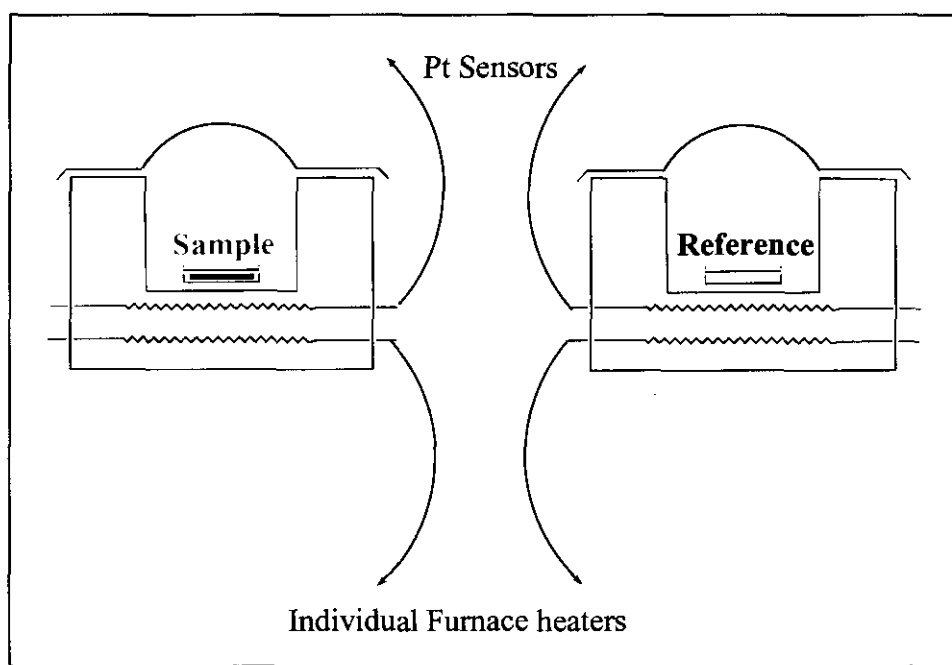
Figure 16:Schematic Representation of a differential scanning calorimeter.

The calorimeter itself has two furnaces, as shown in Figure 16, one to heat the sample in question and one to heat an inert reference material. The two furnaces are heated independently, however they are connected such that the temperature of both remains identical throughout any heating or cooling cycles. If a sample melts, heat will be absorbed from the surroundings. Heat must therefore be supplied to that chamber to prevent any imbalance in the temperatures of the sample and the reference. From the energy supplied on phase change, the enthalpy change can be calculated. The calorimeter must be calibrated prior to use with a sample of known enthalpy change, usually indium metal (t=156.6°C, ΔH=28.45 Jg^{-1})[83]. Transition enthalpies are calculated by measuring the area under the peak produced by the phase change and comparing this to the area derived from the standard. A typical DSC trace is shown in Figure 17.
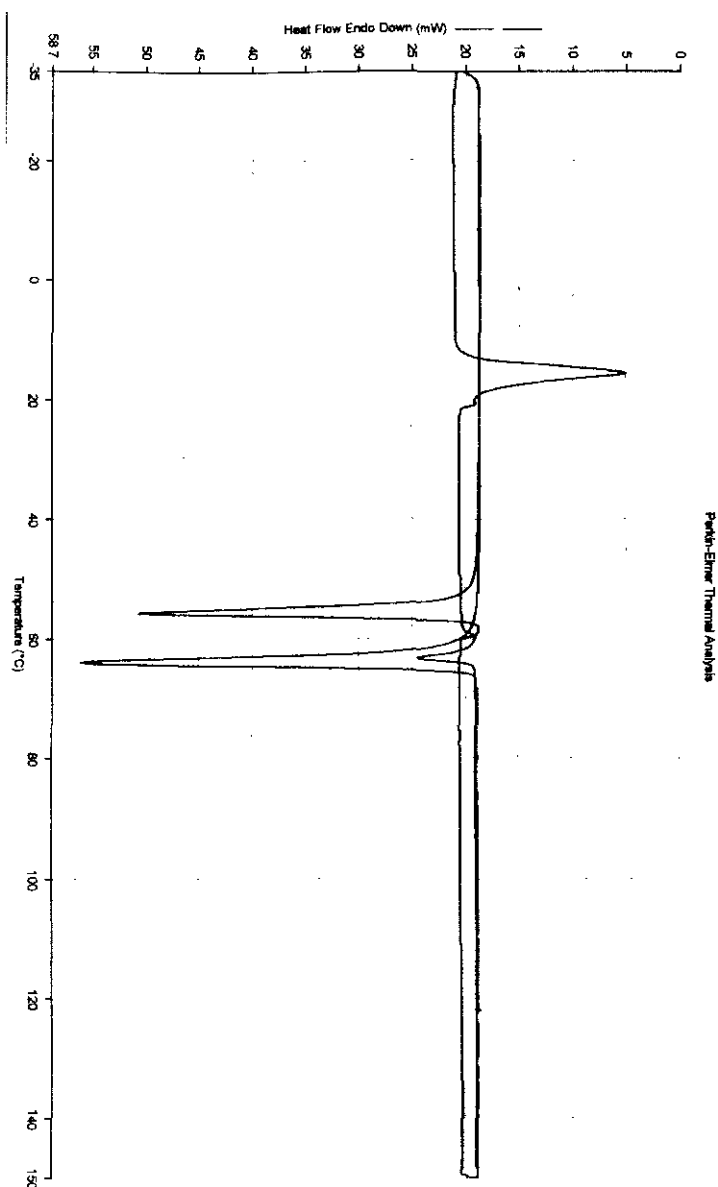
Figure 17: A typical DSC trace, Compound 23

The sample for analysis is weighed out into a small aluminium pan, which is crimp sealed with an aluminium top. Typically 50mg of compound will be used. The pan is placed into a holder on a large chemically resistant block, usually Pt/Ir alloy, to ensure a good control of the temperature. The instrument we used allowed DSC between temperatures of –180 to 600°C.

The magnitude of the enthalpy change associated with the phase transitions is an indication of the degree of structural order involved within the phase. Typical enthalpy changes for a variety of transitions are show in Table 2[78].

TRANSITION	ENTHALPY CHANGE (kJmol^{-1})
Solid $\rightarrow$ Liquid	30-50
$S_A \rightarrow$ Liquid	4-6
$S_B, S_c, \rightarrow$ Liquid	4-6
Nematic $\rightarrow$ Liquid	1-2
$S_A \rightarrow$ Nematic	1
$S_C \rightarrow$ Nematic	<1
$S_C \rightarrow S_A$	0.3

Table 2: Typical enthalpy values for liquid crystalline transitions.

As can be seen from the table, the enthalpy change gives a good indication of the change in structural order. The large enthalpy change observed when a crystalline solid melts to an isotropic liquid reflects the considerable energy change which occurs on loss of short-range order. The smaller enthalpy changes involving phases such as S_A S_B and S_C are indicative of loss of only positional or orientational order, as described earlier.

Optical microscopy and DSC are often used together as reinforcing techniques in the identification of mesophases. In some cases, the structure of the liquid crystalline phase is very difficult to determine precisely using these two techniques, and so X–ray analysis is employed. This enables the exact phase structure to be obtained.

2.5 THE ODD-EVEN EFFECT.

The nature of the most flexible part of the molecule in a tethered mesogen, the spacer group, plays a very important role in phase stability and therefore its formation. When molecules form into liquid crystalline phases they align such that intermolecular attraction can occur. In this way 'like' sections of the molecules can pack together, providing bond angles will permit such conformations. For example, with benzene rings their planarity serves to allow stacking, but how well they pack depends upon the freedom they are allowed by the spacer groups. It is the ability to pack together that creates a stable phase and determines both its formation and the temperature at which it will be seen. Long alkyl chains add flexibility to the compound, reducing melting points and T_{N-I} (temperature of the nematic to isotropic transition). The longer the alkyl chain, the increasingly stable the liquid crystal phase. The length of the chain however reaches an optimum, after which length the increasing flexibility causes disruption and destabilisation to the phase.

The odd-even effect[78] refers to the dependence of the liquid crystal properties on the number of atoms present in the spacer chain, n. The onset temperature of the liquid crystalline phase is noticeably lower for compounds with an even number of carbon atoms in the spacer chain compared to those with an odd number. This can be explained by the fact that the extra carbon in the chain which makes the chain even generates a deviation from the linear structure of the more favourable all-*trans* conformation of the chain[78]. This deviation reduces the melting point and also T_{N-I}.

The odd-even effect is also observed with untethered mesogens, again an alkyl chain with an odd number of carbon atoms attached to the mesogenic core exhibits higher transition temperatures than the corresponding even numbered compound.

2.6 LIQUID CRYSTALLINE SILSESQUIOXANES

The mixing of siloxanes and mesogens has been of interest for many years. The combination of liquid crystalline properties with those of the siloxane species results in novel molecules with potentially interesting features. Liquid crystals have previously been attached as side chains to siloxane polymers[84-87]. A large number of well known mesogens has been used in this way, such as biphenyl and cholesterol derivatives. More recently such mesogens have been coupled with silanes[75], cyclic siloxane[88, 89] and cubic silsesquioxanes[68, 74]. Investigations have focused on existing, well-documented mesogenic units[90] and the effects upon their phase transitions when coupled to silicon compounds.

Liquid crystalline silsesquioxanes are prepared by combining mesogens with spherical silsesquioxanes. Kreuzer, Maurer and Spes [71] prepared a number of these compounds by hydrosilylation, based on $(RSiO_{3/2})_n$ cages where n = 6, 8, and 10. The nematic mesogens were derivatives of cholesterol and a change in liquid crystalline phase was effected by their attachment to the cage. The functionalised silsesquioxanes produced smectic phases. In an attempt to explain the change in phase produced, the molecular arrangement was considered. S_A phases are known to occur when molecules are packed into diffuse layers. Within silsesquioxane systems the mesogen arms can rotate freely about the silicon atoms to which they are attached, in order to lie parallel to each other, resulting in a rod-like structure that can pack together in layers. Thus, the non-mesogenic silsesquioxane cages can be considered to act as 2 cyclic siloxane rings joined by oxygen bridges, resulting in a star-like arrangement as depicted in Figure 18 [71]. The presence of the smectic phase demonstrated the ability of the mesogenic entities to control the molecular packing

arrangement; that is, spherical species are distorted into rod-like structures dictating the liquid crystalline phase formation. This is demonstrated in Figure 18.
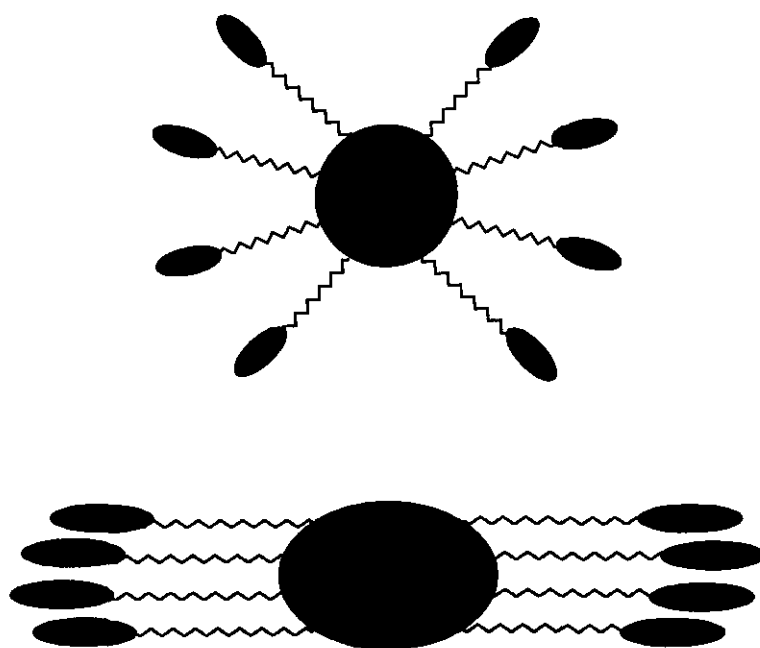
Figure 18: Schematic representation of the star-like arrangement of the non-aligned sample and of the distorted core structure induced by phase alignment.

Goodby and Mehl also supported this explanation of silsesquioxane frame distortion during liquid crystal phase formation for the species formed by coupling compound **10** with tetrakis(dimethylsilyloxy)silane, 1,3,5,7 tetramethylcyclotetrasiloxane, hexakis(dimethylsiloxy)silsesquioxane[79] and octasilsesquioxane[67, 68, 79].


n = 2, 4 or 9
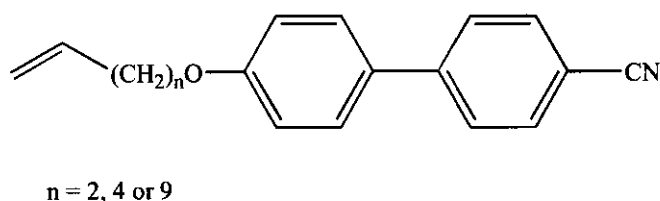
Compound 10: Cyanobiphenyl mesogen

Whilst nematic phase transitions were seen for the free mesogen, Smectic A phases were observed for the adducts. Computer calculated energy minimised structures indicated deformation of the shape of the central core. The volume available about the silicon atom was shown to impose restraints on phase formation. With an increase in the number of mesogen units this volume is reduced, restricting the freedom of movement[74]. This limits the ability of the compound to form a rod-like structure. The outcome of this is a destabilised phase as indicated by a higher temperature of transition.

The transition temperatures observed for these systems were shown to follow a number of trends including increased isotropization temperatures with an increase in the number of methylene groups. The DSC traces showed higher enthalpy change values for transitions where the spacer chain was longer. This suggests that there is more ordering within the layers when long mesogen chains are present.

In contrast to the organisation assumed for the cyclic and cubic derivative, an overlapping mesogen structure was suggested for the molecular packing with the tetrakis(dimethylsilyloxy)silane. The arrangement, shown in Figure 19 indicates how the silicon core is thought to be a monolayer, S_A, whilst the mesogens are considered to be overlapped. The phenyl groups are partially interwoven reducing the interlayer spacing[79]. This formation was referred to as S_{Ad}, implying that in this case the interlayer distance is less than that of the siloxy units.
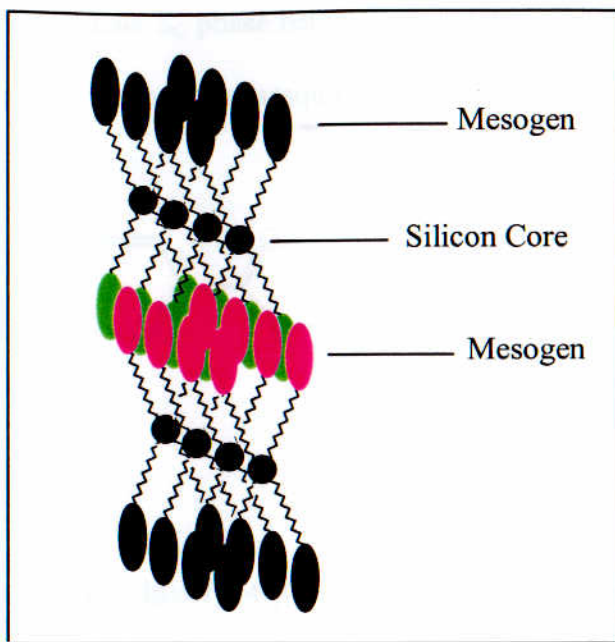
Figure 19. Overlapping aromatic structure proposed by Goodby et al for the tetrakis(dimethylsilyloxy)silane derivative[79]. Mesogenic phenyl groups are shown in different colours for different layers, this should not be confused with a different molecular composition.

The transition temperatures for this set of compounds were in the same region as the T_8 and T_6 cages[68]. However, the difference between the temperatures for the different spacer length was lower in the case of the tetramer[79].

Other mesogens have also been coupled with the these cores[71, 74]. The most interesting of these is the 2-methylpentyl 4-[(4-hexyloxybenzolyoxy)phenyl]benzoate, compound 11[68]. This system requires a significantly higher temperatures to leave the crystalline state compared to the cyanobiphenyl compounds previously discussed. The crystalline state for these molecules appears to be more stable due to the more extensive intermolecular bonding presented by the biphenyl carboxylate group. In contrast to the cyanobiphenyl system, these carboxylate compounds are known to favour formation of a tilted S_C phase.

This resulted in an intermediate S_C phase being observed between the crystalline state and the formation of the S_A phases for the silsesquioxane compound.
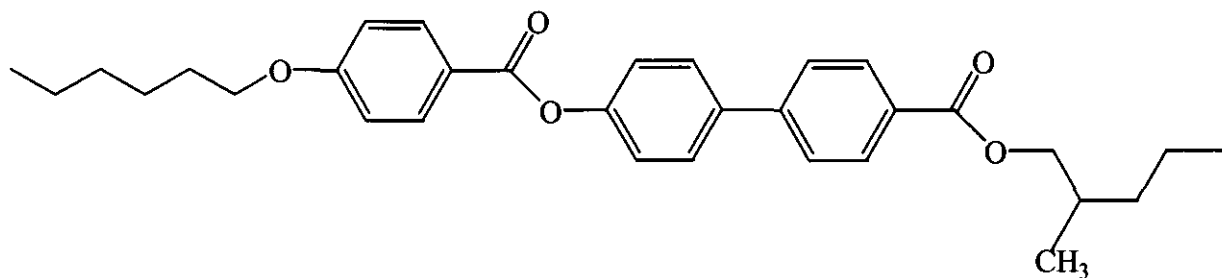

Compound 11: 2-Methylpentyl 4-[(4-hexyloxybenzoyloxy)phenyl]benzoate

Again, trends in increasing isotropization temperatures with increasing chain length were observed for both systems. The cubic cage structure displayed lower isotropization temperatures and higher glass transition temperatures compared to the hexamer. Calamitic transitions for the cage systems occurred at higher temperatures than for the cyclic (D4, D5) derivatives, but lower than for a linear polymer analogue. This would suggest that the liquid crystalline phases formed by the cubic derivatives are destabilised compared to the cyclic systems. This instability arises from the cage deformation necessary to align the mesogens on liquid crystal phase formation. The linear polymer can be expected to give rise to a more stable phase since it has increased flexibility. This flexibility would occur by having more atoms along the polymer backbone between aligning mesogenic units in a linear system compared to the cage structure.

A comprehensive range of silicon containing core species coupled with many liquid crystal side-chains was published by Mehl *et al*[74] in 1999 after our work was completed. Cores included octasilsesquioxanes, cyclic rings and linear polymers, with a selection of side chains producing compounds such as **12, 13** and **14**.

Compound 12

Compound 13
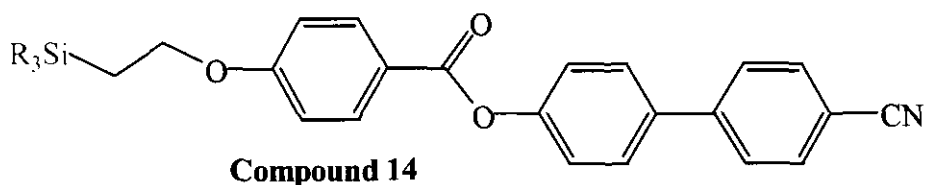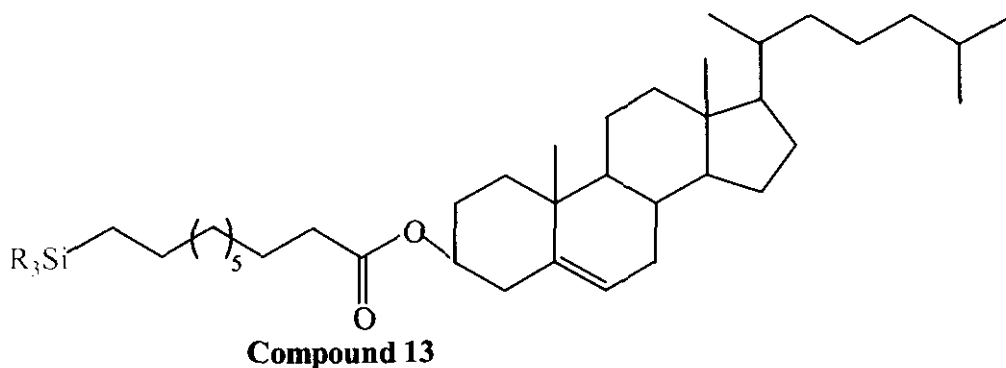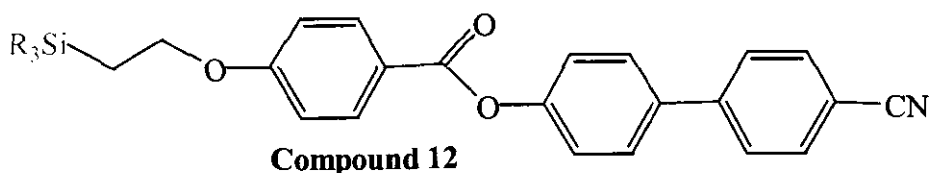
Compound 14

**Compounds 12, 13 and 14: Polyhedral liquid crystal silsesquioxanes**

Similar patterns in phases were achieved and transition temperatures were observed for all systems. The cage compounds generally led to higher temperatures for phase transitions. Linear polymers containing a siloxane backbone were also seen to follow similar trends to the oligomers. This work was completed using X-ray diffraction studies to deduce the exact liquid crystal transitions for these compounds. Liquid crystalline silsesquioxanes prepared with compounds **12, 13** and **14** exhibited the Smectic A phase.

Further work by Mehl and Saez involving a variety of silsesquioxane cores including $[HSi(CH_3)_2\{SiO_{3/2}\}]_8$[89] and $[HSiO_{3/2}]_8$ combined with a number of mesogenic units suggested that the nature of the core played an important role in the observed phase behaviour[68, 74]. Factors affecting the phase production were highlighted as the central core geometry, the proportion of stereoisomers and the actual number of mesogens present. The

observed phase transitions were in line with those seen by other workers[68, 71]. A change from the Q_8 to the Q_{10} core resulted in an increase in isotropization as the crowding of mesogens about the core created additional ordering in the alkyl chains. The difference between Q_8 and T_8 transitions were negligble suggesting that the dimethylsiloxy group plays no role in encouraging order within the system.

Sellinger and Laine[91] prepared a series of silsesquioxane aromatic diester derivatives that showed liquid crystalline phase activity; examples are shown as compounds **15-18**, with the mesogenic units highlighted in blue. These species were prepared using T_8, triethylsilane, TMDS and diphenylsilane, as part of a study of catalytic hydrosilylation.

Liquid crystalline phase transitions were nematic for simple siloxane systems, with a slow transformation into the more highly ordered smectic phase. It was noted that X-ray diffraction was required for a detailed analysis. The nematic phase was also exhibited by the silsesquioxane with four equivalents of mesogenic unit, compound **18**. This disordered phase suggests that the mesogenic arms are too far apart to form the layers required for a smectic transition. This is noticeably in contrast to the results of the octafunctional cages discussed earlier.

Compound 15

Compound 16

Compound 17
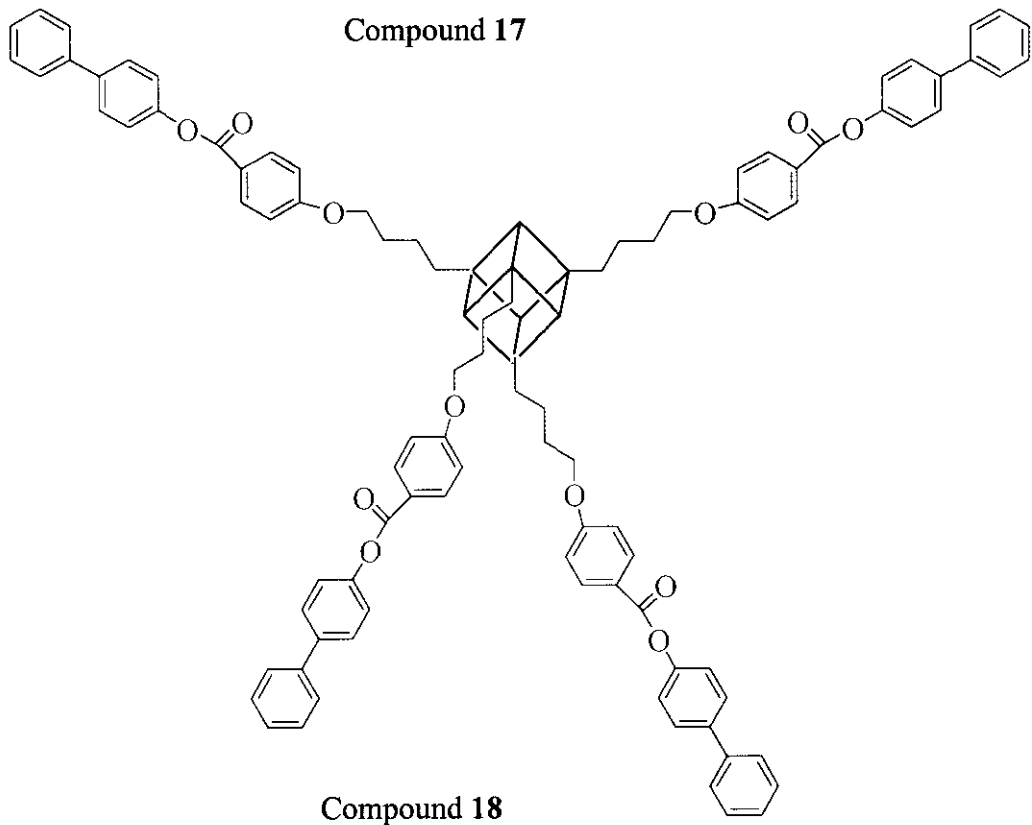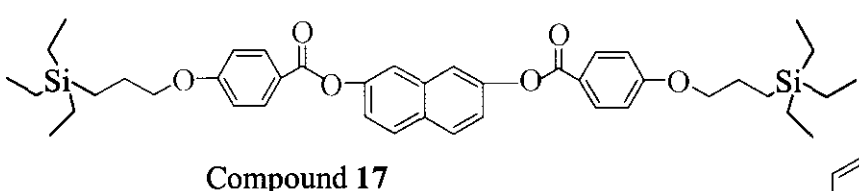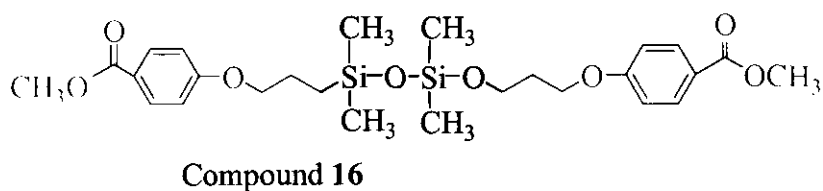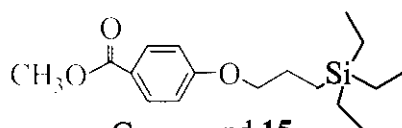
Compound 18

Compounds 15, 16, 17 and 18: Examples of liquid crystalline materials prepared by

Sellinger et al[91]

Recently, work has focused on more complicated systems such as metallomesogens[74].

These species were designed to generate materials of a predominantly inorganic nature

leading to properties more usually associated with metallic materials, such as conductivity

and magnetism. The attachment of a Ni^{2+} complex to $(HSiMe_2)_8[SiO_{3/2}]_8$ resulted in a compound that did not exhibit liquid crystalline phases. The crystalline state was found to be stabilised up to 219°C before decomposition occurred. However, the same mesogen did produce a S_A phase when coupled with 1,3,5,7 tetramethylcyclotetrasiloxane.

Previously, work has been based on complete siloxane substitution, i.e. octasilsesquioxanes have been coupled with eight mesogenic units. Laine has recently experimented with incomplete substitution using four and five mesogenic units coupled to an octasilsesquioxane, $[MesogenSiMe_2OSiO_{3/2}]_x[HSiMe_2OSiO_{3/2}]_{8-x}$ where x = 4 or 5[91, 92]. Liquid crystalline phases were observed for these systems. S_C, S_A and nematic phases were observed. This is thought to be due to the increased volume around the core allowing greater rotational freedom of the mesogens. The S_C phase is possibly encouraged due to incomplete substitution of the cage, reducing steric hindrance between the mesogen arms. Such partial substitution of a cage may also allow tilted layers to form. It is important to note that the mesogens employed displayed either no, or very simple, liquid crystalline properties prior to reaction with the cube.

Linear siloxanes have also been used in mesogen coupling reactions[76]. Although not directly related to the silsesquioxane examples, examination of these systems is useful for considering the factors effecting transition temperatures.

Coles, Newton and Hannington attached a cyanobiphenyl mesogen, compound **11**, to pentamethyldisiloxane[76] . Liquid crystalline transitions were as observed by Goodby, Mehl and Saez[68, 79]. Attachment to the siloxane moiety lowered the Tg values and destabilised the crystalline state. This is due to a reduction in the interchain interactions between the cyanobiphenyl groups because of the size and flexibility of the siloxane end group[93].

Smectic phases were observed, in line with all previous work with analogous systems. The transition temperatures were far lower for these compounds than those of the cyclic and cubic derivatives studied by Goodby[68]. This can be explained by the more significant ordering possible in the linear system. There is also no structural deformation on liquid crystal phase formation, which serves to stabilise these phases.

The cyanobiphenyl mesogen was later attached to a silane core in a sequential manner to produce branched supermolecules. The compounds were such that there were 1, 2, 3 or 4 mesogen units attached to the silane centre[74]. For example, compound 19 is the tetra-substituted species.
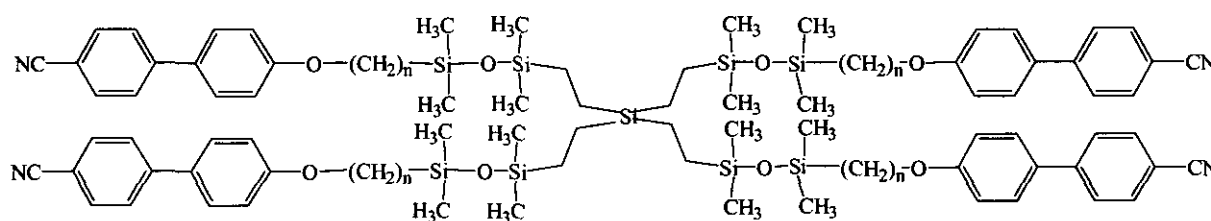
Compound 19: Tetrasubstituted silane prepared by Goodby and Mehl.

Liquid crystalline phases were exhibited and shown to be S_A with increasing degrees of both order and phase for compounds having more mesogenic arms. With just one mesogenic entity the phase was found to exhibit an overlapping layer, similar to that depicted in Figure 19. Ordering of molecules within the structure of the mesophase was seen to be greater for members of the series with an even number of mesogen units. This was considered to be due to symmetry allowing better packing arrangements.

There are many examples of siloxane polymers with liquid crystalline side chains[84, 86]. There is not time in this thesis to discuss these species, however they enable an appreciation of the diverse nature of liquid crystals that have been coupled to silicon

containing species; usually achieving a successful change in liquid crystalline phases exhibited.

In this work, a range of liquid crystal side arms has been prepared and coupled with silsesquioxanes. Both sets of compound were analysed for liquid crystalline properties.

2.7 RESULTS 1 : The mesogens.

The mesogens compounds **20-23** are vinyl terminated phenoxy-esters prepared by a Williamson ether synthesis as shown in Reaction Scheme 6. These mesogens were chosen because of their ellipsoidal shape. It was anticipated that compounds **20-23** would exhibit nematic phase transitions due to their molecular conformation. It was important that compounds **20-23** were terminated with a vinyl group in order that the hydrosilylation reactions could be carried out with the silsesquioxanes.
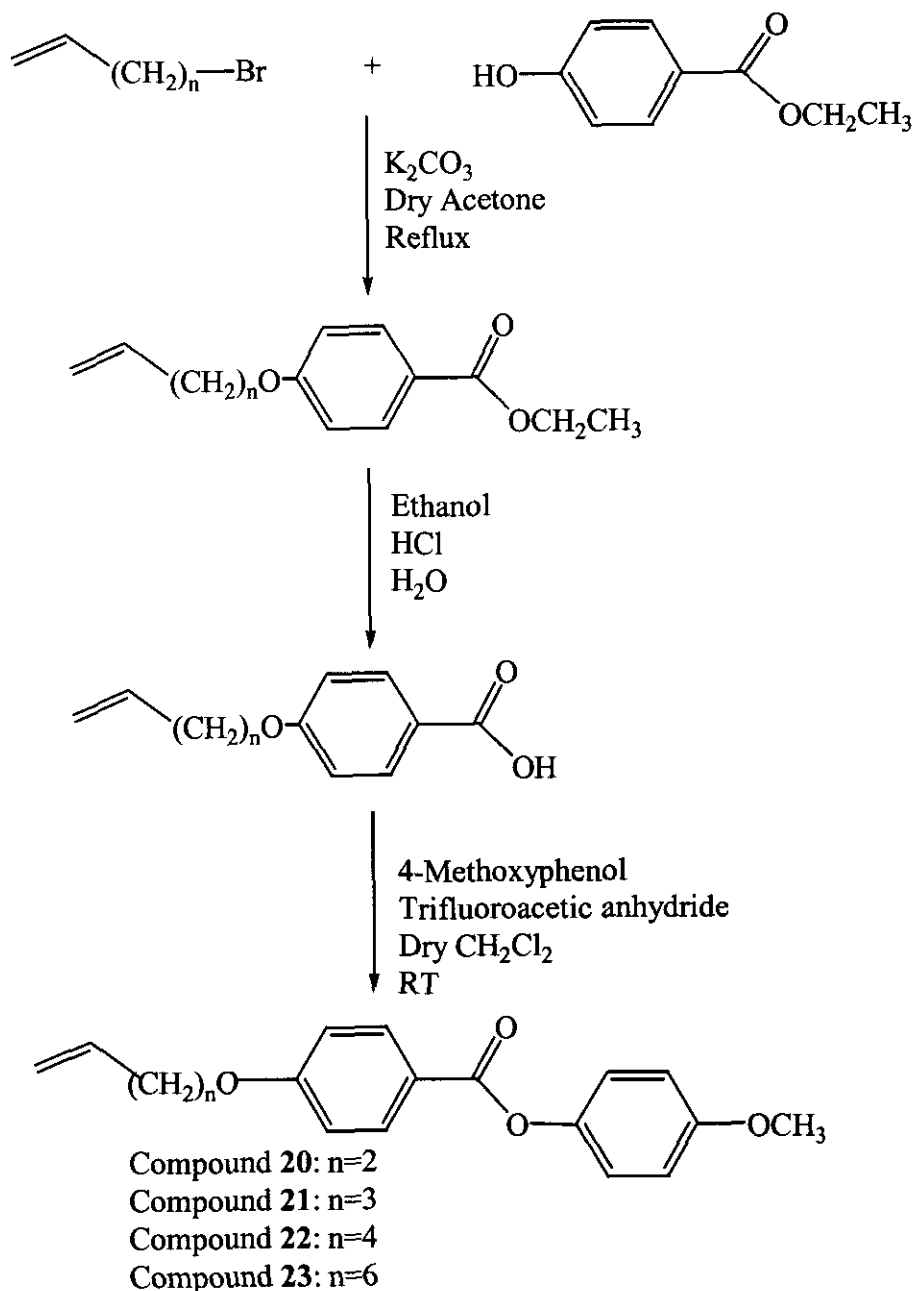
Reaction scheme 6: Preparation of the mesogens.

Compound **20**: n=2
Compound **21**: n=3
Compound **22**: n=4
Compound **23**: n=6

These species were analysed for their liquid crystalline phase behaviour. Compounds **20-23** were found to display the nematic phase as anticipated. These ellipsoidal compounds are well supported in the centre by the ester linkage and the overall structure is analogous to other well-known nematic liquid crystalline species[79]. Several techniques have been applied to identify the phase transitions exhibited by these molecules.

2.8 PHASE IDENTIFICATION OF COMPOUNDS 20-23.

Identification of the nematic phase is relatively easy by optical microscopy; birefringent textures were observed using crossed polarising lenses under a light microscope. The unique textures seen for nematic phases are known as *Schlieren* brushes [78]. These textures are the result of molecules aligning with the polarising lenses, to produce black lines on a coloured background. A typical image is shown in Picture 1.
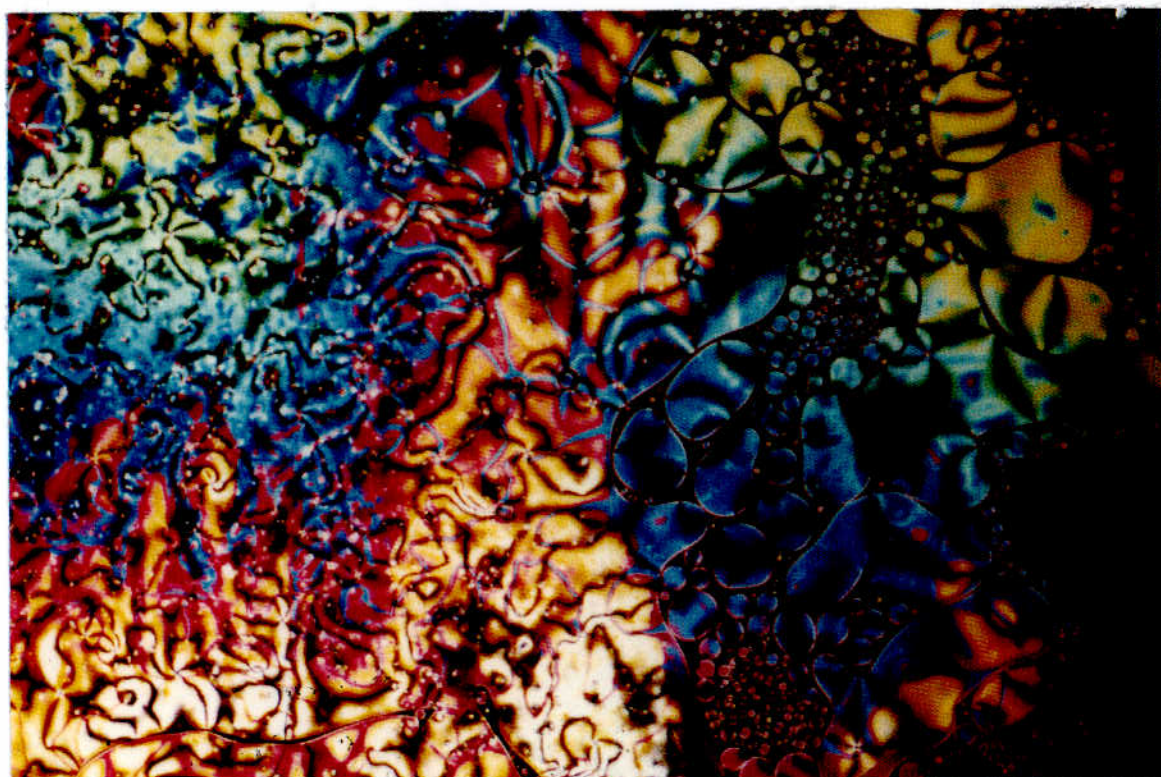

Picture 1: Typical textures of the nematic phase a produced by compound 22.

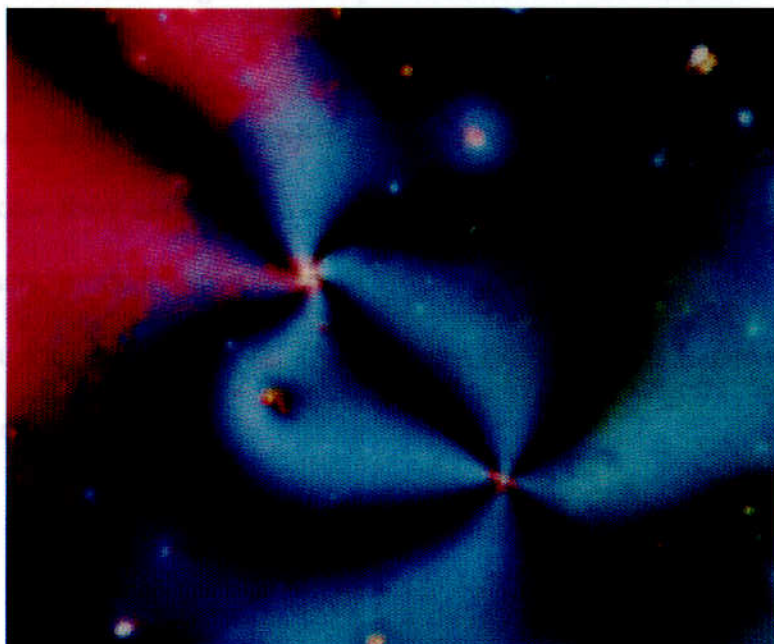**Polarisation: 90° Magnification: ×80**

Compounds **20-23** were clearly shown to produce such thread textures on heating from the crystalline solid. The evidence of multi-thread brushes, indicates the different forms of molecular alignment within the nematic phase. Four brush *Schlieren* textures occur when molecules are radially aligned pointing away from the point defect as shown in Figure 20.
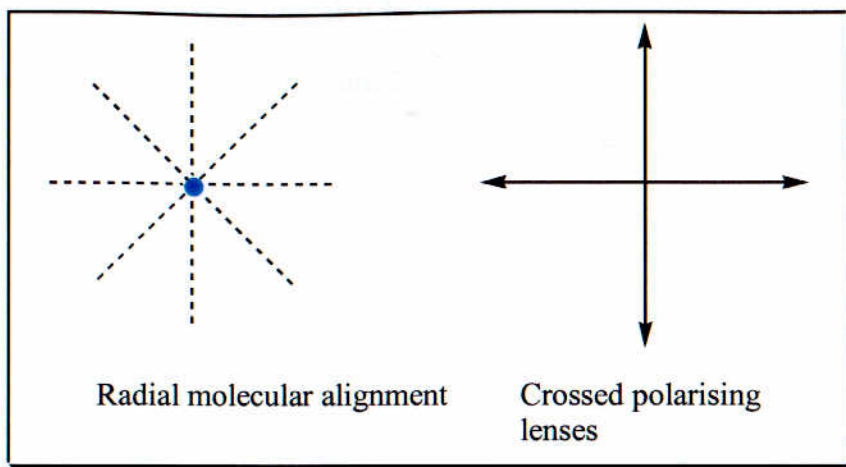
Figure 20: Molecular alignment for production of a 4 brush *Schlieren* texture.

Alignment of the molecules with the crossed polarising lenses creates black lines, known as brushes, in four regions radiating from the point defect. The point defect can be seen as the bright cross in the centre were the brushes join, as shown in Picture 2.

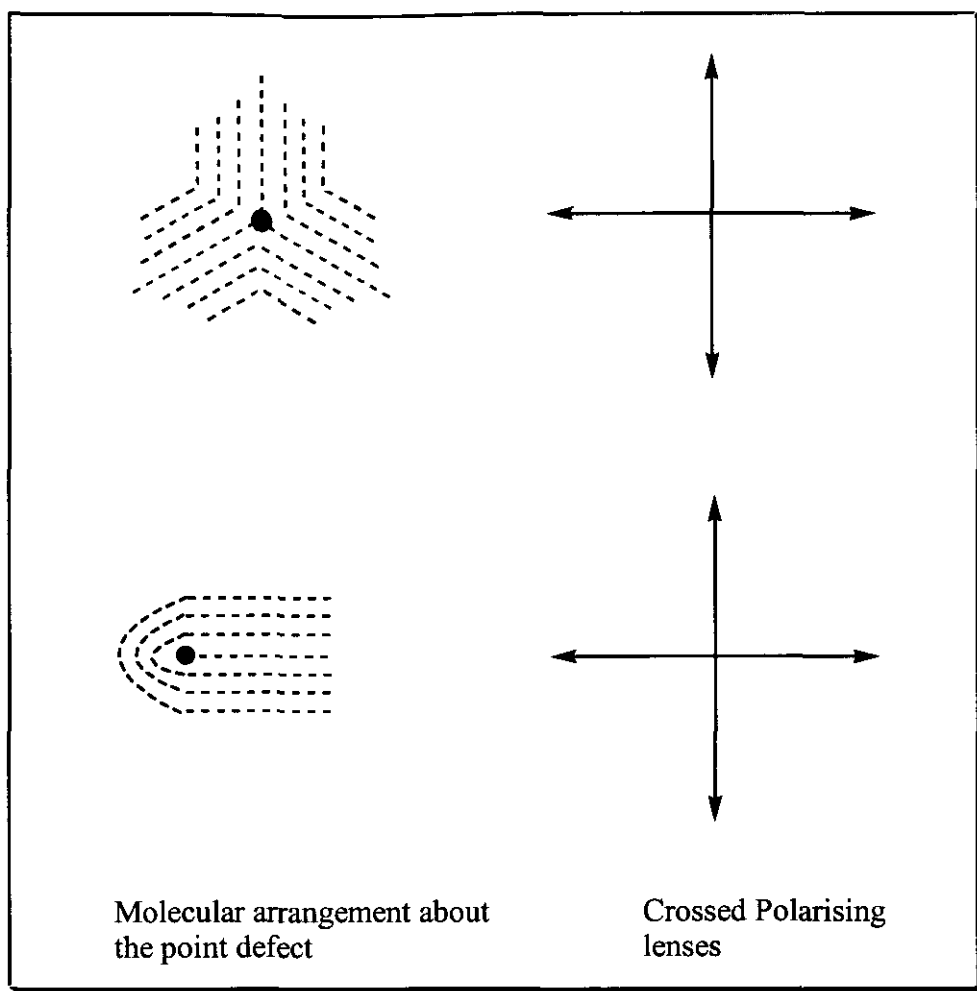**Picture 2: A four brush *Schlieren* texture as seen for the nematic phase of compound 23 Polarisation:270°, Magnification:×200**

A four brush *Schlieren* texture can also be achieved when molecules arrange themselves about the point defect as shown in Figure 21.
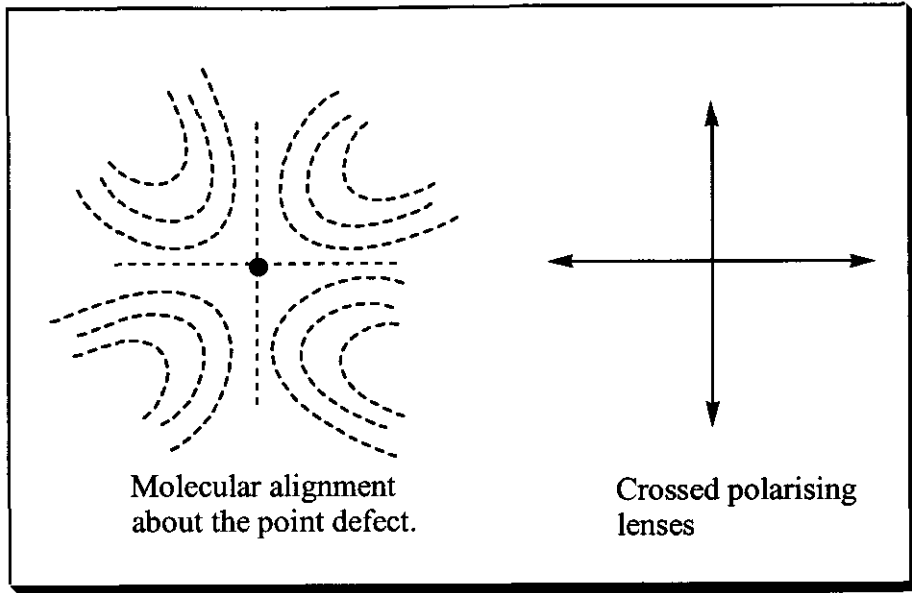
Figure 21: Molecular alignment for production of a 4 brush *Schlieren* texture.

Two brush *Schlieren* textures occur when molecules are organised in an arc about the point defect. In this case there are only two regions were molecules are arranged in line with the crossed polarisers, producing two optically extinguished areas. Examples of how this can be achieved are shown in Figure 22. The thickness of the brushes increase as the distance from the point defect increases.

Molecular arrangement about
the point defect

Crossed Polarising
lenses

Figure 22: Molecular alignment for production of a 2 brush *Schlieren* texture.

Compounds **20-23** exhibited both two and four brush *Schlieren* textures. Phase formation was evident on both heating and cooling cycles, with clear and distinct transitions. The samples passed through only one transition, with no evidence of any other textures. A typical image from the microscopy studies is shown in Picture 3. All the samples analysed were seen to exhibit the same textures.
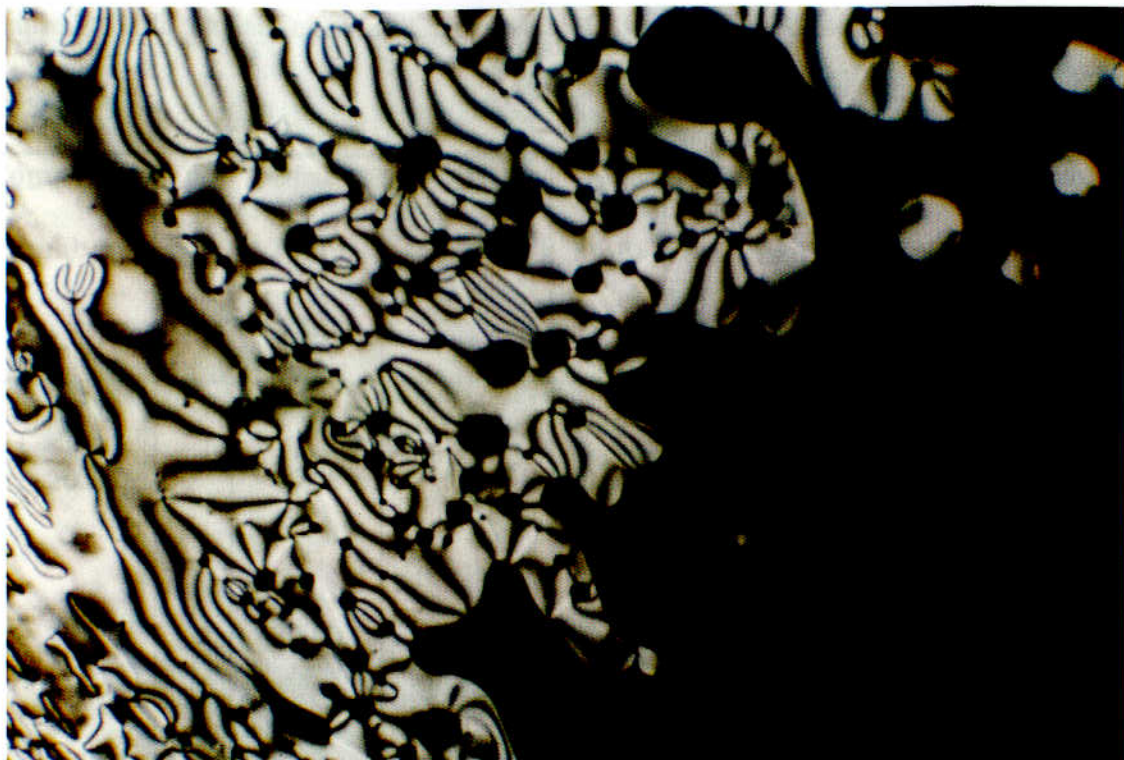
Picture 3: Nematic phase formation exhibited by compound 5-8. Magnification:×80, Polarisation: 180°

These compounds were also analysed by DSC. The data obtained was in line with nematic phase formation. This data is shown in Table 3.

Table 3: Differential Scanning Calorimetry Data For The Mesogens

Compound number	n	Onset Temp (°C)	ΔH (kJmol^{-1})	ΔH (Jg^{-1})	ΔS (JK^{-1}mol^{-1})	ΔS (JK^{-1}g^{-1})	Phase transition
20	2	43.58	0.084	0.28	0.27	0.09	K → N
20	2	76.08	3.29	0.01	9.42	0.03	N → Iso
21	3	75.48	30.45	97.49	87.38	0.28	K → N
21	3	89.80	1.66	5.33	4.58	0.01	N → Iso
22	4	52.95	27.63	84.65	84.77	0.26	K → N
22	4	60.91	1.54	4.34	4.71	0.01	N → Iso
23	6	53.95	24.38	68.82	72.82	0.003	K → N
23	6	61.80	3.01	9.67	8.99	0.03	N → Iso

Both the microscopy and the DSC experiments were repeated 3 times, each time resulting in reproducible values for both the onset temperatures and enthalpy changes. The values shown in Table 3 are the averages of those results.

The transition temperatures quoted are the onset of the phase, i.e. the beginning of molecular disruption. It is advisable to quote these values, as peak centre values determined by DSC can often be affected by both the sample size and heating rate. The heating cycle used in this particular experiment was 10.0°C per min. The entropy values were calculated using the relationship $\Delta G = \Delta H - T\Delta S$. As the process is reversible $\Delta G = 0$ at the melting point, hence $\Delta S = \Delta H/T$.

2.9 DISCUSSION.

A number of trends in the onset temperatures were observed for these compounds. The "odd-even" effect[78] was apparent with compounds comprising an even number of atoms in the spacer group displaying lower transition temperatures than compound **21**, with an odd number of atoms. The onset temperature for compound **21** is 22°C higher than those of compounds **20** and **22**, which differ by just one carbon atom in the chain.

The enthalpy changes for the transitions associated with compounds **20-23** provide a good indication of the extent of change in order when the samples were heated. Dealing firstly with compounds **21, 22** and **23**. It is noticeable that the enthalpy values for the formation of the nematic phases are significantly higher than for the production of the isotropic liquids. The first transition that all the compounds passed through involved a large input of energy. The enthalpy changes correspond to a dramatic reduction in the extent of intermolecular bonding. As was mentioned previously such a nematic phase is the least well-ordered phase where the molecules have lost their positional order. This loss of order from the crystalline solid is substantially greater than any subsequent loss of order, hence a large enthalpy change is observed, with ΔH values of approximately 30 kJmol^{-1}. The transition from the nematic phase to the isotropic liquid involves only the loss of the orientational order of the molecules, involving a minimal disruption at the molecular level. The ΔH values in this situation are approximately 1.5 kJmol^{-1}. The entropy values observed are in line with these results, confirming the magnitude of molecular disruption required at each phase transition.

Turning to compound **20**, where n=2, the values for enthalpy and entropy changes are somewhat ambiguous. These data do not fit with the logic of phase transitions expressed

previously. ΔH for the onset of the nematic phase is very low, only 0.084 kJmol⁻¹. This suggests that very little disruption is required to form a nematic phase from a crystalline sample of this species. This suggests that the positional order in the crystalline solid is readily lost with little input of energy. The onset of isotropy for compound **20** however, required a level of disruption comparable only to compound **23**, where n = 6. Compound **20** required more than twice as much energy to produce an isotropic liquid as either compound **21** or **22**. This evidence implies stronger intermolecular bonding in the nematic phase, a proposal supported by the stability of the phase across 33°C (43-76°C).

Generally ΔH values for liquid crystalline transitions (N→Iso) should be larger for species with longer spacer chains. This is due to enhanced intermolecular bonding between the chains. In the cases examined this trend was only observed with compounds **22** and **23**. The opposite effect was noticeable for compounds **21** and **22**, with the enthalpy of phase transition decreasing with the longer chain length.

The true liquid crystalline nature of these molecules is illustrated by their phase stability, as indicated by the temperature range over which the phase occurs. For example compound **23** was stable across 7°C, whilst with compound **21**, the nematic phase was observed across 14°C. With all compounds **20-23** the nematic phase was seen to occur and be maintained right through to isotropy. The presence of *Schlieren* brushes was noticeable throughout the temperature ranges quoted in Table 3.

2.10 COMPARISON OF COMPOUNDS 20-23 WITH OTHER MESOGENS

Comparison of compounds **20-23** with other mesogens identifies both similarities and differences. Previous mesogens that have been coupled to silsesquioxanes include cyanobiphenyls[67, 73], alkenylbiphenyls[74] and alkenylbiphenylcarboxylates[73]. Examples, and corresponding liquid crystal transitions, are shown in Compounds **24-26.** The values quoted in brackets are the enthalpy changes for the transitions in $Jmol^{-1}$.
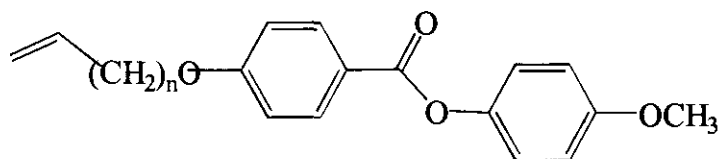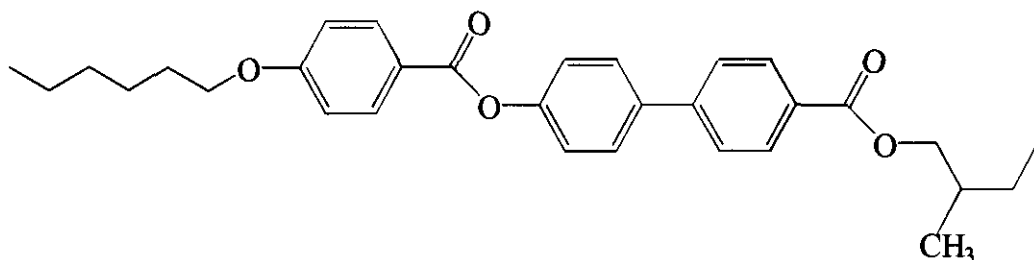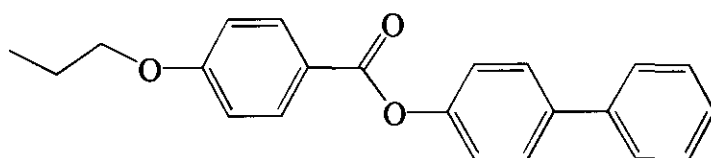
Compound 20 n=2 K 43.58°C N 76.08°C (3.29) Iso
Compound 21 n=3 K 75.48°C N 89.80°C (1.66) Iso
Compound 22 n=4 K 52.95°C N 60.91°C (1.54) Iso
Compound 23 n=6 K 53.95°C N 61.80°C (3.01) Iso
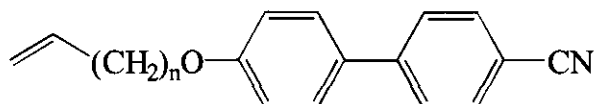
Compound 24[67,73] n=5 K 83.8°C N 89.0°C Iso
Compound 25[67,73] n=6 K 36.8°C N 52.2°C Iso
Compound 26[67,73] n=8 K 36.3°C N 57.3°C Iso

Compound 11[74] K 78.5°C S_C 106.1°C (0.34) S_A 157.2°C (1.41)
N 168.9°C (0.73) Iso

Compound 12[73,74] K 78.5°C S_C 106.1°C S_A 157.2°C N 168.9°C Iso

All of these mesogens have the same overall geometry, in that they are all long, rigid molecules supported by linked phenyl groups and carbonyls. Alkyl chains serve as spacer groups and enable a series of compounds to be prepared for comparison.

Compounds **24-26**[79] were shown to exhibit nematic phases; as with compounds **20-23** no other transitions were evident. The onset temperatures for transitions produced by

compounds **20-23** were higher than those compounds **24-26**. For compound **25**, where n=6, K→N was seen at 36.8°C, whereas the same transition for a comparative species, compound **22**, was observed at 53.9°C. These data suggests that compound **22** is less stable as a liquid crystalline compound than compound **25**. The "odd-even" effect was also noticeable for compounds **24-26**; however, as can be seen from the data, this was considerably more pronounced than for compounds **20-23**.

Both compounds **11**[74] and **12**[73, 74] were shown to produce S_C and S_A phases prior to the onset of the nematic phase. Transitions were observed at considerably higher temperatures than for compounds **20-23**. Compound **12** was shown to produce a nematic phase at 157.2°C, and compound **11**, the same phase, at 168.9°C. The lack of such complex phase transitions for compounds **20-23** suggests these have a simpler liquid crystalline system. This is due to the molecular structure of compounds **11** and **12** and is probably a result of the biphenyl groups.

2.11 RESULTS 2: Silsesquioxane liquid crystals.

The coupling reaction of the mesogen to the cage was carried out using Karstedt's catalyst[65] as shown in Reaction Scheme 7. The hydrosilylation was affected by refluxing in toluene and monitoring by Fourier Transform Infra red spectroscopy, observing the gradual disappearance of the Si-H stretch at 2143cm^{-1}. By attaching the mesogens to the silsesquioxane cage it was hoped that novel materials would be prepared. The pertubation afforded by the mesogen being tethered to a cage should result in the change to a more ordered phase being observed.

Compound 27: n=2
Compound 28: n=3
Compound 29: n=4
Compound 30: n=6
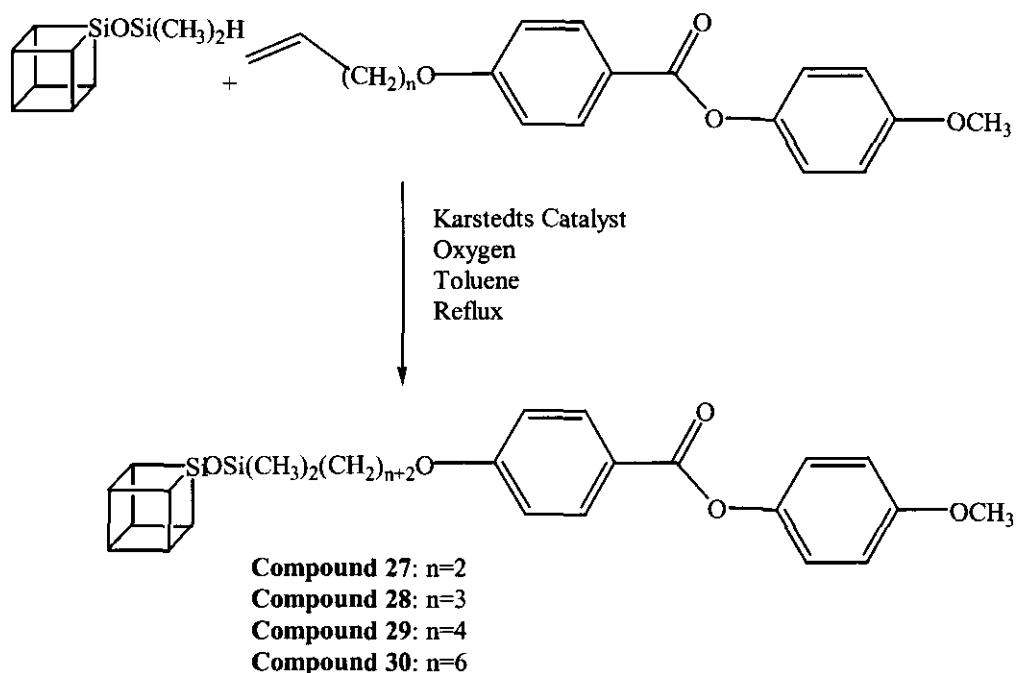
Reaction scheme 7: Hydrosilylation of mesogenic compounds.

The structure of the functionalised silsesquioxane **28** was confirmed by MALDI-TOF mass spectrometry. Samples were analysed using a DHB matrix with NaI. Compound **28**, where n=3, has a calculated mass of 3513.0. A peak of 3538.5 verified the presence of this compound, since this is the equivalent of the target molecule plus sodium (3538.5-22.9 = 3516). A slight mass deficiency of approximately 2.6 amu was observed in the measured masses. However this difference is within the error of the measurement. Isotope distribution calculations were carried out to compare theoretical results with experimental data. The experimental and theoretical distributions were found to correlate well.

A second set of peaks was observed at 3460.4, a difference of 78 compared to the target molecule. Such a peak suggests one R group does not contain a phenyl group. This type of fragmentation would also involve the loss of an OCH$_3$ group, including another 31 mass units. No evidence of such a peak is seen, discounting such a fragmentation. The purity of the individual side arms was confirmed prior to hydrosilylation, removing the possibility of impure starting materials.

It is also possible that such a fragment comes from the absence of one $OSi(CH_3)_2$ linkage. This would present a mass value of 3464.4. However, alternative data for both the starting silsesquioxane and the final product, confirm the structure is compound **28**. An anomaly in the microanalysis for both compounds would be obvious in such a situation. This is not the case and ^1H, ^{13}C and ^{29}Si NMR confirmed the Q_8 nature of the final compound. Discarding the absence of a phenyl group, an alternative explanation for the peak at 3460.4 is a distribution of methylene groups in the mesogen linker. Such a situation has not been previously observed in either starting material or final product. There is a slight possibility that such a 'rearrangement' could occur under MALDI-TOF conditions.

In conclusion, the main peak distributions prove the presence of the target compound, other peaks may represent the presence of a rearranged compound. They are not the result of any impurities in the final compound.

MALDI-TOF mass spectrometry was also carried out on compound **30**, where n=6. Here the measured mass (+Na) was 3871.8, highlighting the nominal mass of 3848.7. This correlated well to the calculated exact mass of 3849.4. The species was therefore identified as the target molecule compound **30**.

A number of other peak distributions were also seen in this spectrum. Masses of 3462.8, 3521 and 3643 were observed. Comparison of the nominal mass and that of the target molecule allowed us to identify these compounds.

The first fragmentation seen in this spectrum involves partial removal of one arm from the functionalised silsesquioxane. The measured mass of 3643.8 corresponds to compound **31**. The nominal mass of 3620.8 correlates, within experimental error, with the calculated mass of 3627.0. This partial fragmentation involves a loss of 227.9 mass units, correlating to a

loss of the phenyl ester unit. This is the first stage of the fragmentation process seen in the mass spectrum of compound **30**.

R = OSi(CH$_3$)$_2$(CH$_2$)$_{n+2}$OH

R = OSi(CH$_3$)$_2$(CH$_2$)$_{n+2}$O—⟨◯⟩—C(=O)—O—⟨◯⟩—OCH$_3$
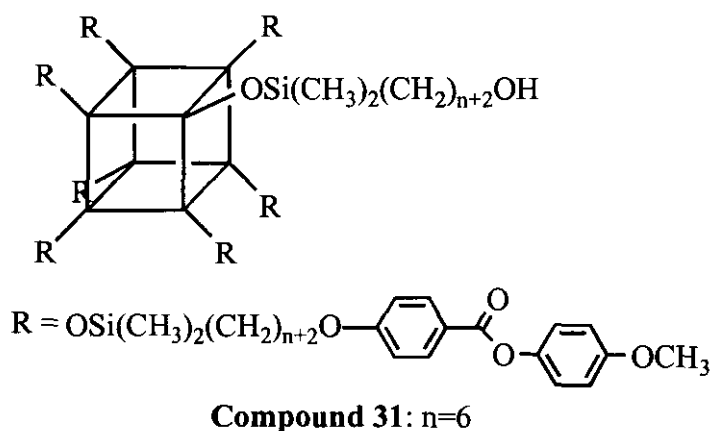
Compound 31: n=6

The peak at 3521.7 was found to correspond to the seven fold functionalised silsesquioxane, compound **32**.

OSi(CH$_3$)$_2$H

R = OSi(CH$_3$)$_2$(CH$_2$)$_{n+2}$O—⟨◯⟩—C(=O)—O—⟨◯⟩—OCH$_3$
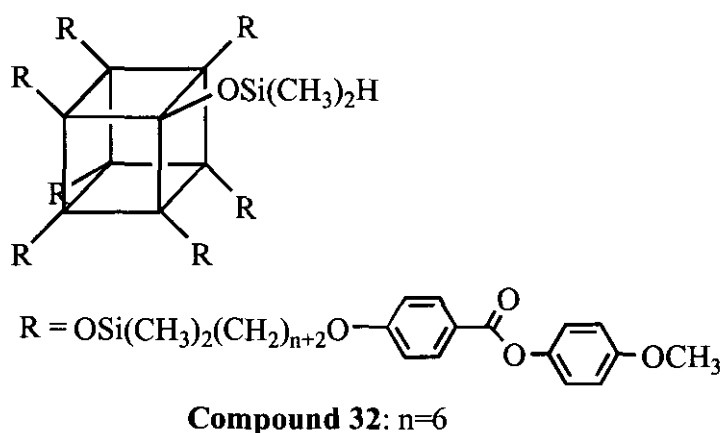
Compound 32: n=6

Here the calculated mass is 3498.7, corresponding to the distribution at 3521.7 (3521.7-22.9). This compound could be formed in two ways. Compound **32** could be a fragmentation species, although a range of peaks would be expected as each arm is removed in turn. However, there is no evidence of further side arm removal. Alternatively this could be a result of incomplete hydrosilylation. If this were the case, a range of peaks in the ^{29}Si NMR would highlight the presence of such a species. The NMR for compound **30** was very simple, with peaks only observed at 12ppm and –108ppm. This suggests that compound **32** is more likely a fragmentation species.

Further fragmentation of compound **32** would produce compound **33**. The mass at 3462.8 is indicative of the [(TR)$_7$T(OH)] were an R group in the original compound has been replaced by an OH group. The calculated mass of this species is 3439.8, corresponding well with the distribution seen at 3462.8 (3462.8-22.9 = 3439.8).


R = OSi(CH$_3$)$_2$(CH$_2$)$_{n+2}$O⟨⟩O⟨⟩OCH$_3$
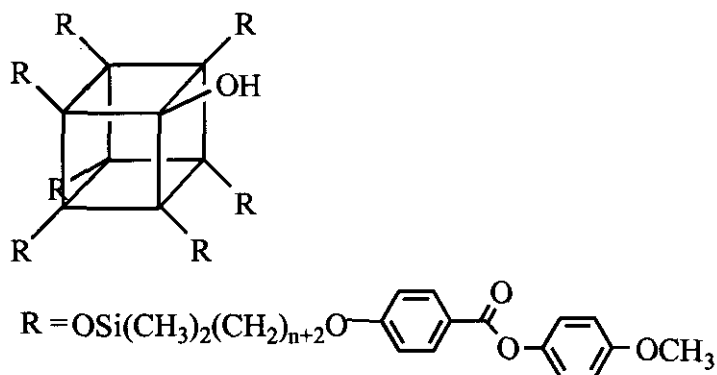
Compound 33: n=6

Analysis of these silsesquioxane compounds was also carried out using hot stage optical microscopy and differential scanning calorimetry in an attempt to ascertain their liquid crystalline properties.

2.12 PHASE IDENTIFICATION FOR COMPOUNDS 27-30.

Smectic A phases were observed for compounds **27-30.** This phase is identified by characteristic textures viewed under a polarising light microscope, known as bâtonnet and focal conic fan textures[78]. Focal conic fan textures are the result of molecules aligning into layers, whereas bâtonnet are the phenomena resulting from the breakdown of these layers. Examples of these two types of textures are shown in Pictures 4 and 5.
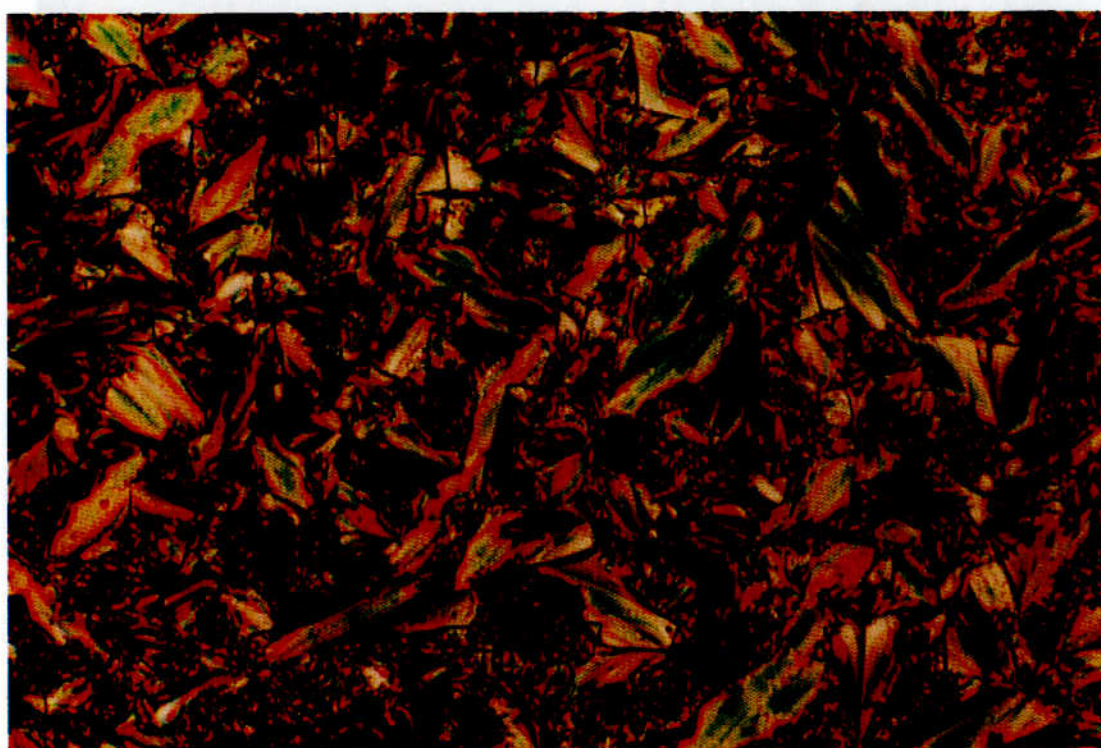
Picture 4. Focal conic fan textures seen for the smectic phase of compound 30.
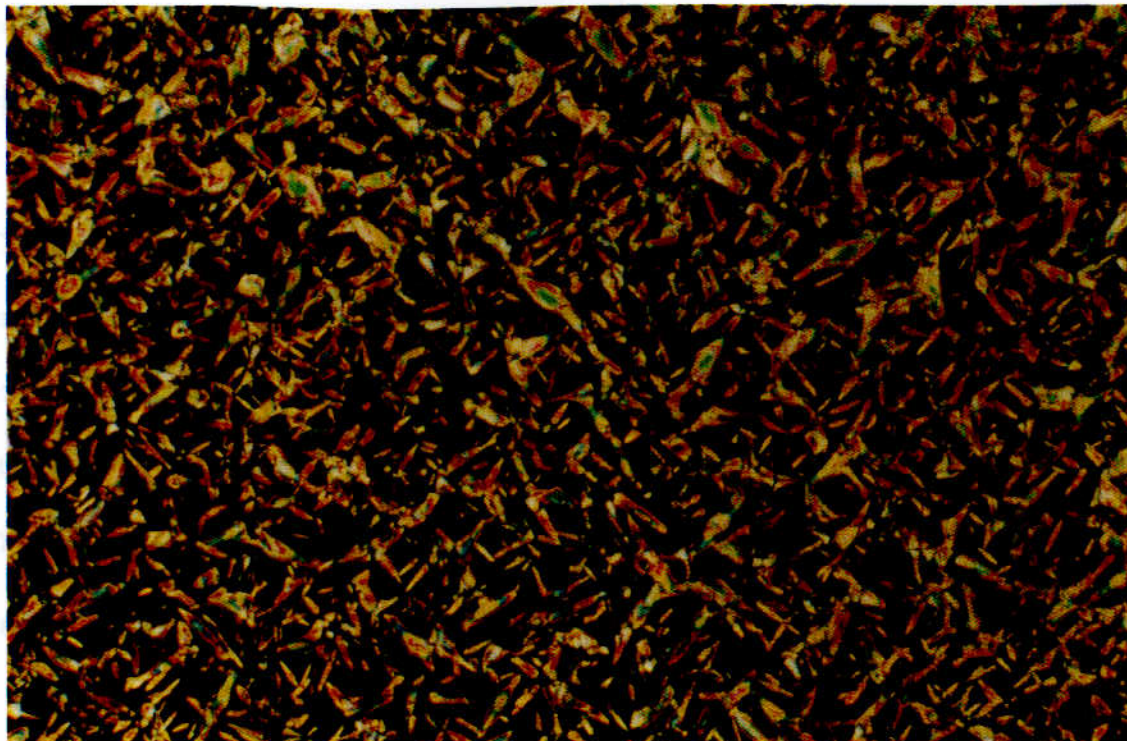
Magnification: ×80, Polarisation: 90°

Picture 5: Batonnet seen for the smectic phase of compound 30. Magnification: ×80, Polarisation:90°

Identification of the smectic phase is slightly more complex than the nematic phase. It is possible to distinguish between the various types of smectic phase formed using optical polarising microscopy because the distinct structural arrangements reveal unique defect textures for each phase. However, the variations in birefringent textures due to tilting of layers and hexagonal packing can be difficult to differentiate between, and so this technique is usually used in conjunction with others

When viewed through a polarising light microscope the smectic A phase exhibits two textures. Molecules that are aligned homeotropically are orientated such that their optical axis is normal to the microscope slide. In this situation the polarised light is unaffected by the sample and the texture appears black. Such homeotropic alignment gives textures that are the same as those seen in the nematic phase, the molecules are aligned with the crossed

polarising lenses and produce optically extinguished black lines. These lines are seen as black crosses.

The second type of texture exhibited by the Smectic A phase arises from the packing in the layered structure. The result, a focal-conic fan texture, as shown in Picture 4, is the result of the energetically favourable packing of the layered structure. The packing gives rise to a set of curved equidistant layers. These layers correspond to the geometric pattern known as Dupin Cyclides[78]. The overall visual effect is a coloured fan with characteristic black crosses on top.

The Dupin cyclides, shown in Figure 23, consist of two sets of concentric circles that merge into each other, usually in an unsymmetrical manner. This produces the fan texture. The visible black lines arise from optical discontinuities, these are called the focal pair. The black lines are ellipses and hyperbola of the Dupin cyclide, and appear as such due to the sharp changes in the direction of the optical axis. Such an area of sudden change is isotropic and hence appears as a black region under polarising light. These regions always appear as crossed pairs, and are referred to as a focal pair. The geometric pattern of the Dupin cyclide is shown in Figure 23.
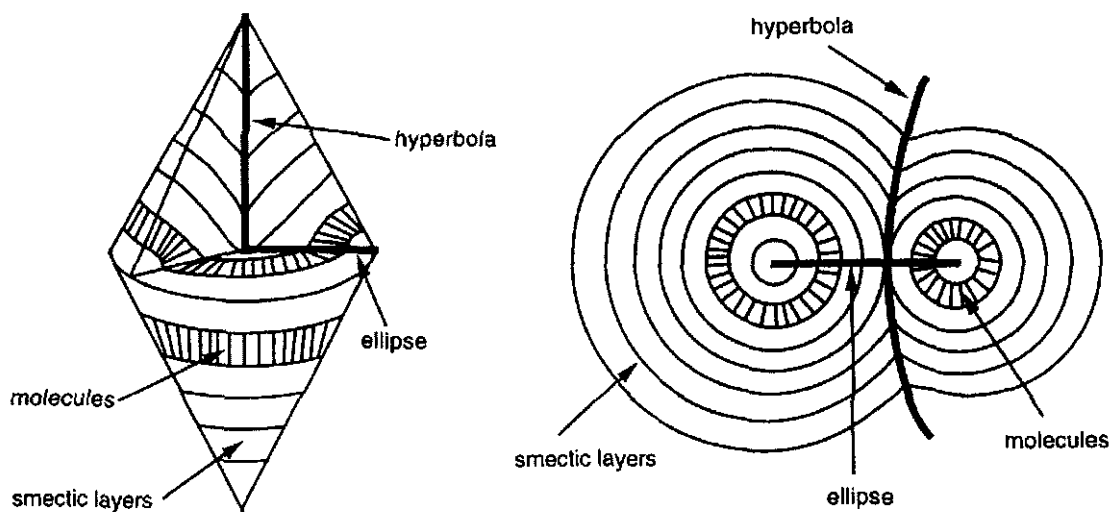
Figure 23: Dupin cyclides[78].

Both sets of textures are usually seen when a Smectic A phase is produced. The most common form of identification is by recognition of the fan texture and the focal pair on heating. Focal conic fan textures gradually give way to isotropy. The increasing disorder involves the break up of the fan textures to produce bâtonnet. These are seen through crossed polarised lenses as bright stars on a black background. This is indicative of the smectic A phase and the gradual loss of the layered structure. Bâtonnet textures are the last traces of the phase seen in a heating cycle and the first sign of a smectic phase when a cooling cycle is being carried out.

At the molecular level the mesogenic arms are thought to rotate about the siloxane spacer chain in order to lie parallel to each other, thus producing the layers necessary to exhibit a Smectic A phase. In the isotropic liquid the mesogen arms are arranged with spherical symmetry. The arms radiate from the central core filling as much space as is conformationally allowed. The onset of the liquid crystalline phase causes the mesogens to align in a rod-like manner. The result is a distorted structure as the phase forms[67].
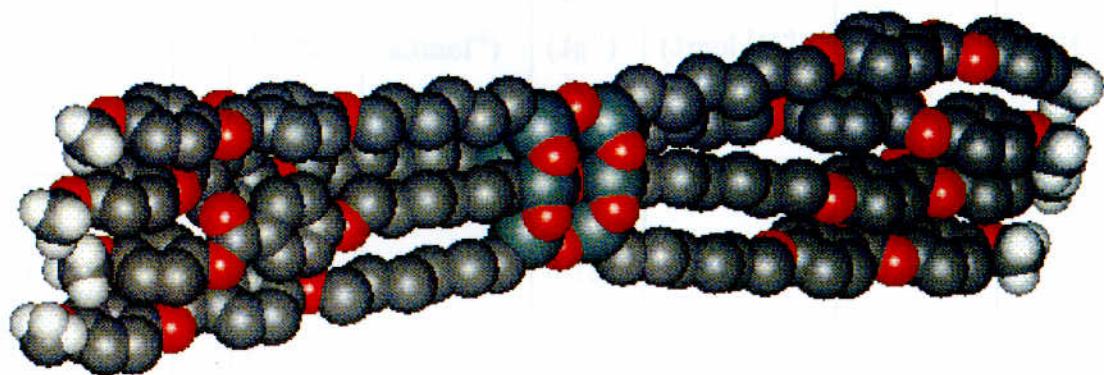
Figure 24: Space Filling Diagram of a Silsesquioxane Liquid Crystal

This molecular distortion was shown through modelling studies carried out by Goodby et al[67, 79]. The studies, involving minimising the energy of the species, revealed that even in the gas phase at absolute zero, a conformation is assumed where the mesogenic arms are aligned, allowing the supermolecules to achieve overall rod-like molecular shapes. Studies were carried out on tetramer, hexamers and octomers, with all species displaying the same effect [67].

The transition temperatures and the data collected using DSC for compounds **27-30** are presented in Table 4. It should be noted that the products actually possess n+2 CH_2 spacer units, as shown in Reaction Scheme 7.

Table 4: Differential Scanning Calorimetry Data

| Compound number	n	Onset Temp (°C)	ΔH (kJmol⁻¹)	ΔH (Jg⁻¹)	ΔS (Jmol⁻¹K⁻¹)	ΔS (Jg⁻¹K⁻¹)	Phase transition
27	2	30.20	0.17	0.05	0.56	1.6×10^{-4}	
27	2	85.84	0.63	0.185	1.76	5.2×10^{-4}	
28	3	86.87	56.86	16.17	158.01	0.044	K → S
28	3	94.03	29.82	8.48	81.25	0.023	S → Iso
29	4	56.47	76.24	21.01	231.41	0.06	K → S
29	4	76.57	24.53	24.53	70.17	0.02	S → Iso
30	6	81.75	6.55	6.55	18.46	0.004	K → S
30	6	97.16	2.93	2.93	7.92	0.002	S → Iso

2.13 DISCUSSION

Samples **27-30** were all seen to exhibit clear focal-conic fan textures as shown in Picture 4. Such textures were visible on heating and at higher temperatures gradually gave way to bâtonnet textures, before the onset of isotropy, as shown in Picture 5. This phase is borne out of the focal conic texture and both the size and brightness of the bâtonnet fade upon isotropy. The change in liquid crystalline phase from the free mesogens, compounds **20-23**, is due to the increased order afforded to the compound by tethering to the cage.

Upon cooling the behaviour was slightly different. The bâtonnet textures were seen to form out of the isotropic liquid and anneal into focal-conic domains. On further cooling the fan

textures were seen to increase in number. These samples were then expected to become crystalline solids as the intermolecular forces increased, and the molecules resume their lattice positions. However, observations by optical microscopy did not show this. The compounds were seen to remain in the liquid crystalline texture through to room temperature, as a result of supercooling.

Supercooling is the effect of 'freezing' a sample into a glass-like solid. The molecular ordering of the sample is not as it would be in the crystalline solid. As the sample is cooled the molecules are 'frozen', such that they do not assume their crystal positions. When observed by microscopy this will appear as if the sample does not return to the crystalline state, hence the focal-conic textures will still be present. The phase transition associated with supercooling will not occur at a sharp temperature, therefore it may also not be obvious by DSC. The glass solid will slowly anneal into the crystal structure, but again this will not occur at a distinct transition. In the case of compounds **27-30** the samples still exhibited liquid crystalline textures after two hours of being cooled. A typical section of a supercooled sample observed by optical microscopy is shown in Picture 4.

As was discussed earlier the smectic phase is more ordered than the nematic phase. By attaching the mesogens to cages a different liquid crystalline phase is observed. The mesogenic arms attached to the silsesquioxane structure can rotate and lie parallel to each other, creating a rod-like structure where molecules can pack together in layers to form a Smectic A phase, as shown in Figure 25.
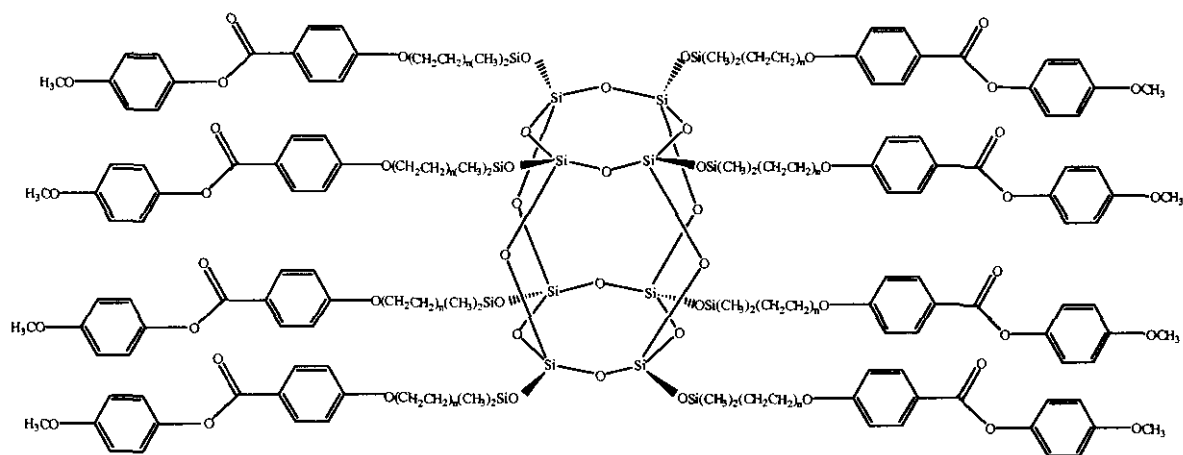
Figure 25: A liquid crystalline silsesquioxane.

The transition temperatures shown in Table 4 raise some interesting points. As with compounds **20-23** the 'odd-even' effect is seen, with compound **28** having the highest K→S transition temperature. This indicates that the phase instability present in the nematic phase has been carried through to the smectic phase for this range of compounds. The K→S transition temperatures for the liquid crystalline silsesquioxanes are generally higher than for the corresponding vinyl mesogens. This suggests that the liquid crystalline phase is not as stable for the silsesquioxane species as for the free mesogens. Increasing the number of methylene units in the spacer group between the ester group and the core unit from four to eight, normally results in an increase in isotropization temperature. This is observed with compounds **29** and **30** where increasing the spacer unit form 6 to 8 results in the isotropization temperature increasing from 76°C to 97°C. (We cannot include compound **28,** because of the odd even effect, or compound **27** because of flexibility problems, that were dealt with earlier.)

The enthalpy changes for the transitions observed provide useful information regarding the changes in molecular forces on production of the liquid crystalline phases. The expected enthalpy change for the transition of a smectic phase to an isotropic liquid is between 4 and 6 Jg^{-1}. First, let us consider compounds **28-30**. General trends in enthalpy values were

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noticeable. Enthalpy changes, in Jg^{-1}, for production of the smectic phases were less than for formation of the nematic phase produced by compounds **20-23**,. In line with this, the enthalpy changes at the onset of isotropy were far greater than the analogous transition in the nematic phases. These data indicate the greater change in order required to produce a nematic phase than a smectic phase. The smectic phase involves a loss of 'in plane' transitional order, whilst the molecules remain packed into their layered positions. As a consequence a higher degree of order remains in the sample which must be lost in order that the isotropic liquid can form. The ΔH values for this transition are therefore lower than the comparative transition of compounds **20-23**.

Enthalpy changes for the transitions of individual species serve to identify the significance of the spacer groups on liquid crystal phase formation. Consider now compound **27**. The enthalpy values are very small indeed. The short spacer group between the cage and the mesogen results in reduced intramolecular and intermolecular bonding. The chains are not as flexible as the longer chains and hence cannot align into layers as readily. This limits the extent of intermolecular bonding achieved. The transitions through smectic phase and on to isotropy involve a loss of this intermolecular bonding; however, there are fewer interactions to disrupt. The result of this would be a smaller value for the associated enthalpy change.

For the larger chain lengths there are significant degrees of both inter and intramolecular bonding. As a result the phase will be considerably more ordered compared to those with the shorter spacer group. At the molecular level this can be explained in terms of the increasing separation of the phenyl groups from the core. Intermolecular interactions are greater with longer chains. The phenyl groups are closer to each other due to the increased flexibility of the chain. This results in more intermolecular interactions between the phenyl groups, increasing the overall order within the structure. The onset of isotropy should

induce a loss of this intermolecular ordering; however, the intramolecular bonding along the chains will not be effected. As the enthalpy change is quite low, it suggests that there is still a certain degree of intermolecular bonding present in the isotropic liquid.

The entropy change values observed for these compounds highlight the difference in the molecular order involved with smectic phases compared to the nematic phase. Typically, entropy changes, in Jg^{-1}, for the formation of a smectic phase from the crystalline state are lower than for the formation of the nematic phase. This confirms the greater order involved with the smectic phase. For the same reason values for the formation of an isotropic liquid are higher for the smectic phase than the nematic. Generally compounds **27-30** show higher entropy values for transitions from crystalline to smectic, than for smectic to isotropic. A greater change in order is observed for formation of the smectic phase, compared to the transition from smectic to isotropic liquid. Compounds **28** and **29** exhibit relatively large entropy changes. The stable crystalline state requires $231 Jmol^{-1}K^{-1}$ to produce the S_A phase. There is still a considerable amount of order within this phase needing $70.17 \, Jmol^{-1}K^{-1}$ to produce isotropy.
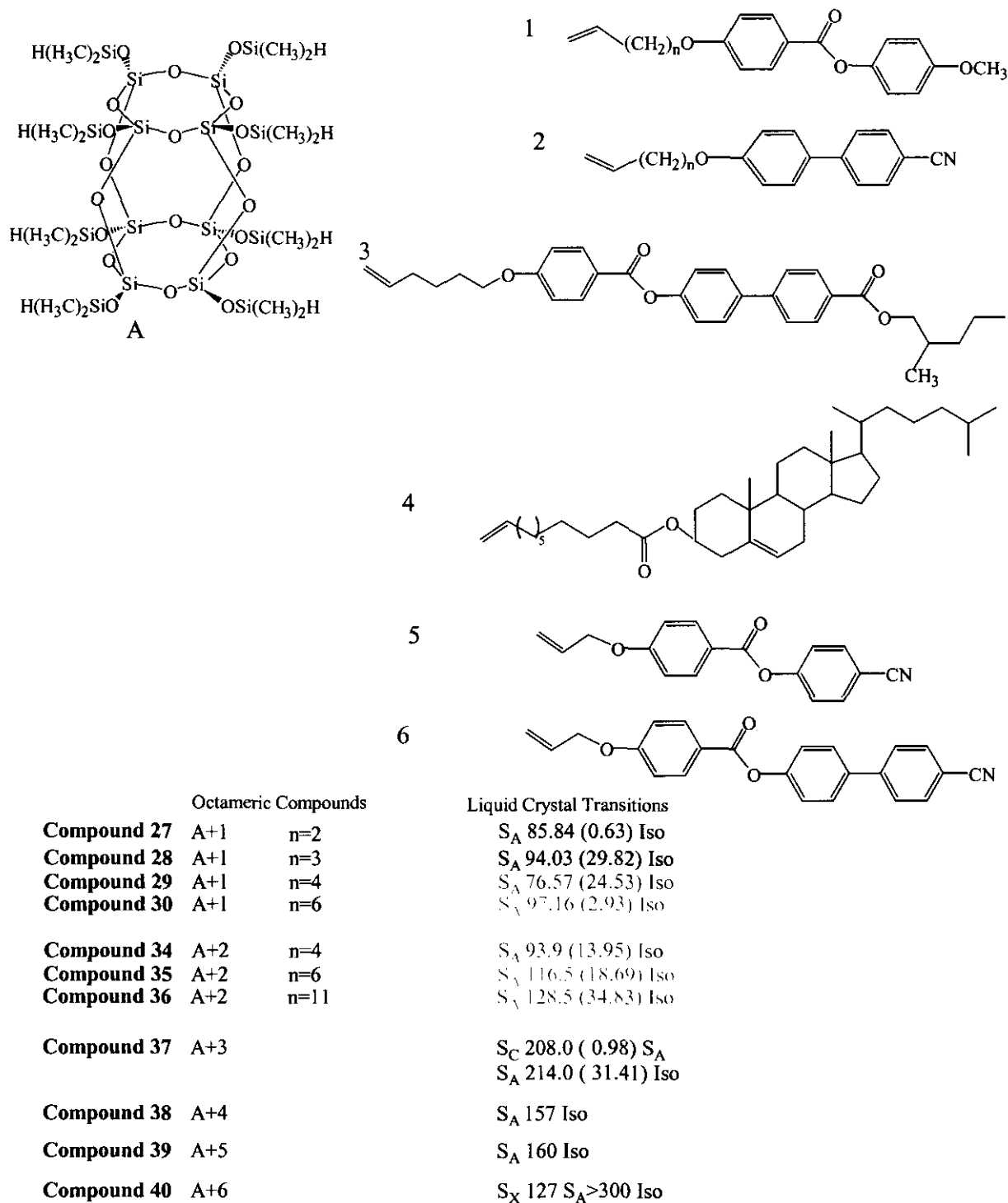
The limited intermolecular bonding due to a shorter spacer chain has already been discussed with respect to enthalpy. This is reflected in the value of the entropy change achieved for this species. Formation and destruction of the S_A phases involve very small entropy changes, confirming the loss of the small proportion of intermolecular bonding.

2.14 COMPARISON OF COMPOUNDS 27-30 WITH OTHER SILSESQUIOXANE LIQUID CRYSTALS.

Other workers have observed similar trends with compounds comparable to **27-30**. With the octasilsesquioxane compounds the mesogenic arms were found in each case to 'overpower' the conformational constraints of the cages distorting their shapes from spherical to tactoidal. The onset transition temperatures for compounds **27-30** were lower than those of similar species. A comparison with compounds of Goodby[67] and Kreuzer[71] can be seen in Figure 26.

Figure 26: Transition temperatures (°C), enthalpy changes (kJmol^{-1}) and liquid crystalline phases formed for silsesquioxane liquid crystals.

Octameric Compounds			Liquid Crystal Transitions
Compound 27	A+1	n=2	S_A 85.84 (0.63) Iso
Compound 28	A+1	n=3	S_A 94.03 (29.82) Iso
Compound 29	A+1	n=4	S_A 76.57 (24.53) Iso
Compound 30	A+1	n=6	S_A 97.16 (2.93) Iso
Compound 34	A+2	n=4	S_A 93.9 (13.95) Iso
Compound 35	A+2	n=6	S_A 116.5 (18.69) Iso
Compound 36	A+2	n=11	S_A 128.5 (34.83) Iso
Compound 37	A+3		S_C 208.0 (0.98) S_A
			S_A 214.0 (31.41) Iso
Compound 38	A+4		S_A 157 Iso
Compound 39	A+5		S_A 160 Iso
Compound 40	A+6		S_X 127 S_A>300 Iso

Liquid crystalline phases were generally in line with compounds **27-30**. The exception to this was the use of a S_C inducing mesogen by Goodby, producing compound **37**[67]. In most cases a different liquid crystalline phase was observed with the mesogen compound to the silsesquioxane liquid crystal. The phases typically observed for silsesquioxane liquid

crystalline species include Smectic A and Smectic C. Occasionally other less defined smectic phases were noticed, usually highlighted by DSC, the true phases not being clearly identified by optical microscopy. These phases are denoted as S_X transitions.

Compound 39[74] is directly analogous to the series 27-30. Production of a S_A phase at 160°C, a far greater temperature than for our series, suggests the liquid crystalline transition is less stable than for compounds 27-30. One possible explanation for this is the shorter spacer chain, allowing less freedom of rotation and less intermolecular bonding.

A range of compounds analogous to the series 27-30 is the cyanobiphenyl silsesquioxane compounds 34-36[67]. These species were observed to display a number of smectic phases for the longer chain length of n=11, with the shorter chains producing only the S_A transitions as with compounds 27-30. Noticeable trends include the increase in isotropization temperature when longer chain length mesogens are coupled to the cages. These phase transition temperatures are greater than those of compounds 27-30. The free mesogen, compounds 20-23, also exhibit lower transition temperatures than the corresponding cyanobiphenyls and it is thought that this effect is being carried through to the silsesquioxane compounds. This trend is also seen with the cholesterol silsesquioxanes synthesised by Kreuzer, compound 38[71].

A comparison of ΔH values for these two systems raises some interesting points. First, let us consider compounds 29 and 34, where n is 4 in both systems. The enthalpy change for the production of an isotropic liquid from the smectic phase is greater for the ester compound than the cyanobiphenyl species. This represents the greater order involved in the aligned sample of compound 29 compared to compound 34. This situation is reversed when considering compounds 30 and 35[67], where n is 6 for both species. The

cyanobiphenyl compound now has far greater order than the ester. This degree of order is representative of the extent of intermolecular bonding present within the aligned sample. This fact is highlighted with compound **36**. The ΔH value for isotropization is 34.83 kJmol⁻¹. This species has a much longer spacer chain than those of compounds **27-30**. The greater value of ΔH for compound **36** compared to compound **30** is due to more energy being required to disrupt the greater degree of intermolecular bonding on isotropization, associated with the longer chain length of compound **36**. As with compound **30** a level of order will remain in the isotropic liquid.

Compounds **37-40**[68, 74] represent a variety of species that have been attached to the silsesquioxane cage. Compound **40** was shown to exhibit a very high temperature of isotropization, greater than 300°C, whilst the cholesterol based species, compound **40**, showed liquid crystalline transition at 157°C.

2.15 SUMMARY

A series of mesogenic compounds **20-23** has been prepared. The molecular architecture was such that the species were ellipsoidal and displayed simple liquid crystalline phases. They were successfully shown to display nematic phase transitions.

Optical microscopy and DSC were used to determine and analyse the liquid crystalline phase behaviour of these compounds.

Transition data for compounds **20-23** highlighted some common trends. Evidence to support the 'odd-even' effect was observed with the onset temperatures of the compound

having an even number of atoms in the spacer chain being lower than those with an odd number of atoms.

The nematic phases were identified by the birefringent nature of the samples. Two and four brush *Schlieren* textures were clearly visible with crossed polarised lenses. Enthalpy and entropy change calculations for the transitions were also in line with the literature values. These values represented the degree of molecular order present within each phase, and the extent of loss of such order when undergoing transitions.

These mesogens were coupled with octasilsesquioxane to produce a novel silsesquioxane liquid crystals. This was achieved by hydrosilylation using the platinum containing Karstedt's catalyst[65]. The compounds prepared were expected to produce more ordered liquid crystalline phases than compounds 20-23, due to the increased order afforded to the mesogens when tethered to the cage. This was seen to be the case with S_A phases being exhibited.

Optical microscopy analysis and DSC data confirmed S_A phases were produced. Focal conic fans were seen to form out of the crystalline phase and give way to bâtonnet textures before the onset of isotropy. On cooling the samples were seen to undergo 'supercooling' providing the appearance of focal conic fans, even at room temperature. The silsesquioxanes are thought to support the model proposed by Goodby et al[68], in being distorted spheres in the liquid crystalline phase due to the aligning of the mesogens overpowering the cage structure.

DSC data highlighted the 'odd-even' effect again. Enthalpy and entropy calculations highlighted the difference in order between the nematic and Smectic A phases. The extent of order within the phases produced by shorter chains, i.e. compound 27, is considerably

less than those with longer spacers. This is due to a lack of flexibility within the chain, such that it can not align into layers as readily, limiting the intermolecular bonding. This is reflected in the smaller values of ΔH and ΔS. The longer spacer chain compound **30,** was also seen to exhibit smaller energy changes associated with phase transitions.

Comparisons with comparable molecular systems show compounds **27-30** to be in line with similar compounds in the literature. The phases and ΔH and ΔS changes for these liquid crystalline silsesquioxanes were as similar to those reported in the literature[67, 68, 71, 72, 76, 79,]

CHAPTER THREE

General Hydrosilylations

3.0 INTRODUCTION

Octopus molecules are high molecular weight compounds built upon silicon containing cores. These compounds are typically prepared via a multiple step process and are similar to star molecules. A star molecule is a compound with pendant groups radiating from a central atom. Octopus molecules possess pendant groups attached to a slightly more complex core, as indicated in Figure 27.
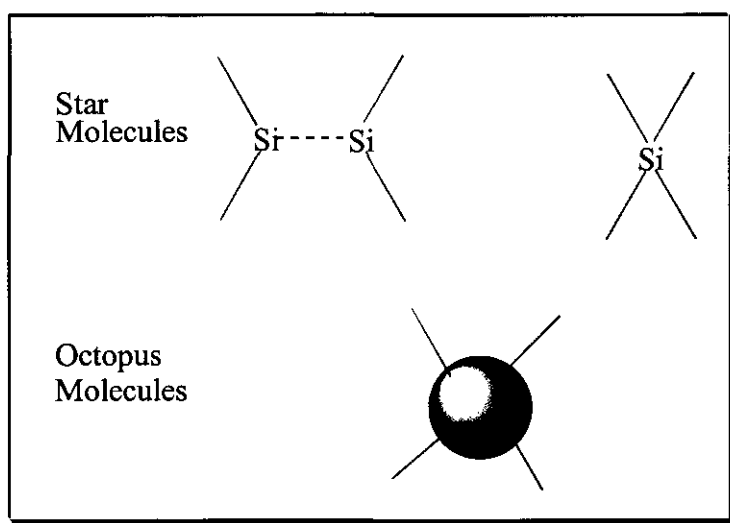
Figure 27: Representation of star and octopus molecules.

Examples of central cores include benzene [94], SiH_4 and the more complicated silsesquioxane ($HSiO_{3/2}$) derivatives [59, 63, 95]. A planar octopus molecule synthesised by Conner et al is shown in Figure 28 [96]. This derivatised benzene was originally named 'octopus' because it was used to encase a metal ion in its 'tentacle' pendant groups.
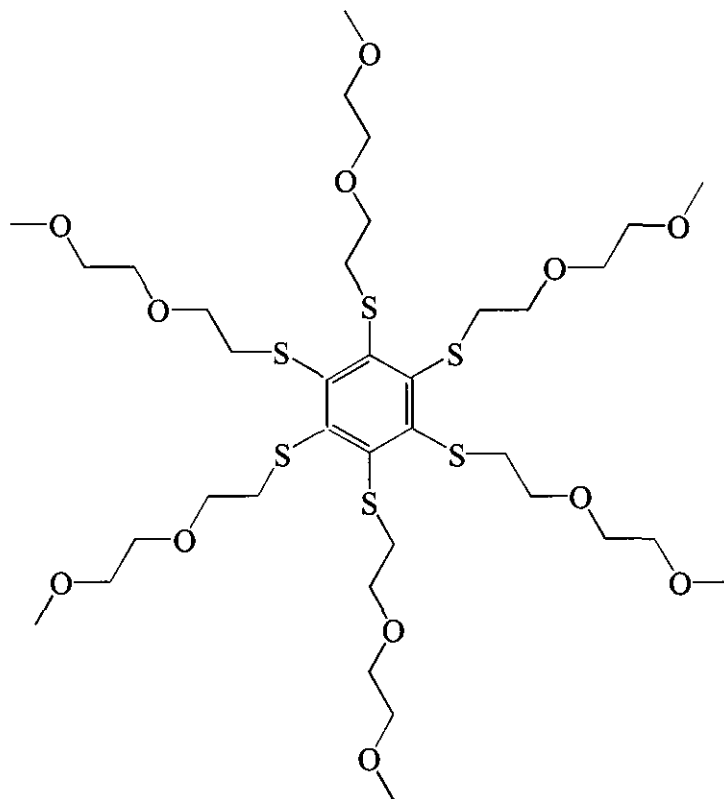
Figure 28: Planar octopus molecule based upon benzene

A great deal of work has been carried out on systems of this type [63, 97]. Octopus molecules have been prepared with organic and siloxane arms, and the work has been extended into dendrimer synthesis[49, 50]. Recent development of these macromolecular species has resulted in materials with controlled molecular formulae and thus specific physical properties. A number of different functionalities can be attached to a central silicon core and thus a range of octopus molecules can be prepared. Such arms are typically synthesised through a lengthy multi-step process. Hydrosilylation [62] has been used to attach the arms to the silsesquioxane cores and produce octopus molecules. Thus octopus molecules based upon silicon, particularly silsesquioxane compounds, have the advantage of only requiring one-step to achieve complete functionalistion.

3.1 HYDROSILYLATION: INTRODUCTION AND LITERATURE SURVEY

Hydrosilylation is one of the most fundamental methods of laboratory and industrial scale synthesis of organosilicon compounds. It is analogous to hydrogenation, involving addition of R_3SiH across a π bond [62]. Such processes typically occur with functional groups such as C=C, C=O and C=N.

Hydrosilylation was first developed in 1947 when trichlorosilane was reacted with 1-octene [98]. This was shown to be a free radical reaction, and, based on this mechanism, a number of refinements and developments were achieved.

In 1957 Speier discovered a catalytic variant. The homogeneous catalyst, known as Speier's catalyst, is hexachloroplatinic acid, which contains a Pt^{IV} centre that can be readily reduced to provide the catalytically active species [99]. However, it wasn't until a reasonable mechanism was defined that catalytic hydrosilylation was truly understood and thus could reach its full potential.
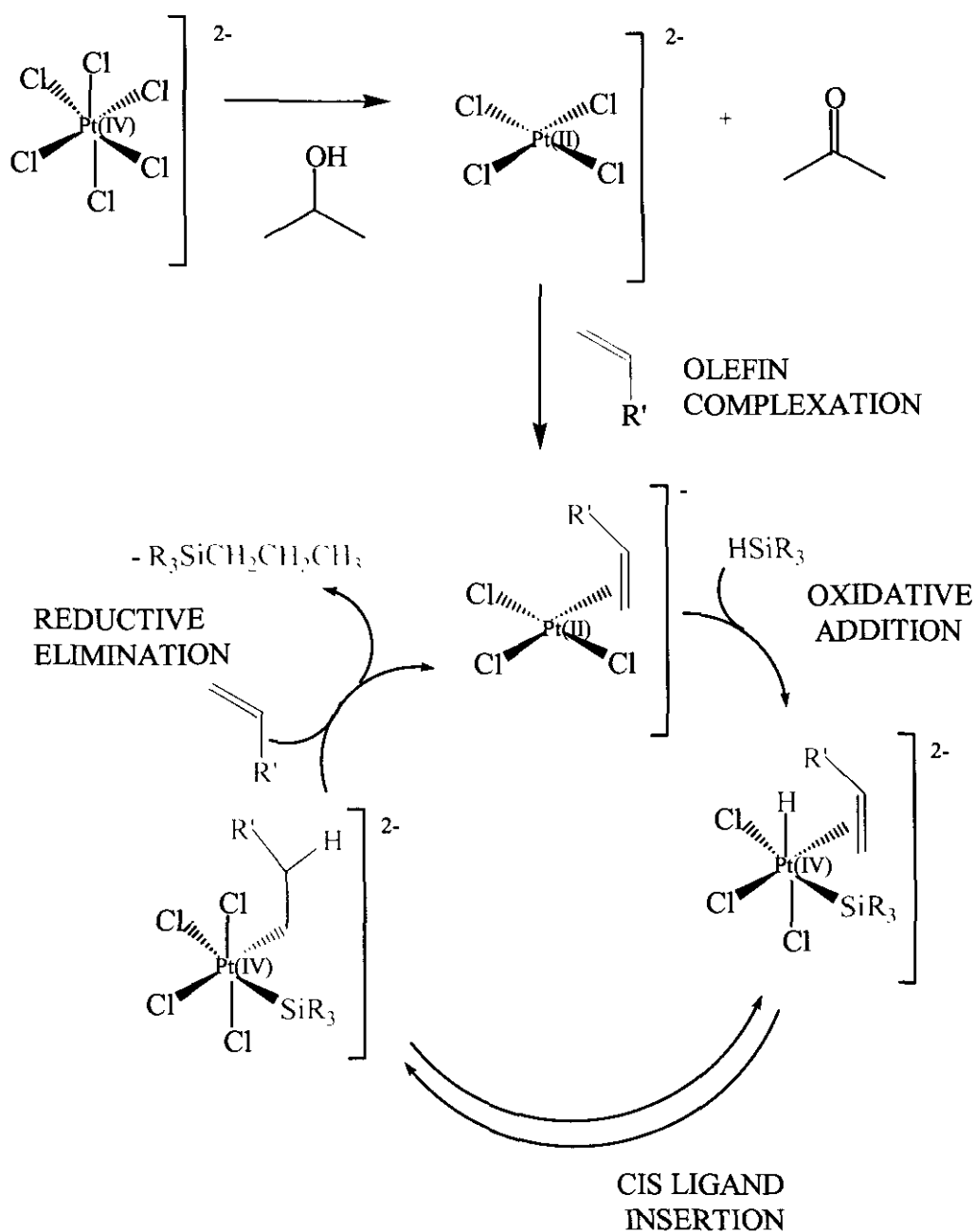
Figure 29: The Chalk-Harrod Hydrosilylation Mechanism.

The exact mechanism of the reaction has been the subject of much debate. The Chalk-Harrod mechanism [100], shown in Figure 29, is often quoted as the definitive mechanism, and has generally been accepted as the mode of addition for silicon hydrides to alkenes catalysed by platinum complexes. The initial induction stage of the mechanism involves a reduction of a Pt^{IV} complex to the Pt^{II} by isopropanol. This is followed by co-ordination of

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the unsaturated olefin to the metal centre, followed by oxidative addition of the hydrosilane. *Cis*-ligand insertion provides the rearrangement that was thought to be the rate-determining step of the process. Reductive elimination forms the organosilicon compound and regenerates the Pt^{II} species for further complexation with the olefin. There are however a number of issues that are not addressed by this mechanism. For example, the reaction mixture often becomes discoloured, a change from colourless to yellow, and in extreme cases black, being observed. A requirement for the presence of oxygen within the reaction system was also noticed. The steric and electronic effects of functional groups can also determine the mode of addition observed, which is, again, not considered in the Chalk-Harrod mechanism.

Variations on this mechanism were later proposed, the most significant involving platinum colloid formation. This was thought to be the crucial stage in a catalytic procedure outlined in the Lewis mechanism, which was postulated in the 1980's [101]. The catalytically active species was suggested to be colloidal particles of platinum, their formation preceding the rapid exothermic hydrosilylation reaction. Lewis reported that his proposed mechanism was intrinsically *the same as the Chalk-Harrod mechanism; for example, both have an* induction period. This involves the reduction of the platinum complex for both mechanisms. In the Lewis mechanism the catalyst is the free metal, as shown in Reaction Scheme 8. Catalysts based on the Pt (0) oxidation state have proven to be useful, an example being Karstedt's catalyst, the divinyltetramethyldisiloxane complex of Pt(0) [65, 102].

$$PtXL \xrightarrow{HSiR_3} HL + XSiR_3 + [Pt_0]x$$
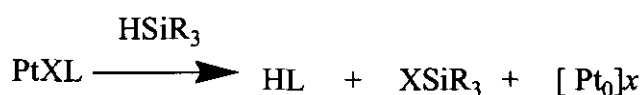
Reaction scheme 8: Formation of the platinum active species in the Lewis mechanism.
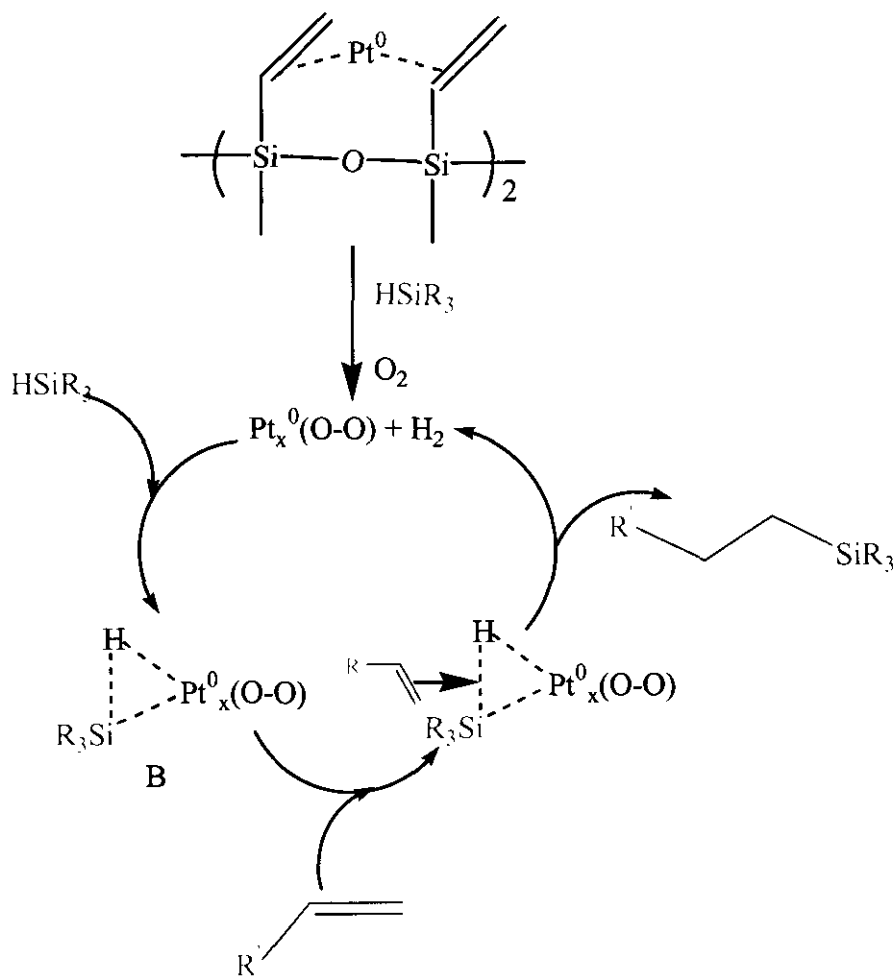
Figure 30: Lewis Mechanism Of Platinum Catalysed Hydrosilylation[101].

In the catalytic cycle the attack of R_3SiH preceeds the attack of the olefin, the opposite to the order of events in the Chalk-Harrod mechanism. In contrast to the Chalk-Harrod process, the Lewis mechanism includes oxygen binding to the active catalyst species. This presence of oxygen was shown to be truly catalytic in that it was not consumed during the reaction [101].

The fact that colloidal platinum is the active catalyst can be used to explain the factors known to limit the reaction. The aeration of the hydrosilylation reaction was shown to prevent severe colouration of the system. In the absence of oxygen dark colours are

observed, due to the formation of large colloids. Oxygen prevents this irreversible agglomeration. The physical size of the colloid formed had been found to play an important role, as large colloids are catalytically inactive. It is therefore vital to minimise the platinum aggregation in order to maintain the catalyst activity.

More recently Brook et al have described a platinum catalyst system which reduces colloid accumulation and which is able to turn over many times without catalytic degradation[103, 104]. A supported Pt^0 catalyst was prepared by reacting triethoxysilane with silica in the absence of water to produce a mobile hydridosilsesquioxane layer. Platinum complexes react with this mobile layer to provide an effective hydrosilylation catalyst. Investigation into the mechanism of platinum colloid formation suggested that the pendant Si-H groups play an important role. The network of 'T' silane species formed on the silica surface, shown in Figure 31, hinders the size of the aggregated metal. Without extensive metal aggregation the catalyst can be recycled several times.

Other variations, based upon the Chalk–Harrod mechanism, [105, 106] involve different metal species such as the transition metals; Rh, Co, Ru and Pd. However, despite varying degrees of success Speier's and Karstedt's Platinum based catalysts are still the most commonly used in hydrosilylation[100].
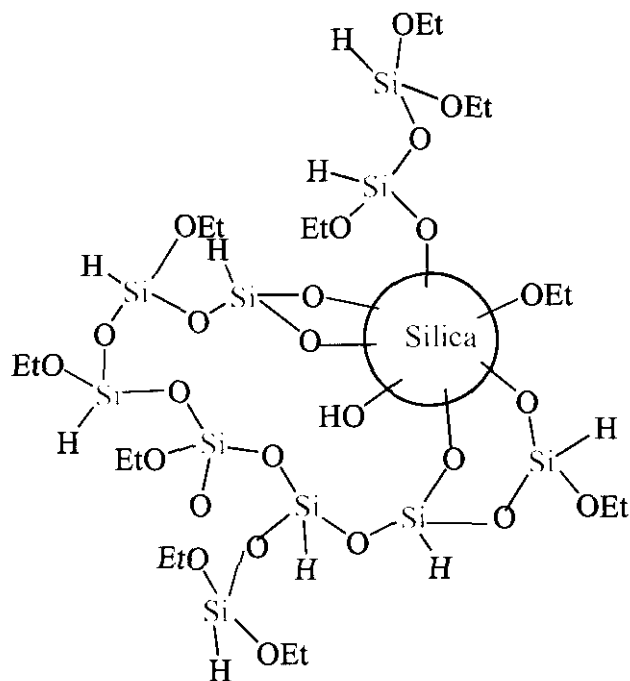
Figure 31: Representation of the silica surface prior to attachment of the catalyst, as proposed by Brook et al[103, 104].

In general hydrosilylation reactions are accompanied by a series of side reactions that reduce the yields of the desired products. The main side reactions are [62]:

a) α and β Addition of the silane to the alkene.

b) Alkene isomerisation.

c) Disproportionation of the hydrosiloxane.

d) Metal catalysed cleavage of the Si-C bond.

a)   Alkene compounds usually couple to silanes through hydrosilylation involving anti-Markovnikov addition. This is known as Farmers rule [107]. This attachment of the silicon to the β carbon produces a straight chain alkane coupled to the silicon species. An

alternate mode of addition involves attachment of the silicon to the more substituted α carbon of the vinyl group. This involves the production of a CH_3 group. Whilst β addition is the most common, occasionally the α product is seen as an impurity. Exact ratios depend on the nature of both the alkene and silane. Examples of α and β adducts are shown in Reaction Scheme 9.

$$H_2\overset{\beta}{C}=\overset{\alpha}{C}HR + HSiR'_3 \quad \xrightarrow{\text{α addition}} \quad H_3C-\underset{SiR'_3}{\overset{H}{\underset{|}{\overset{|}{C}}}}-R$$

$$\xrightarrow{\text{β addition}} \quad R'_3SiCH_2CH_2R$$
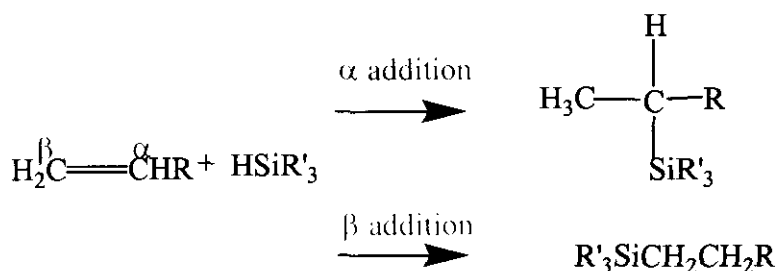
Reaction Scheme 9: Alkene addition to a silane by hydrosilylation.

b)   Hydrosilylation of internal alkenes often involves isomerisation of the alkene. Speier et al investigated hydrosilylations of 1,1,3,3-tetramethyldisiloxane (TMDS) with isomers of hexene [108]. Hex-1-ene produced the expected 1-hexyl product, however hex-2-ene and hex-3-ene provided a mixture of isomers. Similarly when 3-heptene was hydrosilylated with TMDS a mixture of the 3-, 4-, and to a lesser extent the 1- and 2-heptyl derivatives was observed[62]. The platinum complexes used in hydrosilylation reactions have been shown to catalyse alkene isomerisation. Examples are shown in Reaction Scheme 10 and 11.

$$R_3SiH + \quad \text{(alkene)} \quad \xrightarrow{\text{Pt}} \quad R_3Si\text{(alkyl chain)}$$
$$+$$
$$\text{(alkene)}$$
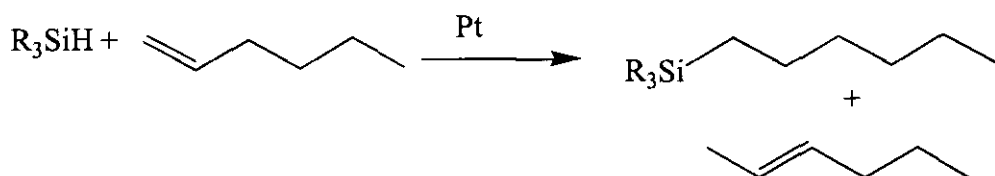
Reaction Scheme 10: Isomerisation of an alkene by Platinum catalysis

Alkene isomerisation can be both welcome and non-productive. The product of β addition is usually the major product; however, double bond migration can cause problems [108]. Internal double bonds are much less reactive than terminal alkenes, resulting in mixtures. In some cases isomerisation to a thermodynamically less stable alkene is reasonably quick and results in the terminal product being trapped as shown in Reaction Scheme 11.

$$HSiCl_3 \; + \quad \text{(alkene)} \quad \xrightarrow{H_2PtCl_6} \quad \text{(product)} \; SiCl_3$$

90%
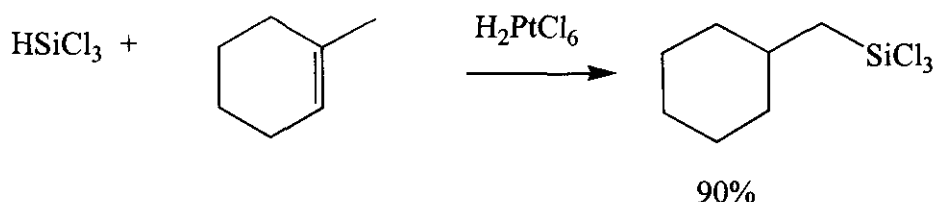
Reaction Scheme 11: Isomerisation of an alkene by platinum catalysis leading to a rearranged product

c)   Redistribution to give oligomeric silanes has been caused by chloroplatinic acid [109-111]. The resulting chain branching reactions have produced high molecular weight by-products, as shown in Figure 32.

$$m \; H-Si(CH_3)(H_3C)-[OSi(CH_3)_2]_n-OSi(CH_3)_2-H \quad + \quad m \; \text{(diallyl silyl phenylene silyl)}$$

$$\downarrow H_2PtCl_6 / Toluene \quad 90^0C$$

$$\left[-Si(CH_3)_2-[O-Si(CH_3)_2]_n-O-Si(CH_3)(H_3C)-\cdots-Si(CH_3)_2-\text{(phenylene)}-Si(CH_3)_2-\cdots- \right]_m + \text{side products}$$
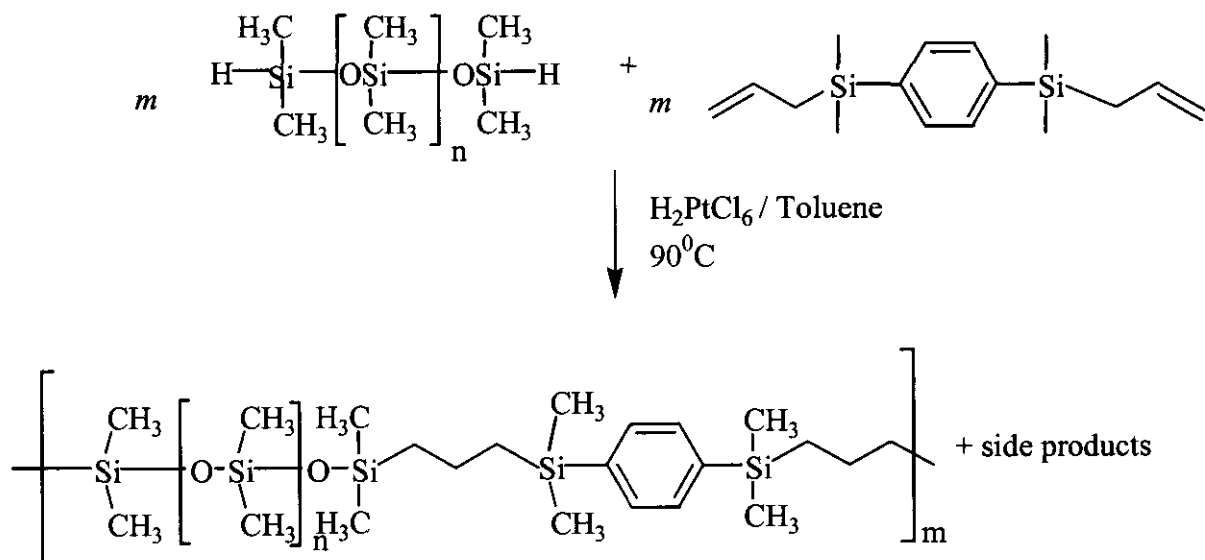
Figure 32: Example of Redistribution of products achieved by Hydrosilylation

d)   Cleavage of Si-C bonds is also possible at elevated temperatures in the presence of transition metals [112]. Platinum is known to effect such cleavage and this can sometimes become a major side reaction of hydrosilylation.

The side reactions described above are generally far slower than the actual hydrosilylation; hence such by-products are usually seen in relatively low quantities [113, 114].

Hydrosilylation has become a very important tool in preparing organosilicon compounds. The range of compounds prepared in this way is still expanding. The limitations of the process are far outweighed by the benefits of the reaction. Nevertheless, determining the cause of such by-products and potentially overcoming them is still an important area of research.

3.2 HYDROSILYLATION IN PRACTICE

The regiochemistry of hydrosilylation has been investigated as part of our studies on using hydrosilylations to produce functionalised silsesquioxanes.

In a series of reactions T_8H_8 and $[Si_8O_{12}][OSi(CH_3)_2H]_8$ were reacted with a number of alkenes to produce octopus molecules. The range of alkenes reacted with the silsesquioxanes was chosen to reflect the versatility afforded to the core via hydrosilylation reactions. Species such as hydrocarbons, amines, ethers, esters and aromatics have been successfully coupled with the silanes [63, 95, 108, 115, 116]. Compounds such as the amine are also useful for further functionalisation to produce more complex silsesquioxanes as demonstrated by Feher in the synthesis of silsesquioxane dendrimers [49-51].

3.3 INVESTIGATION INTO α AND β ADDITION.
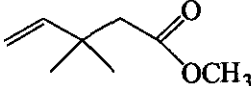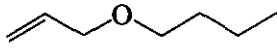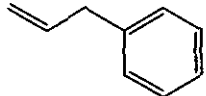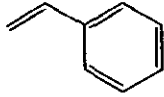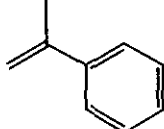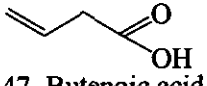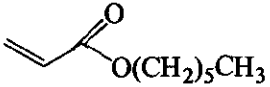
In order to probe the factors effecting α and β addition of silicon species to alkenes a series of hydrosilylation reactions have been carried out. The specific factors effecting α and β addition to silsesquioxanes have not been discussed in the literature. The size of the silsesquioxane cage may mean that steric factors could control product formation. Alternatively the oxygen atoms attached to the silicons may well have an electronic effect upon the hydrosilylation reaction. In order to probe the factors controlling the modes of addition to vinylic and allylic compounds, such species were also reacted with triethoxysilane $(CH_3CH_2O)_3SiH$, and triethylsilane $(CH_3CH_2)_3SiH$. The derivatised silane analogues are shown in Figure 33.

Derivatised   Derivatised Octa(silsesquioxane)   Derivatised
triethylsilane   triethoxysilane
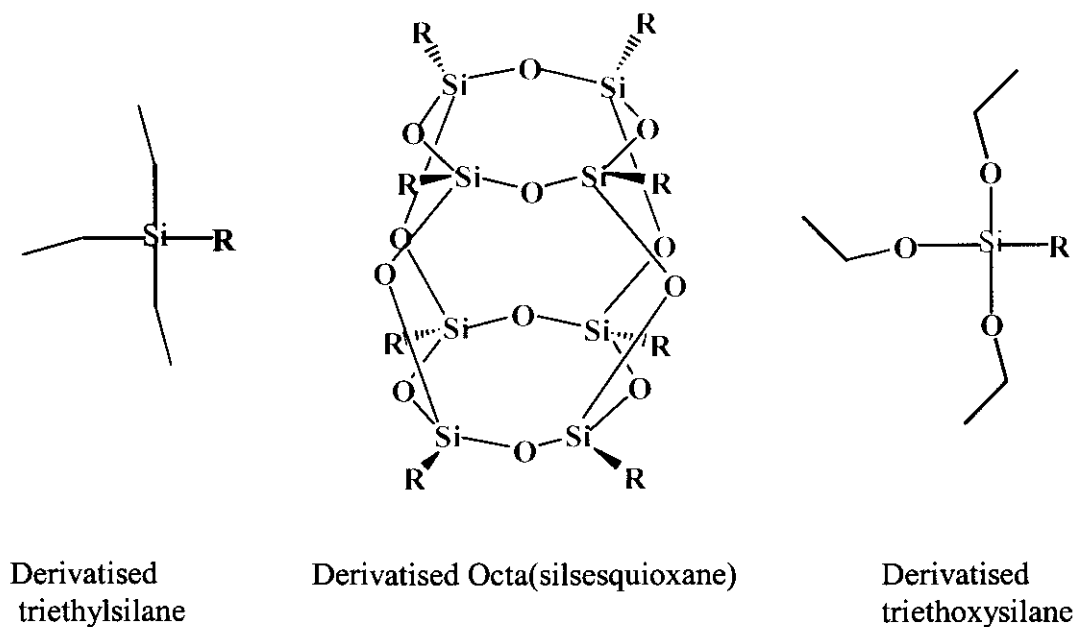
Figure 33:Derivatised Triethylsilane, T_8H_8, and triethoxysilane

Triethoxysilane was selected as a probe in order to mimic the silicon-oxygen arrangement at one corner of the T_8H_8 cube. Triethylsilane was used as a standard, in order to achieve a suitable comparison for the cage results, and with other data in the literature.

The alkene compounds used in the hydrosilylation with the simple silanes and the silsesquioxanes are shown in Table 5, along with a list of generic products for all reactions. In the table R_3Si represents any of the silicon containing core species. β products are highlighted in blue, with α products shown in red.

Alkene compound	General products
 41 1-Hexene	$R_3Si(CH_2)_5CH_3$ $R_3Si(CH)CH_3(CH_2)_3CH_3$
 42 Methyldimethylpentenoate	$R_3Si(CH_2)_2C(CH_3)_2CH_2CO_2CH_3$ $R_3Si(CH)CH_3C(CH_3)_2CH_2CO_2CH_3$
 43 Allylbutylether	$R_3Si(CH_2)_3O(CH_2)_3CH_3$ $R_3SiCH(CH_3)(CH_2)_2O(CH_2)_3CH_3$
 44 Allylbenzene	$R_3Si(CH_2)_3C_6H_5$ $R_3SiCH(CH_3)CH_2C_6H_5$
 45 Styrene	$R_3Si(CH_2)_2C_6H_5$ $R_3SiCH(CH_3)C_6H_5$
 46 α-Methylstyrene	$R_3SiCH_2CHCH_3C_6H_5$ $R_3SiC(CH_3)_2C_6H_5$
 47 Butenoic acid	$R_3Si(CH_2)_3CO_2H$ $R_3SiCHCH_3CH_2CO_2H$ $R_3Si[OCO(CH_2)_3]Si(CH_2CH_3)$
 48 Hexyl Acrylate	$R_3Si(CH_2)_2CO_2(CH_2)_5CH_3$ $R_3SiCH(CH_3)CH_2CO_2(CH_2)_5CH_3$

Table 5: General Products possible through hydrosilylation

The ratios of products for each reaction [Et$_3$SiH, (EtO)$_3$SiH, T$_8$H$_8$ and [Si$_8$O$_{12}$][OSi(CH$_3$)$_2$H]$_8$], were compared in an attempt to assess the exact structural effects of the silsesquioxane cage. Hydrosilylations were carried out to ensure complete substitution. To this effect the cage compounds were reacted in an 8:1 molar ratio of alkene

to silsesquioxane, whilst the simpler species were reacted in a 1:1 ratio. The catalysts used were chloroplatinic acid (Speier's catalyst)[62] and [bis-(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)platinum(0)] (Karstedt's catalyst) [65]. The Speiers catalyst was a solution of 0.02 moldm^{-3} chloroplatinic acid in propanol, with 4×10^{-5} mol of chloroplatinic acid being used per reaction. Karstedts catalyst was a solution of [bis-(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)platinum(0)] as provided by Dow Corning. Approximately 50μmol of platinum were used per reaction. The Karstedts catalyst was premixed with D3 and D4 oligomers and was further diluted in toluene. Triethylsilane, triethyoxysilane and T_8H_8 reactions were incubated at 80°C with Speiers catalyst, whilst the $Q_8[OSi(CH_3)_2H]_8$ reactions were carried out in refluxing toluene with Karstedt's catalyst.

It should be noted that α/β ratios have been shown to be dependent upon a number of factors including the nature of the catalyst, the nature of the olefin, the nature of the Si-H compound and reaction conditions such as solvent and temperature[100]. Therefore when dealing with T_8, $(RO)_3SiH$ and R_3SiH reactions the catalyst and reaction conditions were kept the same. The study therefore focused on the effect of the olefin and Si-H compound. When dealing with the $Q_8[OSi(CH_3)_2H]_8$ compound Karstedts catalyst was used therefore studying the effect of the different catalyst. The Karstedts catalyst was activated prior to use by bubbling oxygen through the reaction mixture.

The extent of hydrosilylation was estimated by the gradual disappearance of the SiH stretch in the FTIR spectrum at approximately 2100cm^{-1}. The disappearance of the vinyllic protons of compounds 41-48, and the Si-H resonance of the silsesquioxane in the ^{1}H NMR, was also indicative of a successful reaction (4.24ppm for T_8H_8, and 4.72ppm for $Q_8[OSi(CH_3)_2H]_8$). Similarly the position of peaks in the ^{29}Si NMR compared to the

starting materials indicates a successful reaction (-84.7ppm for T_8H_8, 12.97 and −108.58 for $Q_8[OSi(CH_3)_2H]_8$, 0.28 ppm for triethylsilane, and −58.82ppm for triethoxysilane).

Table 6 shows the results of all reaction carried out, including the yields of α and β products achieved. These ratios were determined by NMR analysis and are not purified yields. In the following discussions each reaction will be dealt with individually, initially considering the simple model systems based on triethylsilane and triethoxysilane.

Table 6: Products of general hydrosilylations

Compound Number	Reactant	Silane	Yield (%)	% α/β
49	Hexene	$(CH_3CH_2)_3SiH$	99	100
50		$(CH_3CH_2O)_3SiH$	99	100
51		T_8H_8	98	100
52		$Q_8[OSi(CH_3)_2H]_8$	98	100
53	Methyl 3,3-dimethylpent-4-enoate	$(CH_3CH_2)_3SiH$	98	100
54		$(CH_3CH_2O)_3SiH$	99	100
55		T_8H_8	95	100
56		$Q_8[OSi(CH_3)_2H]_8$	99	100
57	Allyl butyl ether	$(CH_3CH_2)_3SiH$	87	5:95
58		$(CH_3CH_2O)_3SiH$	95	5:95
59		T_8H_8	98	30:70
60		$Q_8[OSi(CH_3)_2H]_8$	97	100
61	Allylbenzene	$(CH_3CH_2)_3SiH$	93	5:95
62		$(CH_3CH_2O)_3SiH$	85	5:95
63		T_8H_8	85	30:70
64		$Q_8[OSi(CH_3)_2H]_8$	95	100
65	Styrene	$(CH_3CH_2)_3SiH$	74	5:95
66		$(CH_3CH_2O)_3SiH$	90	40:60
67		T_8H_8	72	40:60
68		$Q_8[OSi(CH_3)_2H]_8$	100	100
69	α- Methylstyrene	$(CH_3CH_2)_3SiH$	83	5:95
70		$(CH_3CH_2O)_3SiH$	85	5:95
71		T_8H_8		Insoluble

72		$Q_8[OSi(CH_3)_2H]_8$	100	100
73	Butenoic acid	$(CH_3CH_2)_3SiH$		Oxysilylation : β
74		$(CH_3CH_2O)_3SiH$		Oxysilylation : β
75		T_8H_8	61	25:75
76		$Q_8[OSi(CH_3)_2H]_8$	96	100
77	Hexyl Acrylate	$(CH_3CH_2)_3SiH$	74	5:95
78		$(CH_3CH_2O)_3SiH$	84	5:95
79		T_8H_8	76	10:90
80		$Q_8[OSi(CH_3)_2H]_8$	98	100

3.4 RESULTS OF TRIETHYLSILANE AND TRIETHOXYSILANE REACTIONS.

It can be seen from Table 6 that all the alkenes selected reacted in good yields with both triethylsilane and triethoxysilane. The alkenes without vinyl or allyl substituents, hexene and methyl 3,3-dimethylpent-4-enoate, reacted to provide only β adducts, whilst the remaining alkenes produced mixtures of both α and β adducts in varying yields.

3.4.1 Hex-1-ene and Methyl 3,3-dimethylpent-4-enoate.

Alkenes without vinyl or allyl substituents other than CH_2 coupled only by β addition. These unhindered alkenes reacted in excellent yields for all the silicon species studied. These results were expected, as the alkyl chain affords little control over the addition stereochemistry. Little difference in reaction yield or time was observed for the

triethylsilane compared to the triethoxysilane, indicating that the SiO plays no observable role in promoting these reactions.

These results are in line with previous investigations in the literature[117]. Early work suggested exclusive terminal addition. Chalk reacted hex-1-ene with triethylsilane reporting 80% yield of the β product using RhCl(PPh$_3$)$_3$ as catalyst[106]. Similarly 74% yield of the β adduct from the reaction between hex-1-ene and triethoxysilane also using RhCl(PPh$_3$)$_3$ has been reported. Analogous systems to the methyl 3,3-dimethylpent-4-enoate derivative have also been studied. Examples of this work are the 84% β addition of 3-methyl-4-penten-2-one with dimethylchlorosilane[118] and the somewhat lower yield of 54% β addition of ethylbutenoate with triethylsilane[119] as shown in Figure 34. In all cases no α addition was reported.
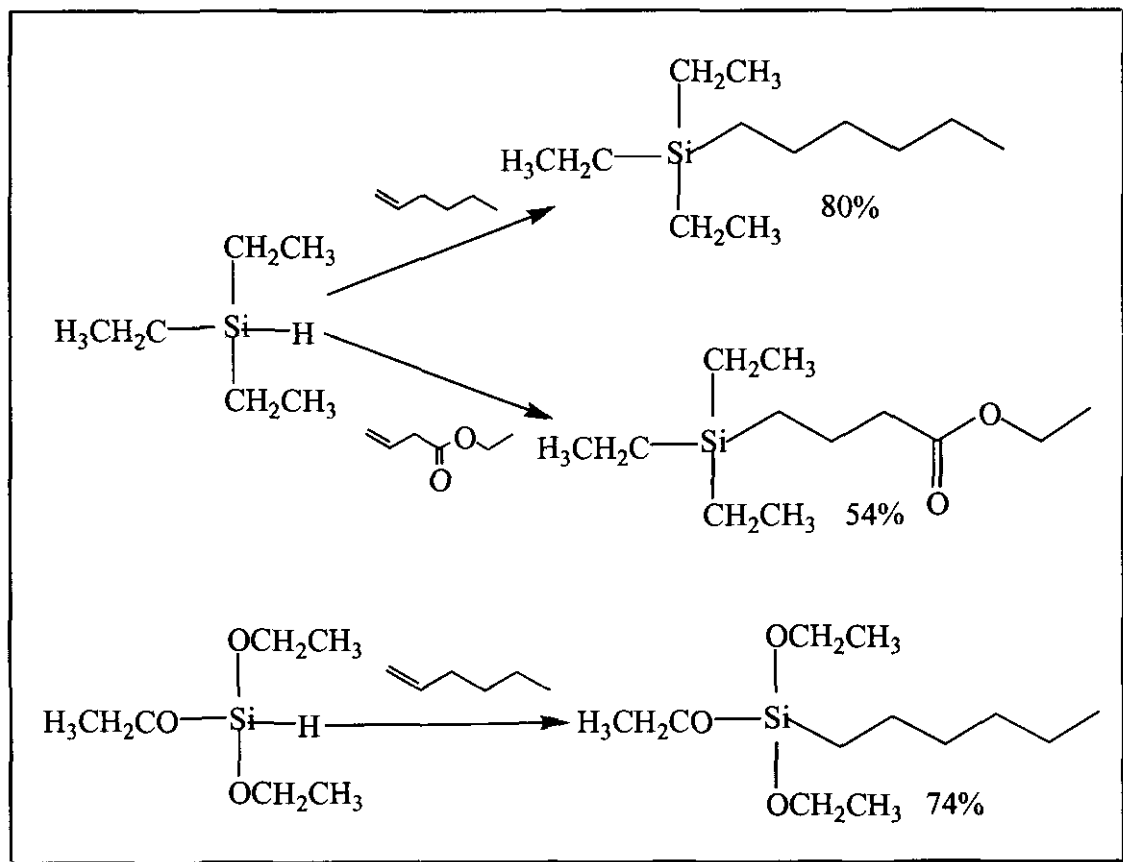
Figure 34: Hydrosilylations involving straight chain alkenes and esters

Work has also been carried out using different catalysts. Rhodium catalysts were shown to limit the degree of isomerisation of internal double bonds. Relevant examples include the reaction of triethoxysilane with hex-1-ene[120], oct-1-ene[121] and pent-1-ene [106]. Yields of β product with the Wilkinson catalyst [122], RhCl(PPh₃)₃, were 74%, 90% and 84 % respectively.

3.4.2 Allyl butyl ether

Allyl butyl ether produced both α and β adducts with Et_3SiH and $(EtO)_3SiH$. Evidence from ^1H, ^{13}C and ^{29}Si NMR indicated distinct resonances for the α and β adducts. The ^{29}Si NMR confirmed the two products of hydrosilylation for these compounds. The α-product of compound **57** was seen to be less than 5% of the reaction mixture by ^1H NMR, and ^{29}Si NMR peaks were observed at 7.15ppm and 7.21ppm. The ^{29}Si NMR for compound **58** showed peaks at –45.95ppm and –46.29ppm.

Analogous results to those in our study include the work of Murai[123]. Murai reacted Me_3SiH with allyloxymethyloxirane using $Co_2(CO)_8$ as catalyst. The result was 9% of the α- regioisomer, though the β addition product was not separated from the byproducts.[123].

Literature examples of this reaction showing different results to our studies include the work of Eaborn[125]. Allyl acetate was hydrosilylated with $PhCH_2SiMe_2H$ using H_2PtCl_6 and 48% of the β product was isolated by distillation . No α addition was reported, however it was not looked for. Similarly, Plueddemann found that triethoxysilane reacted with allyloxymethyloxirane using a Pt catalyst to give only β addition, no α addition was observed[124].

General examples from the literature show triethylsilane and triethoxysilane to give mainly β products when Pt catalysts are used[122, 125, 126]. The only sign of α addition was when R₃SiH was hydrosilylated using Co catalysts[123]. These results are in contrast to the results shown in Table 6, where (RO)₃SiH produced mainly β products with a small quantity of α addition with R₃SiH.

3.4.3 Allylbenzene

Allylbenzene reacted with both the silane and siloxane to produce α and β derivatives. Product identification was confirmed by ²⁹Si NMR with chemical shifts of –45.18ppm and –46.46ppm for the mixture 62 and 6.81ppm and 6.52ppm for mixture 61. The ²⁹Si NMR spectrum suggested that the α-product was present in about 5% yield for both reactions. ¹H and ¹³C NMR also indicated two modes of addition for both silicon species. This was seen by peaks at 0.82ppm and 1.13ppm in the spectrum of the triethoxysilane derivative. These peaks represent the SiCH and SiCH₃ of the α adduct and were observed alongside the peaks of the β product.

Similar work carried out by Petrov in the 1960's involved a series of reactions with methyldichlorosilane and ethyldichlorosilane [128]. Reaction Scheme 12 shows the reactions carried out. In general terms it was observed that the further away the double bond is from the benzene ring, the greater the proportion of β adduct formed. Hence addition if allylbenzene produced more β adduct than that of styrene. This observation is in line with our own results. Specific examples include the 100% β addition of all the phenyl alkenes when trichlorosilane was reacted, and when styrene was reacted with methyldichlorosilane a 68:32 ratio of products were achieved, with β addition being more prevelant, as shown in Reaction Scheme 12.

$$RCl_2SiH \quad + \quad$$

benzene ring with $(CH_2)_n\text{—CH=CH}_2$ substituent

$$n= 0, 1, 2$$

↓

benzene ring with $(CH_2)_{n+2}SiCl_2R$ substituent

β adduct

benzene ring with $(CH_2)_nCHCH_3SiCl_2R$ substituent

α adduct

When n=0   β:α   68:32   R= CH_3 or CH_2CH_3
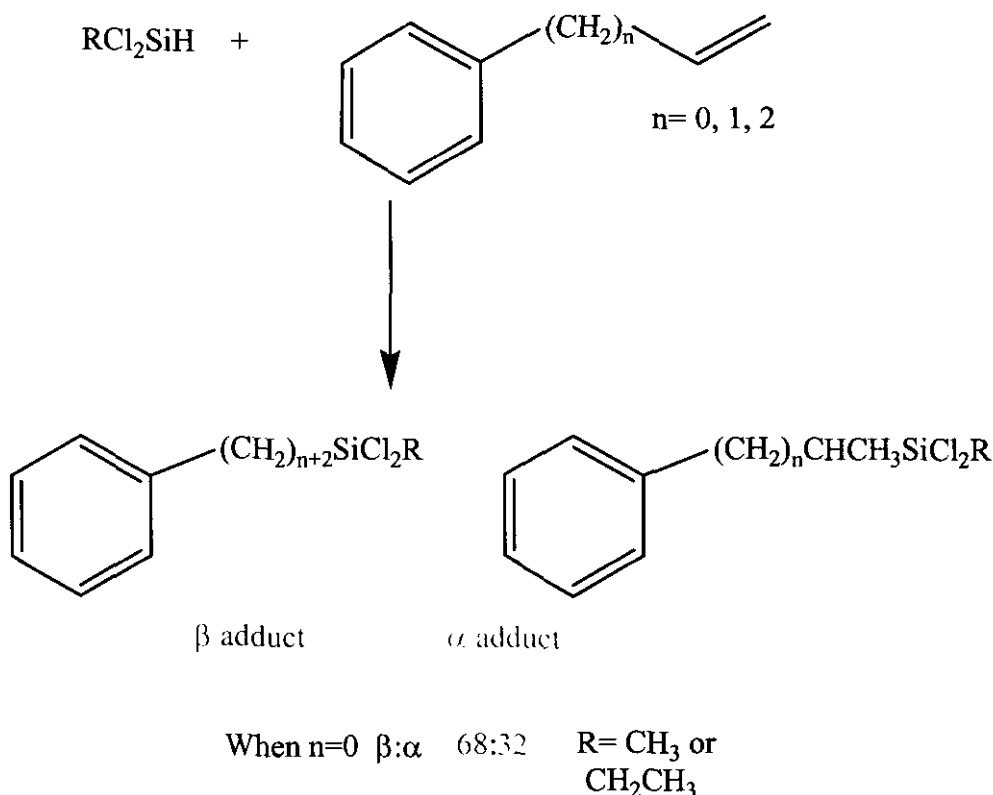
Reaction Scheme 12: Hydrosilylations carried out by Petrov[128].

3.4.4 Hexyl acrylate

Reaction of triethylsilane and triethoxysilane with hexyl acrylate again produced mixtures; however, very little α addition was observed by NMR, less than 5% in each case. Product solubility was good, enabling clear identification of the product compounds. Again the ^{1}H and ^{13}C NMR evidence provided a good indication of the products and overall yields.

The hydrosilylation of α/β unsaturated esters has been studied in depth, showing complex results. The outcome of the reaction of acrylates and methacrylates using H_2PtCl_6 has been shown to depend upon the nature of the ester and silane, as discussed by Ojima[129]. Chlorosilanes have been shown to give mixtures of α and β addition, as well as 1,4 addition products. Triethylsilane reacts to give exclusively the β product[119]. The selectivity

of the reactions is substantially affected by the substitutents of the ester groups and the β carbon.

In contrast to our results some examples from the literature show prevelant α addition. Sommer reacted methyldichlorosilane and acrylates, using 5% Pt/C catalyst to give only α addition in 75% yield[130]. Goodman found only α addition when vinyl acetate was hydrosilylated with methyldichlorosilane. Again the catalyst was 5% Pt/C producing 76% yield[131]. In a similar manner Speier found that α addition was dominant in his reaction of methydichlorosilane with methylacrylate, catalysed by Pt/C. Both α and β addition was observed, with the α regioisomer present in the greater yield[99]. The hydrosilylation of ethylacrylate with triethylsilane gave 100% β addition. This was reported by Ojima in 1976, using (Ph$_3$P)$_3$RhCl as catalyst with a yield of 80%[129]. Similar results were obtained when phenyldimethylsilane and ethyldimethylsilane were also reacted. However when ethylacrylate was hydrosilylated with chlordimethylsilane the yield was 100% of the α adduct[129].

3.4.5 Styrene

Styrene was observed to react in two ways with both triethylsilane and triethoxysilane, however in somewhat differing proportions. With triethylsilane, compound **65**, about 5% of the α adduct was present, identified by COSY and DEPT NMR experiments. However, with the triethoxysilane example, the α product made up 40% of the final reaction mixture. The exact composition of the mixture produced by triethoxysilane was again confirmed by NMR, with conclusive evidence from the ^{29}Si NMR spectrum. Two peaks were observed

in the same ratio as the products at –45.93 and –46.47ppm, corresponding to the β and α adducts respectively.

These results are supported by those already reported in the literature. Reports by Lappert show 24% β addition with triethylsilane and no evidence of the regioisomer[132]. Triethyoxysilane produced 39% β addition, with 7% of the α product. The catalyst used here is [Rh(acac)$_3$]AlEt$_3$. These results reflect our study; little α addition for R$_3$SiH, a substantial amount when (RO)$_3$SiH. Similarly Földes reported reactions of styrene and triethylsilane using a variety of catalysts[133]. The results supported those found in our study, with 69% β adduct and 3% α product using PtCl$_2$(PhCN)$_2$ as the catalyst. Other catalysts used provided similar results, such as 76:2, β:α for PtCl$_2$ and 23:10, β:α for RhCl(PPh$_3$)$_3$ [133]. Speier reported an 83% addition of chlorodimethylsilane to styrene, with a small amount of impurity observed [116]. It is presumed that this impuirty was the product of α addition.

Examples that do not agree with our results have also been reported. Green observed only β addition using the diplatinum complex [{Pt(SiR$_3$)(μ-H)[(C$_6$H$_{11}$)$_3$P]}$_2$]. The exception to this was when chlorodimethylsilane was used. In this case 78% of the β adduct was observed, with 22% of the regioisomer[134].

Petrov's work has already been mentioned, whereby a mixture of two isomers were observed in a 70:30 β:α ratio with hydrosilylation of styrene with MeCl$_2$SiH [128]. Yamamoto also reported the reaction between dichloromethylsilane and styrene, affected with a Ni catalyst to give a β:α of 54:46. [135]. Other reports involving hydrosilylation of styrene include a 58.7% β addition with trichlorosilane, with the regiosiomer present in

38.5%. The proportion of β-isomer could be increased to 92% by adding triphenylphosphine or pyridine to the catalyst[136].

3.4.6 α-Methylstyrene

α-Methylstyrene also reacted to produce two products with both of the silanes; however, the α species was not more than 5% by NMR. The lack of significant α addition is thought to be due to the steric restraint imposed upon the system by the presence of the α methyl group.

These results were in line with those published by Földes[137]. Triethylsilane was hydrosilylated with α-methylstyrene, showing only β substitution, with 98% conversion.

3.4.7 But-3-enoic acid

But-3-enoic acid reacted in two ways with triethylsilane. The expected product was achieved, compound **73**, but the product of an oxysilylation reaction, compound **81**, was also observed. Initial attachment of one triethylsilane group through hydrosilylation would leave an OH group free to undergo further reaction. Oxysilylation to a second triethylsilane molecule would result in compound **81**. CI+ mass spectrometry and accurate mass calculations confirmed the presence of this compound. Two distinct ^{29}Si sites were also observed in the NMR, one corresponding to the SiC$_4$ site, at 6.6ppm, (for both compounds), and the other at 24.7 ppm corresponding to compound **81**. ^{1}H and ^{13}C NMR data analysed using COSY and DEPT techniques confirmed the presence of these two compounds.

Oxysilylation was also observed with triethoxysilane. The proportion of this disilylproduct was 20% compared to just 5% in the triethylsilane reaction. It should be noted that the silanes and acid were reacted in a 1:1 ratio, therefore any oxysilylation would be as a result of a competing reaction, and not due to the excess silane.

CH_3CH_2—$Si(CH_2CH_3)_2$—$CH_2CH_2CH_2$—$C(=O)$—OH

Compound 73
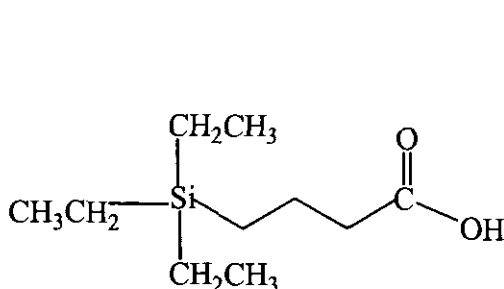
$(CH_3CH_2)_3Si$—O—$C(=O)$—$CH_2CH_2CH_2$—$Si(CH_2CH_3)_3$
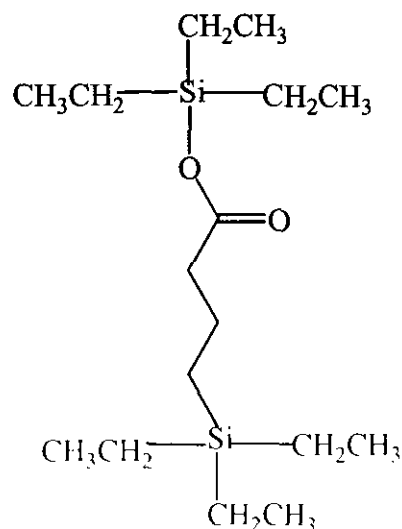
Compound 81

Hydrosilylation and Oxysilylation Products of triethylsilane with vinyl acetic acid

Both T and Q regions were seen in the ^{29}Si NMR, corresponding to the O_3SiC and $OSiO_3$ sites. The expected β adduct was confirmed by the OH stretch in the FTIR spectrum. β addition with oxysilylation was confirmed by the presence of two OCH_2 peaks in the ^1H NMR, at 3.73ppm and at 4.04ppm, as demonstrated in Figure 35. The latter CH_2SiOCH_2 peak had the larger integration reflecting the fact that this chemical environment is present in both products. In all examples of hydrosilylation of the carbon-carbon double bond no α substitution was observed.
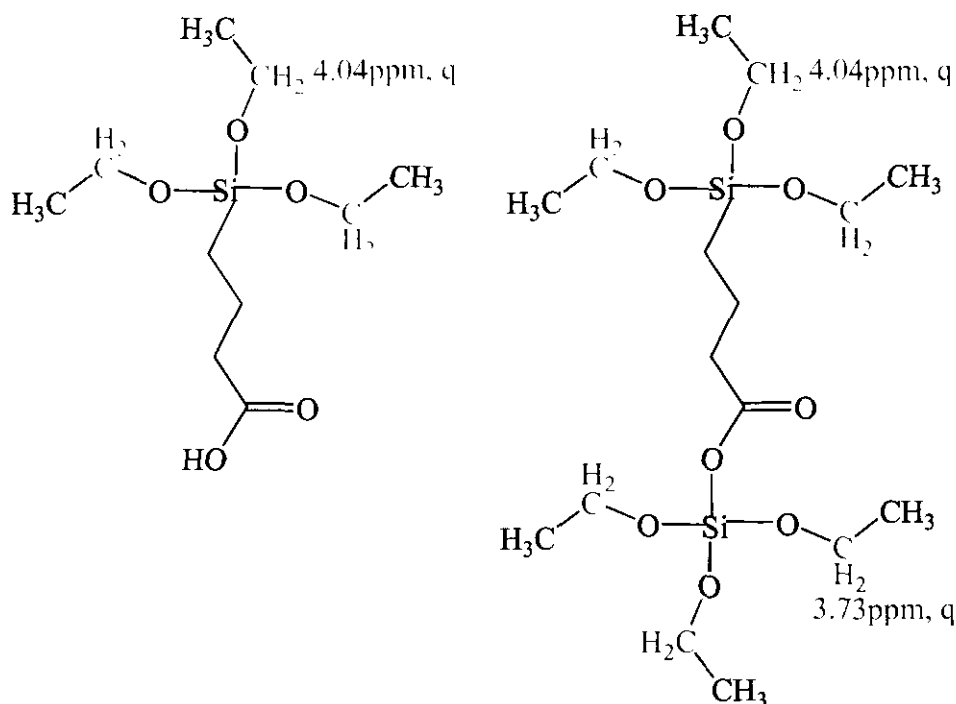
Figure 35: Products of the reaction between triethoxysilane and butenoic acid.

3.5 SUMMARY OF HYDROSILYLATION REACTIONS USING TRIETHYLSILANE AND TRIETHOXYSILANE .

A series of compounds has been attached to triethylsilane and triethoxysilane using hydrosilylation reactions. The proportions of α and β addition were estimated using NMR techniques such as DEPT and COSY, along with mass spectrometric analysis to identify the products achieved.

Straight chain alkenes, compounds **41** and **42**, were seen to react exclusively by β addition with both the silane and siloxane.

Allyl and vinyl substituents led to both α and β addition. Typically the α by-product made up just 5% of the reaction mixture for both reactions. The exception to this was triethoxysilane addition to styrene were the ratio of products was 40:60, α:β.

The one unusual case involved compounds **73** and **74**, the but-3-enoic acid examples. Reaction with triethylsilane and triethoxysilane produced both the β adduct and the product of an oxysilylation reaction. Oxysilylation was found to be 5% of the overall reaction involving triethylsilane and 20% when triethoxysilane was used. These products were confirmed by NMR and mass spectrometry. These data suggest that oxysilylation is promoted when triethoxysilane is used. A comparison with the silsesquioxane compounds will highlight any preference for the oxysilylation process in the same electronic environment, providing identical conditions are assumed.

Comparison of these results with work published in the literature shows some good correlations. The results from reactions involving triethyl and triethoxysilane provide no conclusive evidence for the factors affecting α and β addition. The nature of the alkene has a larger effect on the α/β ratio of the products than the structure of the silane used.

Of those species providing both α and β products a number of features stand out. Evidence shown in Table 6 suggests that conjugation may serve to encourage α addition, as shown in Figure 36.
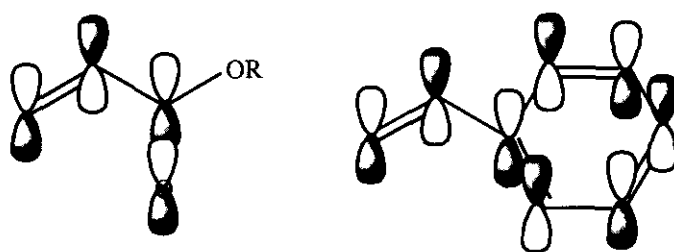
Figure 36: Conjugation seen to encourage α addition

A phenyl or oxygen at the allyl position also led to some α substitution but not a carboxylic acid group, as shown in Figure 37.
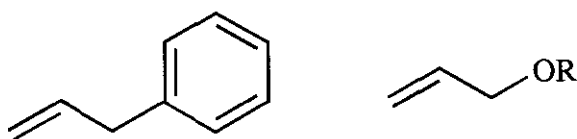
Figure 37

The Chalk Harrod mechanism suggests that the regiochemistry is determined by the mode of the *cis* ligand insertion which is thought to be rate limiting, as shown in Figure 38.
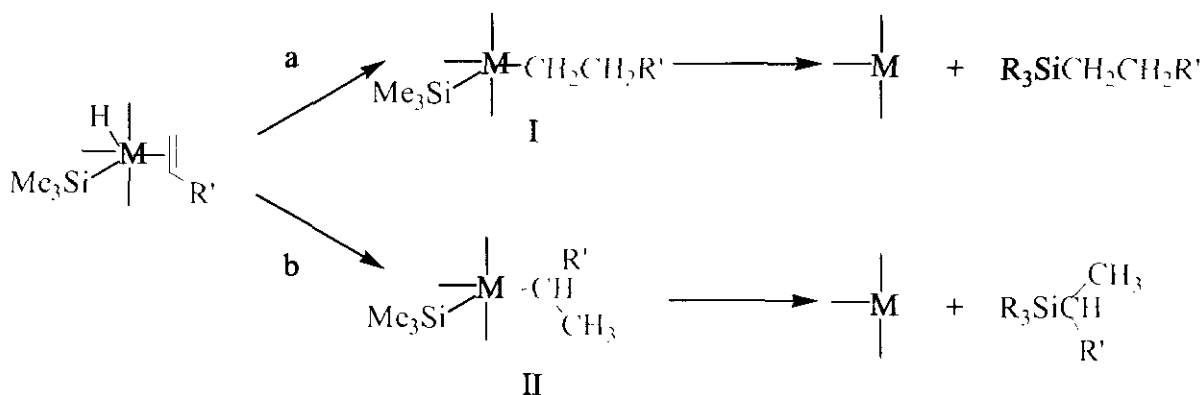
Figure 38: Regiochemistry of the Chalk-Harrod Mechanism

Where R is alkyl, route a is favoured on steric grounds. In a typical transition metal π complex the species is stabilised through π bonding and back-bonding as shown in Figure 39.

Donation from filled
π orbitals to vacant
metal orbitals

Back-bonding from
filled metal orbitals
to π* of the alkene
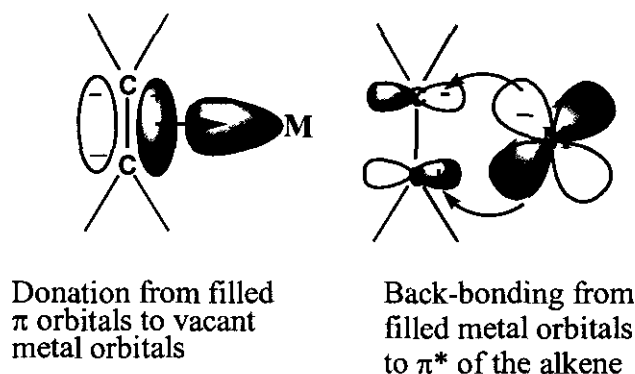
Figure 39: Typical bonding in a transition metal complex such as the Platinum π complex formed in the hydrosilylation reaction.

The complex is stablilised by donation of the π electron density of the olefin to the σ type acceptor orbital of the metal. Back bonding is also present involving electron density flow from the filled d_{xz} metal orbital to the antibonding orbital of the alkene species.

When the substituent is an alkyl group the electron distribution in the π complex is fairly symmetrical such that the H transfer is controlled by steric factors to give the thermodynamically more stable linear compound.

The presence of a conjugated double bond will cause a polarisation of the carbon-carbon double bond such that electronic factors start to become important. For example, the hydrogen in the platinum complex is hydridic in nature and the presence of an adjacent COOR group makes the terminal carbon more electrophilic. This is shown in Figure 40.
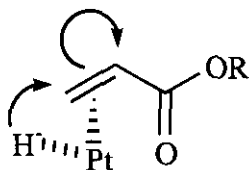
Figure 40: Addition of the hydrosilane to a vinyl-platinum complex

Thus addition tends to mirror 1,4 addition of nucleophiles to eneone systems, favouring route b and thus α addition. Similarly the presence of a phenyl group will stabilise charge build up on the adjacent carbon, again favouring α additions. Whilst electronic factors favour α addition, steric factors generally dominate such that β addition predominates. However, this is not the case with (EtO)₃SiH and styrene.

If the reductive elimination were the rate limiting step, the regio chemistry will be determined by the relative concentration of the two species I and II and the rates of silicon carbon bond formation. The predominance of the β product for most alkenes suggests the regiochemistry is determined by the thermodynamic stability of I and II; the linear form I being favoured for steric reasons. If the previous steps are equilibria any electronic control exerted in the *cis* ligand insertion will not be important. Hydrosilylation is faster with X_3SiH species than R_3SiH and thus the reductive elimination step may be faster for $(RO)_3SiH$ than R_3SiH. If this is the case, the *cis* ligand insertion may become more kinetically significant for $(RO)_3SiH$ and in extreme case rate limiting. Thus, the electronic factors that control the regio chemistry of *cis* ligand insertion become more significant leading to substantial α addition. The literature also suggests that high α addition occurs mainly with X_3SiH addition.

The presence of some α addition when there is a substituent in the allyl position is not easy to rationalise. Arguments based on hyperconjugation are difficult to sustain. A more likely explanation is that the substituents coordinate with the platinum reducing the energy difference between III and IV and thus allowing more α addition to be observed, as shown in Figure 41.

It is clear that the factors controlling the amount of α and β addition are finely balanced and thus it is interesting to examine the effect of the bulky cage.
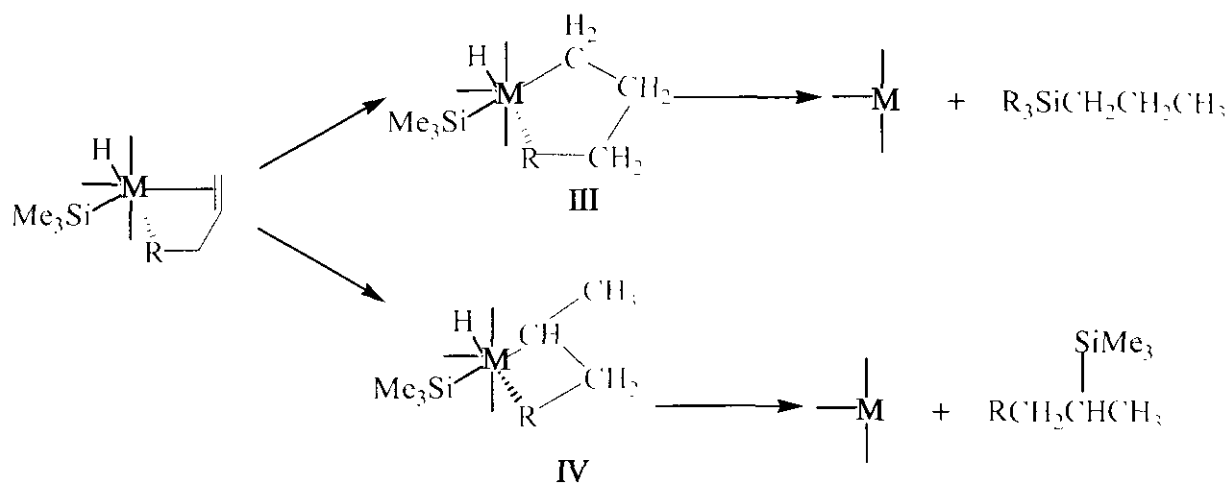
Figure 41: Steric Factors Controlling α addition of Allyl Compounds to Silanes.

3.6 RESULTS OF HYDROSILYLATION REACTIONS INVOLVING SILSESQUIOXANES.

It was hoped that by attaching compounds **41-48** to the cages, synthetically versatile silsesquioxanes could be obtained. In a series of reactions Speier's catalyst[62] was used as a 0.02 mol dm^{-3} solution in isopropyl alcohol, while Karstedt's catalyst[65] was used as a 3% solution in toluene. Karstedt's catalyst was activated by means of aeration prior to incubation. The hydrosilylation of the alkenes in Table 5 were carried out using Speier's catalyst for T$_8$H$_8$ and Karstedt's catalysts for Q$_8$[OSi(CH$_3$)$_2$H]$_8$.

The proportions of regioisomers (α and β adducts) vary, depending upon the side arm in question. Ratios of α and β addition also depend upon the structure of the silane, and the reaction conditions employed. In general Q$_8$ gave only the β isomer. Of the five compounds that gave mixtures with T$_8$ cage compounds, three achieved approximately 30:70, α:β addition. The styrene and hexyl acrylate derivatives, compounds **67** and **79**, differed slightly, the former exhibiting a higher α content and the hexyl acrylate compound

showing a suprisingly low α content. A comparison of the measurable ratios of α and β

products achieved throughout this investigation is shown Table 7.

Table 7: Comparison of α addition products for T₈H₈, triethylsilane and triethoxysilane.

Compound Number	Reactant	Silane	% α addition
57	Allyl butyl ether	$(CH_3CH_2)_3SiH$	<5
58		$(CH_3CH_2O)_3SiH$	5
59		T_8H_8	30
61	Allylbenzene	$(CH_3CH_2)_3SiH$	5
62		$(CH_3CH_2O)_3SiH$	5
63		T_8H_8	35
65	Styrene	$(CH_3CH_2)_3SiH$	<5
66		$(CH_3CH_2O)_3SiH$	40
67		T_8H_8	40
69	α-Methylstyrene	$(CH_3CH_2)_3SiH$	<5
70		$(CH_3CH_2O)_3SiH$	<5
71		T_8H_8	Insoluble
73	But-3-enoic acid	$(CH_3CH_2)_3SiH$	Oxysilylation
74		$(CH_3CH_2O)_3SiH$	Oxysilylation
75		T_8H_8	25
77	Hexyl acrylate	$(CH_3CH_2)_3SiH$	<5
78		$(CH_3CH_2O)_3SiH$	<5
79		T_8H_8	10

3.7 DISCUSSION OF SILSESQUIOXANE REACTION PRODUCTS AND COMPARISON WITH THE TRIETHYL AND TRIETHOXYSILANE DERIVATIVES

3.7.1 Hex-1-ene

The reaction of hex-1-ene with both T_8H_8 and $Q_8[OSi(CH_3)_2H]_8$ was shown to proceed via predominant β addition. This result was expected in light of the literature and the products achieved with $(CH_3CH_2)_2SiH$ and $(CH_3CH_2O)_3SiH$. Hex-1-ene addition to T_8H_8 has previously been reported by Herren et al, who observed the same results[59]. All reactions involving hexene gave excellent yields of approximately 99% of the β product.

3.7.2 Methyl 3,3-dimethylpent-4-enoate

Methyl 3,3-dimethylpent-4-enoate also coupled to the cages by solely β addition producing compounds **55** and **56**. The products here are, perhaps, the most synthetically useful of the range prepared. The versatility of the ester functionality suggests that such species will be useful precursors to more complex compounds, as shown in Figure 42[138]. This has been demonstrated by the reaction of these compounds with ethylenediamine to produce an amine terminated side arm. The nucleophilic nature of this side arm prevented it from being attached directly to the cage, since hydrogen substituted silsesquioxane cages have previously been shown to be unstable in the presence of amines.
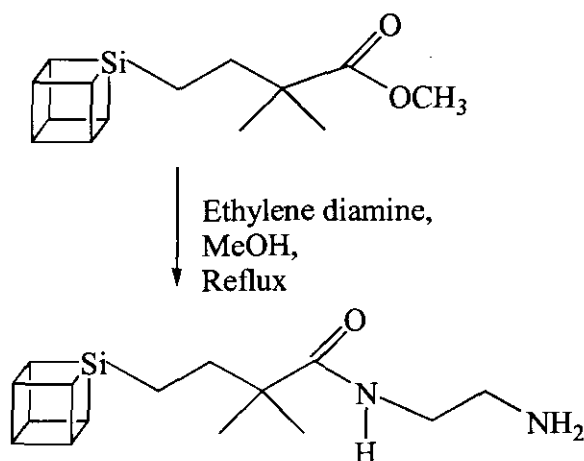
Figure 42: Amine functionalisation of the silsesquioxane cage.

Again, all reactions involving methyl 3,3-dimethylpent-4-enoate proceeded with excellent yields. No obvious difference in reactivity was noticeable between the cage compounds and the simpler silane and siloxane. Yields for all reactions were typically 98% of the β product.

These results were in line with those reported in the literature. All straight chain alkenes that have been hydrosilylated with silsesquioxane cages have produced the β product[60]. Examples include the series carried out by Bassindale et al that involved attaching alkenes ranging from hex-1-ene through to octadec-1-ene, all with the same result[61].

3.7.3 Allyl butyl ether

The reaction of allyl butyl ether provided a more interesting result. Allyl butyl ether was shown to undergo α and β addition with triethoxysilane, as demonstrated by mixture **58**. A similar situation was anticipated with the cage compounds. Both modes of addition to T_8H_8 were obvious by NMR. Evidence was clearly seen for the linear alkyl chain resulting from β addition, as shown in Figure 43.
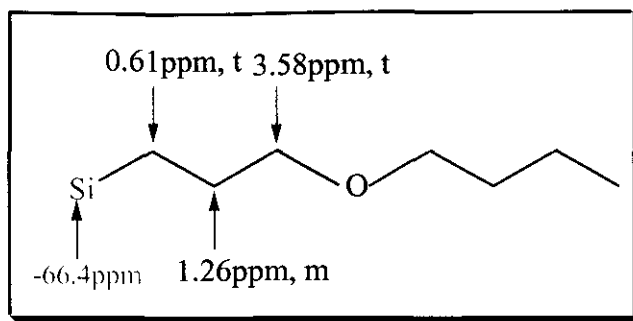
Figure 43: [29] Si and ^{1}H NMR chemical shifts for β addition of allyl butyl ether

A peak for the –CH₃ produced by α addition was also clearly seen as indicated in Figure 44.
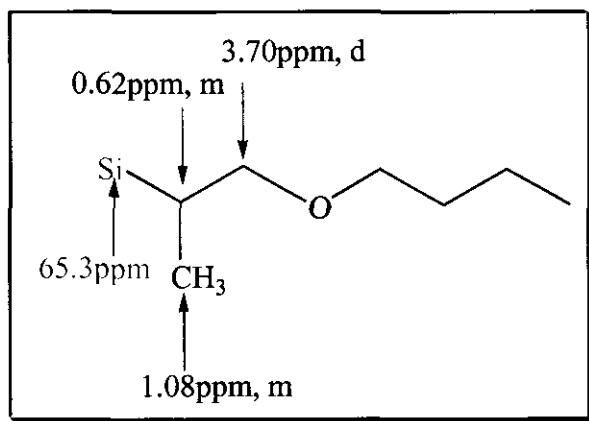
Figure 44: [29] Si and ^{1}H NMR chemical shifts α addition of allyl butyl ether.

Only two ^{29}Si NMR resonances would be expected if the product were a mixture of just octa(4-oxaoctyl)silsesquioxane and octa(1-methyl-3-oxaheptyl)silsesquioxane. The ^{29}Si NMR in fact showed multiple signals around –66.7 ppm for this T₈H₈ derivative, which was in line with the hydrosilylations of other ether compounds as described by Gentle[97]. These multiple peaks arise from both α and β addition occurring on the same cube without any particular preferences, giving mixtures of compounds with different extents of α/β

substitution. The major peak in the cluster for the T_8H_8 derivatives was at –66.4ppm, indicative of the octa(4-oxaoctyl)silsesquioxane.

The extent of α addition was far higher with T_8H_8 than previously seen with the triethylsilane or triethoxysilane. 30% of the reaction mixture was shown to result from α addition with the silsesquioxane, compared to less than 5% with the silane. The $T_8[OSi(CH_3)_2H]_8$ produced compound **60**, the β adduct, exclusively.

3.7.4 Allylbenzene

Reaction of allylbenzene with the octa(hydrido)silsesquioxane cage produced a mixture of products. As before the α and β adducts were observed by NMR. ^1H NMR data of the T_8H_8 derivative is shown in Figure 45.
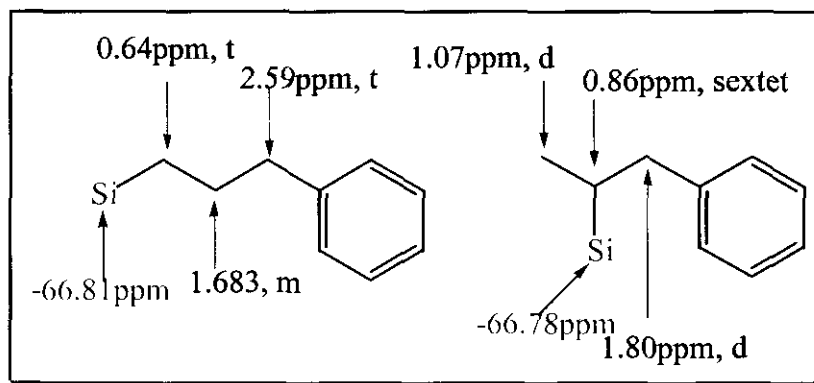
Figure 45: ^{29} Si and ^{1}H NMR chemical shifts confirming two modes of addition for allylbenzene to silsesquioxane cages.

The ^{29}Si NMR also provides evidence of multiple products. Peaks at –66.78 and –65.82ppm indicate two unique T_8H_8 cage systems. The proportion of α addition was far greater in this example than for the simple silanes. 35% of the α product was observed

with T_8H_8, compared to no more than 5% with the triethyl and triethoxysilanes. In fact, compound **82** is the product of both α addition of allylbenzene and β addition of the isomerised alkene, as shown in Figure 46. Under the conditions of the reaction the platinum catalyst could isomerise the allylbenzene into the more thermodynamically favoured conjugated isomer. The proportion of the α species present in the reaction mixture would therefore be larger.

Route A   Route B

β addition   α addition   β addition

Octa(1-phenyl propyl)silsesquioxane   Octa(1-methyl-2-phenylethyl)silsesquioxane

COMPOUND 82
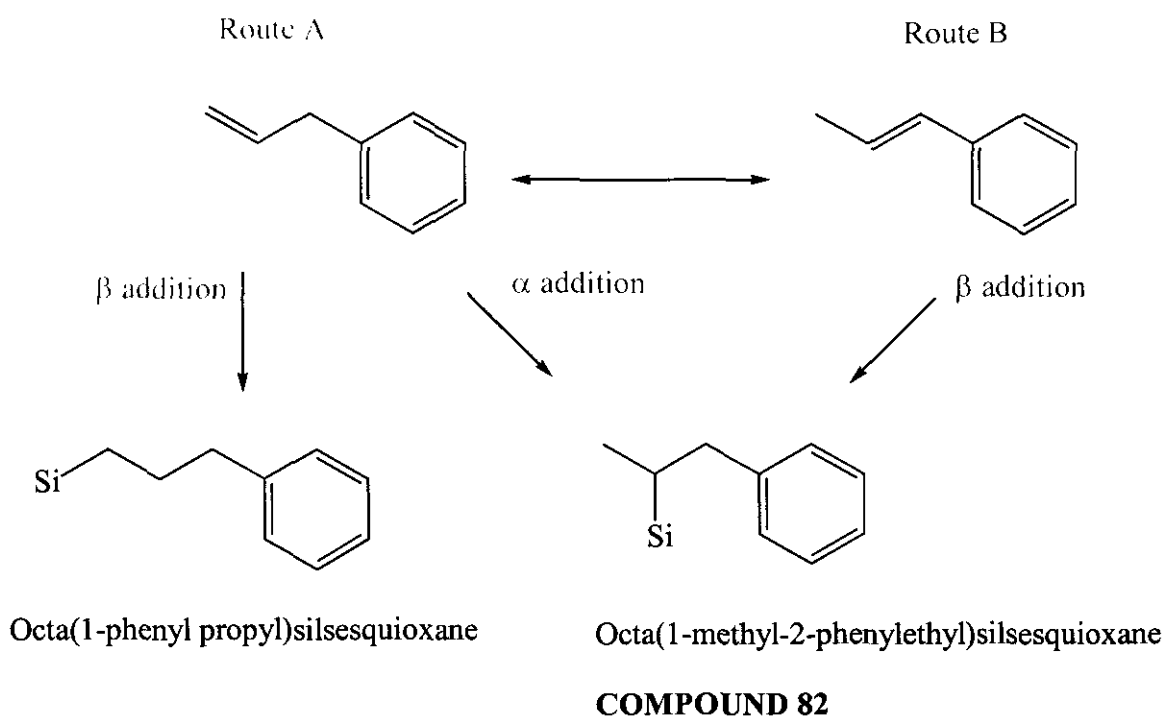
Figure 46: Isomerisation of allylbenzene and subsequent hydrosilylation products.

The presence of the isomerised alkene was confirmed by ^1H NMR. Allylbenzene was mixed with the catalyst in the absence of the silane. The ^1H NMR revealed the absence of the benzyllic CH_2 and the presence of the methyl group as a doublet, integrating to 3H. Such isomerisation was not seen to be important with R_3SiH and $(RO)_3SiH$. These species reacted faster than T_8H_8, before isomerisation could occur, hence producing the β product. The $T_8[OSi(CH_3)_2H]_8$ derivative, compound **64**, presented a simpler picture, since only β addition of allylbenzene was observed by ^1H and ^{13}C NMR.

The lack of α addition in compound **64** was somewhat surprising, since the platinum could still facilitate an alkene isomerisation. The obvious reason for this is the use of Karstedt's catalyst with all $Q_8[OSi(CH_3)_2H]_8$ reactions. One explanation may be that $Q_8[OSi(CH_3)_2H]_8$ reacts faster than T_8H_8 before isomerisation could occur.

Hydrosilylations of allyllic species with T_8H_8 and $Q_8[OSi(CH_3)_2H]_8$ cages have been reported in the literature and only β addition was observed. For example in 1998 Provatas reacted allylbromide with the silsesquioxane detecting 49.7% of the eightfold β product[139]. A similar situation was achieved with the analogous T_8H_8 reaction. More sterically hindered allyl compounds from the literature also provide the same result. Examples include those of Jutzi, with a 85% yield of the β substituted cage when 1-allyl-2-methyl-1,2-dicarbadodecaborane was used[66]. Karstedts catalyst was used, affording yields of 85%, with no evidence of the regioisomer.

3.7.5 Styrene

Hydrosilylation reactions involving styrene have been shown to undergo polymerisation and to produce more than one adduct. For example, reaction with chlorosilicon hydrides were seen to form 1- and 2-phenylethyl chlorosilanes[116]. Multiple products were therefore anticipated when hydrosilylating styrene with cage compounds.

When styrene was reacted with the silsesquioxanes the result was similar to that of the allylbenzene reaction. The T_8H_8 derivative, compound **67**, produced both α and β adducts in a ratio of 40:60, whereas the $Q_8[OSi(CH_3)_2H]_8$ derivative, compound **68**, was only seen to undergo β addition. If steric hindrance were considered to be the main driving force it should be greater with α addition to the styrene reaction than with allylbenzene. In the

styrene derivative the benzene ring would interfere with the bulky SiO groups. However, the extra CH_2 group in the allyl derivative provides increased separation between the siloxane cage and the benzene ring and for this reason a greater difference in the proportions of $\alpha{:}\beta$ compounds might have been expected. However, as can be seen in Table 6, both allylbenzene and styrene react with T_8H_8 to produce approximately 40% of the α adduct. The same result was observed with the styrene and triethoxysilane derivative, highlighting the importance of electronic factors.

3.7.6 α-Methylstyrene

A similar situation was observed with α-methylstyrene. The $Q_8[OSi(CH_3)_2H]_8$ derivative, compound **72**, produced only the product of β addition, in 100% yield.

The reaction of α-methylstyrene with T_8H_8 yielded an insoluble gelatinous product. The gel was found to be insoluble in all common solvents and was therefore assumed to be a highly cross-linked polymer. Polymerisation was thought to have occurred as a result of the reaction temperature and the platinum catalyst. Such polymerisation was not observed with styrene and must occur prior to hydrosilylation, and suggests that either the α-methylstyrene is polymerised more quickly than the styrene or that the α-methylstyrene undergoes hydrosilylation less readily than styrene.

This situation was not observed in the preparation of compound **72**. This is probably due to the different reaction conditions employed. The hydrosilylation involving $Q_8[OSi(CH_3)_2H]_8$ was carried out in refluxing toluene and this dilution will limit any polymerisation, assisting hydrosilylation to take place. Hydrosilylation with $Q_8[OSi(CH_3)_2H]_8$ also occurs faster than with T_8H_8, again reducing the proportion of

polymerisation. The effect of the catalyst activity was investigated by using Karstedt's catalyst in a T_8H_8 reaction with α-methylstyrene, however the insoluble gel was produced in all these reactions.

A general trend was obvious throughout all hydrosilylations involving α-methylstyrene, in that α addition to the silanes was rare. Less than 5% was observed when triethyl and triethoxysilane were reacted and this was thought to be due to steric factors. As there was no indication of insoluble gelatenous material with Et_3SiH or $(EtO)_3SiH$, it is thought that these silanes react faster than $Q_8[OSi(CH_3)_2H]_8$ and thus polymerisation was a minor slower reaction.

3.7.7 But-3-enoic acid

The range of functionalities attached to silsesquioxane cages was further extended by the addition of but-3-enoic acid to both T_8H_8 and $Q_8[OSi(CH_3)_2H]_8$. Previous attempts to couple carboxylic acids with silsesquioxanes have been unsuccessful[138], producing insoluble gel-like products as we obtained in the addition of pentenoic acid to T_8H_8.

Reactions with butenoic acid were found to yield soluble products. Predominant β addition was identified for both T_8H_8 and $Q_8[OSi(CH_3)_2H]_8$ compounds. Close analysis of the ^1H NMR for the T_8H_8 derivative, compound **75**, provided evidence of possible cage coupling compounds, thought to be less than 25% of the mixture. Close analysis of the ^{29}Si NMR identified no 'Q' peaks present, suggesting minimum oxysilylation in this case.

Nevertheless, the presence of peaks developing from vinyl groups in both sets of NMR spectra provides an indication that hydrosilylation may be compete. The catalyst

concentration was increased and further silsesquioxane was added to the reaction mixture to complete hydrosilylation.

Eventually the vinyl signals were reduced considerably. The only peaks visible in the 'T' region of the ^{29}Si spectrum were at –66.72 ppm and –66.46ppm, indicating the presence of only two types of T compound, probably arising from α and β addition. The α product was considered to be 25% of the final mixture in light of the ^{29}Si NMR evidence. The ^{1}H and ^{29}Si NMR data for these products are shown in Figure 47.
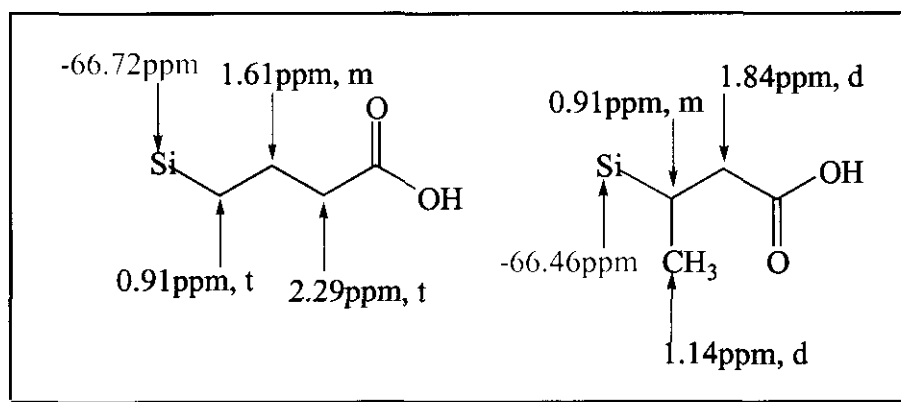
Figure 47: ^{29} Si **and** ^{1}H **and NMR shifts confirming** α **and** β **addition of vinyl acetic acid to** T_8H_8.

The product of the reaction between vinyl acetic acid and $Q_8[OSi(CH_3)_2H]_8$ was the result of exclusive β addition.

3.7.8 Hexyl acrylate

Reaction of hexyl acrylate with T_8H_8 was observed to give two modes of addition. The product mixture for the hexyl acrylate was dominated by the β adduct; however, the α

addition product comprised 10% of the reaction mixture. Evidence for the α-product was seen in the NMR data for the reaction as shown in Figure 48.
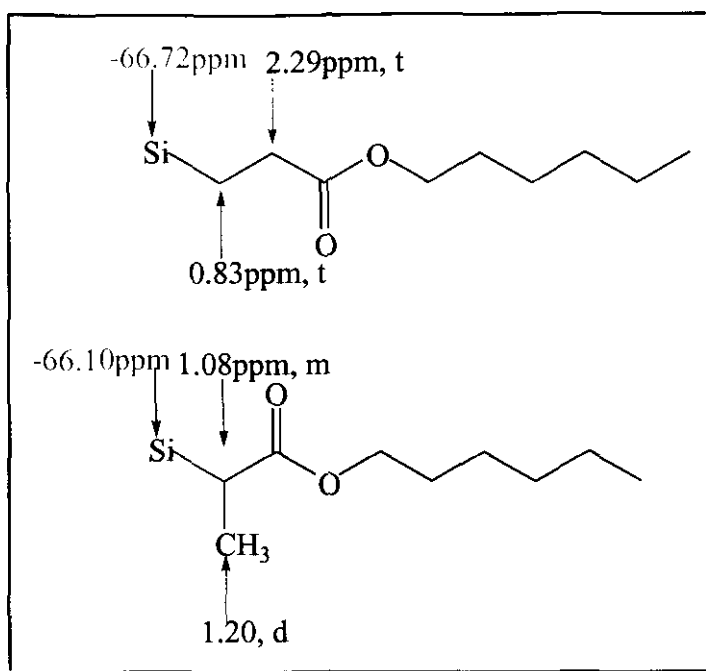
Figure 48: [29] Si and ^{1}H NMR shifts confirming two modes of addition for hexyl acrylate to T_8H_8.

Reaction of hexyl acrylate with $Q_8[OSi(CH_3)_2H]_8$ was found to proceed exclusively by β addition of the alkene. The overall reaction yield was 98%, with the structure of the product being confirmed using NMR techniques and mass spectrometry. This was in line with the regiochemistry of addition exhibited by methyldimethylpentenoate.

3.8 SUMMARY OF SILSESQUIOXANE HYDROSILYLATION REACTIONS.

A series of compounds has been attached to T_8H_8 and $Q_8[OSi(CH_3)_2H]_8$ cores using hydrosilylation reactions. The proportions of α and β addition by the alkene species have been estimated using NMR techniques. All reactions involving $Q_8[OSi(CH_3)_2H]_8$ reacted exclusively via β addition of the alkene to the silane. Reactions with T_8H_8 varied in outcome, depending upon the alkene structure. Straight alkyl chain compounds such as hexene and methyl 3,3-dimethylpent-4-enoate reacted to give purely β products. Vinyl and allyl substituted compounds, such as allylbutylether and styrene, produced α adducts as well as β. The proportion of the α by-product was seen to vary depending upon the structure. Typically α:β ratios were 25:75, with anomalies such as hexyl acrylate giving ratios of 10:80 and styrene producing 40:60.

The results achieved in this study provide a good correlation with those seen previously in the literature.

Bassindale reported production of a mixture when vinylsiloxanes were hydrosilylated with T_8H_8, with approximately 21% of the reaction mixture comprising the α product[63]. Similar results were observed when vinylferrocene was reacted with $Q_8[OSi(CH_3)_2H]_8$ in the presence of Karstedt's catalyst[64]. The ratio of isomers was 1:9 with the β adduct being most prevelant. In this case the yields were determined by the peak intensity of the methylene protons in the ^1H NMR spectrum.

The common theme within this group of reactions is that greater quantities of α adducts are produced from the T₈ cage reactions compared to the simple analogues. This implies that the cage itself plays a crucial role in this reaction. It is unlikely that this effect is an electronic one since reactions involving triethoxysilane do not exhibit such high yields of α isomers. If anything the steric bulk of the cage would have been expected to hinder α addition of these alkenes. Thus, the enhanced α addition observed must be due to the specific geometric constraints exhibited by the rigid cage.

As discussed in Section 3.5, the regiochemistry is determined by the interplay of electronic and steric effects. With linear alkyl substitutents the polarisation of the π complex is small and thus the thermodynamically more stable β product is observed in all cases. α addition was observed with conjugated alkenes owing to the polarisation of the π complex such that electronic factors favour α addition. The extent of α addition depends upon relative rates within the catalytic cycle. With bulky cage structures relief of strain in the platinum complex V on reductive elimination may speed up this reaction so that the *cis* ligand insertion becomes more kinetically significant, as demonstrated in Figure 49. This leads to a greater importance of the electronic effect of the substituent and thus more α addition is observed in the case of hexyl acrylate.

V
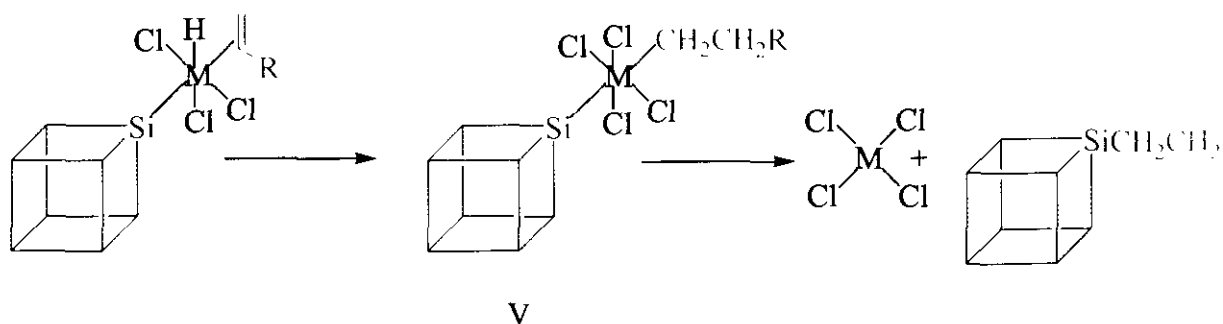
Figure 49: *Cis* **Ligand insertion due to the bulky cage**

The increase in α addition with the substituted allyl compounds may be due to specific intramolecular interactions of these groups which are enhanced by the steric demand of the cage in the complex, or a reduction in the rate of hydrosilylation due to steric effects such that isomerisation is possible to the conjugated alkene which undergoes β addition.

Interestingly the reaction with but-3-enoic acid suggests that whilst the rate of hydrosilylation is reduced by the bulk of the cage, oxysilylation is removed completely.

$Q_8[OSi(CH_3)_2H]_8$ gave only β addition with all the alkenes. In this core the cage-$OSiMe_2H$ group is less sterically demanding and only has one electronegative group attached to the silicon, so should behave similarly to Et_3SiH. The complete lack of α substitution may reflect the different conditions and catalyst employed, which ensure that steric effects dominate leading to just the β addition product.

3.9 SUMMARY

Hydrosilylation reactions are known to yield a mixture of products consisting of two modes of addition of the alkene to the silane. An investigation has been carried out to probe two aspects that may effect the proportions in which the two products are made.

A series of compounds has been coupled with four silicon containing species, $(CH_3CH_2)_3SiH$, $(CH_3CH_2O)_3SiH$, $[HSiO_{3/2}]_8$ and $[Si_8O_{12}]\{OSi(CH_3)_2H\}_8$. The variety of compounds used served to highlight the different functionalities that can be attached to silsesquioxane cages by means of hydrosilylation.

Straight chain alkyl compounds were seen to couple by just β addition to all the silanes. Allyl and vinyl terminated compounds were found to react by β addition with the $Q_8[OSi(CH_3)_2H]_8$ species, however T_8H_8, $(CH_3CH_2)_3SiH$ and $(CH_3CH_2O)_3SiH$ produced varying proportions of the α adducts.

The common themes observed in controlling the outcome of a hydrosilylation reaction were highlighted as 1) the nature of the alkene and 2) the exact structure of the silane. A greater proportion of α adducts were produced when the alkene exhibited π-bond orbital overlap and when the T_8H_8 cage was employed. In all cases the degree of α addition did not exceed 40%, resulting in the expected β adduct remaining the most common product.

The compound that did not follow this general trend was the but-3-enoic acid series. Reactions with the simple silane were shown to undergo hydrosilylation followed by oxysilylation. This was not observed with the cage compounds, with both α and β addition occuring to T_8H_8, whilst only β addition was achieved with $Q_8[OSi(CH_3)_2H]_8$. Within this set of reactions the expected isomers were produced in reasonable yield, with the α or oxysilylation products never exceeding 25%.

CHAPTER FOUR

Polyether Functionalised Silsesquioxanes

4.0 INTRODUCTION

Supramolecular chemistry is the investigation of molecular systems in which the components are held together reversibly by intermolecular forces and not covalent bonds[140]. The key concept is complementarity. Many examples can be drawn from biological systems, such as enzyme catalysis. Enzymes will catalyse a single reaction with total specificity, because the active site is complementary to the substrate. The size, shape and position of the binding sites are ideally set up for substrate recognition. This has been described as the 'lock and key' principle and has been extended to help our understanding of macrocyclic chemistry[141, 142].

The majority of receptors involved in supramolecular chemistry contain macrocyclic rings. In nature macrocyclic structures are used for metal ion binding in antibiotics such as *valinomycin*[143, 144]. *Porphyrin* macrocycles are seen to bind iron in haem groups and magnesium in chlorophyll[144]. A *corrin* macrocycle binds cobalt in vitamin B12[145]. These natural ionophores can complex the metal ion via oxygen atoms or nitrogen atoms. In fact many macrocycles exhibit their binding characteristics through oxygen, most commonly polyether derivatives.

Polyether derivatives are available both naturally and synthetically[146-152]. These species have the extraordinary ability to solvate metal cations and their host-guest chemistry is well documented. Non-bonding pair donation between heteroatoms within the host and the charged guest, 'hold' the cation in the cavity created by the shape of the host. The most common of these species are the crown ethers[147-150]; however, non-cyclic systems are also known to behave in this way, with varying degrees of efficiency[151, 154].

There are a number of commercially available crown ethers but recently more diverse macromolecules have been prepared[140, 154-159]. Traditionally macrocycles contain oxygen atoms[149, 150], but they have also been prepared with nitrogen[155, 156 157] and sulfur atoms[158, 159, 150], as well as more than one kind of heteroatom[151]. Bicyclic species, cryptands, capable of surrounding the complexing cation in three dimensions, have also been prepared[161-163]. The three dimensional structure provides a tighter binding space, and shows greater affinity than crowns for some cations. Other synthetic variations on the crown ethers include spherands[162, 164], where the cavities are only occupied by spherical entities, podands[140], where two or more arms come out of a central core structure, and finally lariat ethers[156, 140], which consist of a crown with one or more side chain that also serves as a ligand.

4.1 NATURAL IONOPHORES

Natural ionophores are involved in cation transport across cell membranes. Their role in translipid ion transport has long been of interest in understanding cell physiology. Naturally occurring ionophores are usually highly organised, allowing them only to complex particular cations for which they have evolved. An example is the highly functional dodecadepsipeptide *valinomycin*. This is one of a group of natural neutral ionophores. It complexes potassium ions and is made up of twelve sub-units, consisting of amino acids and hydroxy carboxylic acids linked by alternate amine and ester bonds, as shown in Figure 50. First isolated in 1955[143], this species selectively transports potassium cations across mitochondrial membranes in the presence of sodium cations.
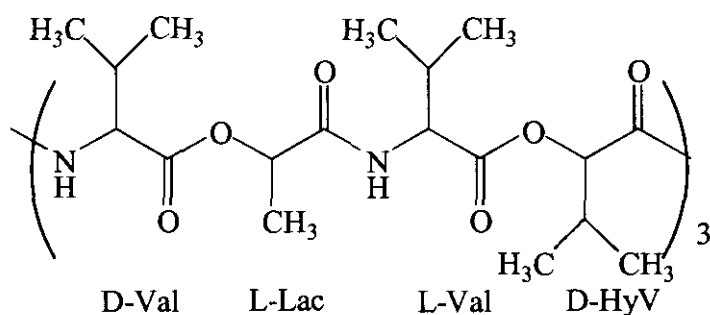
Figure 50: Chemical structure of Valinomycin.

D-Val, L-Val represent the D and L enantiomers of valine, D-HyV is D-

Hydroxyvaleric acid, L-Lac is L-Lactic acid.

This species has a very high selectivity for potassium over sodium, even when there is up to 10^4 times as much sodium as potassium. Such selectivity is important in biological systems and antibiotic action. When complexed the potassium ion is at the centre of a thirty-six membered ring, which is itself stabilised by intra-molecular hydrogen bonding, forming a series of ten membered rings. Further hydrogen bonding between the amide carbonyls binds the cation through the ester groups. When *valinomycin* is bound to a potassium ion, the molecule is 'locked' into a conformation where the exterior consists of isopropyl groups. The cell membrane that *valinomycin* has to pass through is predominantly non-polar. The system is perfectly arranged for complexing potassium, but could not complex any smaller ion as efficiently. The overall hydrophobic exterior aids translipid transport to deliver the potassium where needed.

Other naturally occurring ionophores include *monensin*[165], *nigericin*[166] and *boromycin*[167]. Their most common use is as antibiotics, however some are also excellent pesticides.

4.2 SYNTHETIC IONOPHORES

Synthetic ionophores use chemistry that mimics their natural counterparts. The general structure of these species is the same, using ether and azo links to create the host compound. Some typical examples of synthetic ionophores are shown in compounds **83, 84** and **85**[149, 150].

Compound 83
18 Crown 6

Compound 84
Dibenzo 18 Crown 6

Compound 85
15 Crown 5
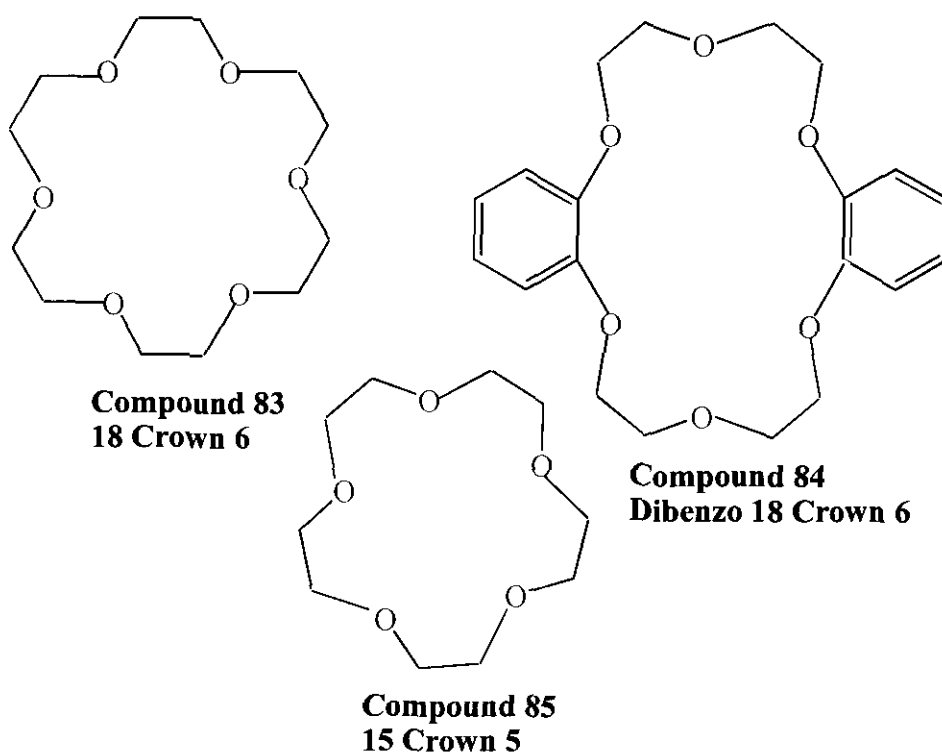
Crown ethers are built up of 1,4 dioxabutylunits, O-C-C-O, for which the minimum energy conformation is staggered. The O-C-Φ-C-O angles are *gauche* and the C-O-Φ-C-C angles are *anti*. This results in the lone pairs pointing away from the ring in the uncomplexed species. However, when a metal ion is bound, the O–C-Φ-C-O bonds are almost always gauche. This brings the ether heteroatoms closer to the metal ion for successful binding.

The most well known synthetic ionophore is 18-Crown-6, compound **83**, which was first prepared by Pedersen in the 1960's[148, 150, 151]. This compound consists of an 18 membered ring comprising six –OCH$_2$CH$_2$- links. Pedersen observed, from a space filling model, that a sodium ion can sit in the cavity of the crown, being held by attractive electrostatic ion-dipole interactions between the alkali metal ion and the six oxygen atoms in the polyether ring. He recognised that the increased solubility of the macrocycle in hydroxylic solvents in the presence of Na$^+$ was due to the crown binding the ion.

A relationship exists between cavity size, cationic radius and the stability of the resulting complex. Structural evidence for this relationship is seen in the crystal structures of the complexes. The cavity size of 18-Crown-6, 2.6-4.2Å, is complementary for potassium ions, which has an ionic diameter of 2.66Å; therefore 18-Crown-6 forms a 1:1 complex with the potassium ions sitting perfectly in the middle of the macrocycle. Those complexes formed between 18-Crown-6 and other alkali metal cations are much less favoured. For example, with sodium ions the crown actually distorts, wrapping itself around the metal in an attempt to maximise the electrostatic interactions. At the same time the strain within the ligand is increased. The ionic diameter of a sodium ion is 1.94Å, significantly smaller than the cavity size of 18-crown 6. This ion, however, is perfectly suited for complexation with 15-crown-5, compound **84**, where the cavity diameter is 1.7-2.2Å. Larger cations perch above one face of the macrocycle because they are too large to fit into the cavity.

Occasionally crown ethers form complexes with metal cations with non 1:1 stoichiometry. An example of this is the potassium ion complex of (benzo-15-crown-5)$_2$[140]. The potassium ion is sandwiched between the two crown ether molecules, as it is too large to fit in the cavity. The opposite situation is also possible, with large crowns capable of binding more than one cation at once[140].

Crown ethers also have a tendency to complex with transition metals and lanthanide cations[140]. Replacing oxygen atoms with softer donor atoms, such as sulfur or nitrogen, can enhance the affinity of the crown for transition metals. Crown ethers can also bind ammonium and alkylammonium cations. 18-Crown-6 is a receptor for primary ammonium cations, as it possess three oxygen atoms, ideally orientated to form three hydrogen bonds with the guest. The overall result is an ammonium ion held by a combination of electrostatic interactions and hydrogen bonds.

Crown ethers are not the only class of synthetic ionophore. Cryptands and spherands are more complicated than crown ethers. Cryptands are cage-like bicyclic species and therefore have a three dimensional structure[160, 163]. They are synthesised by high dilution techniques and are named according to the number of oxygen atoms in each nitrogen-nitrogen linker. Compared to the crowns this structure offers enhanced selectivity and stability for complexation. Examples of cryptands are shown in compounds **86** and **87**[160].
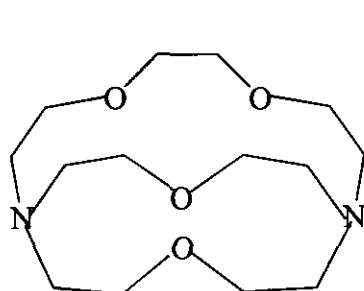
Compound 86
[2,1,1]
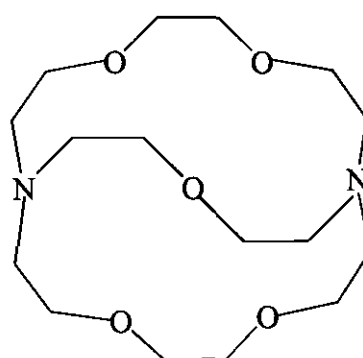
Compound 87
[2,1,2]

Cryptands have been found to complex metal cations from groups 1 and 2 with very large stability constants, higher than those of the analogous crown ethers. Those high stability constants have been attributed to a number of factors. Once bound in the cryptand cavity,

the cation is poorly solvated, resulting in a positive entropy effect, since the solvent is released on binding[161]. Compared to the crown ethers there is also less re-organisation of the structure on metal ion co-ordination, thus providing a favourable enthalpic contribution.

Spherands and calixarenes are more examples of species with complexing abilities[160, 162]. Spherands were designed by Donald Cram in order to create a ligand containing an enforced spherical cavity. These species are highly pre-organised and undergo minimal changes prior to the uptake of a metal ion. Lone pairs are focused to the centre of the cavity, as shown in Figure 51.
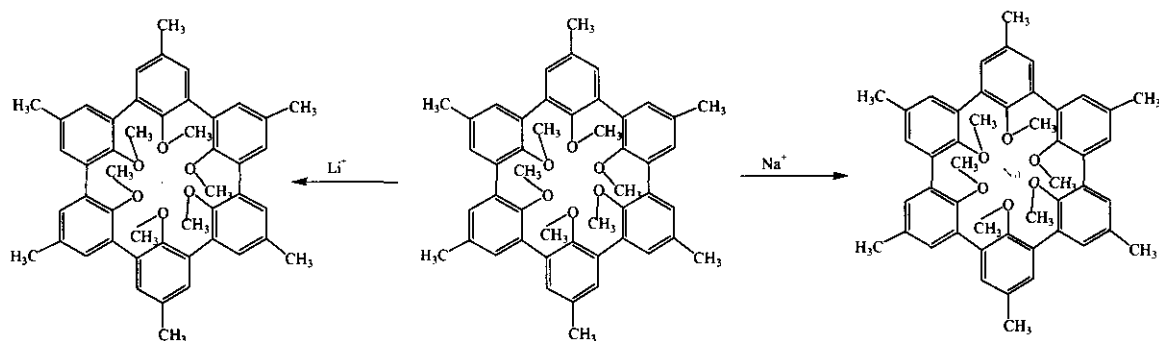
Figure 51: Spherand molecules prepared by Cram

Cram identified that the key factor for complexation with spherands was the principle of 'pre-organisation'. This states that 'the more highly hosts and guests are organised for binding and low solvation prior to complexation, the more stable their complexes will be'. Pre-organisation is therefore a crucial determining factor of binding power.

4.3 USES OF SYNTHETIC IONOPHORES

Synthetic ionophores have many uses, including their role as phase transfer agents, molecular sensors and supramolecular catalysts[168]. The most interesting recent developments are in the field of pharmaceutical research. These species have been used in magnetic resonance imaging (MRI) and X-ray computed tomography techniques (CT), where three-dimensional images are produced which can assist in the diagnosis of disease[168]. Contrast agents are designed to accumulate in a particular part of the body, for example in the cardiovascular system, the liver or in tumours. This enhances the visibility in MRI, allowing abnormalities to be seen more clearly. Radioisotopes with physical properties suitable for imaging and therapeutic application are mostly metal ions such as Ga^{3+}, Ca^{2+} and Na^+. An essential feature of these complexes is that they are kinetically inert and therefore do not release toxic ions into the body before they are excreted. For safe in vivo use, these metals need to be administered as a co-ordination complex. Examples of ligands used in such applications are Compound **88**, marketed as *dotarem*,[169] and Compound **89**, marketed as *prohance*[170].

Compound 88
Dotarem

Compound 89
Prohance
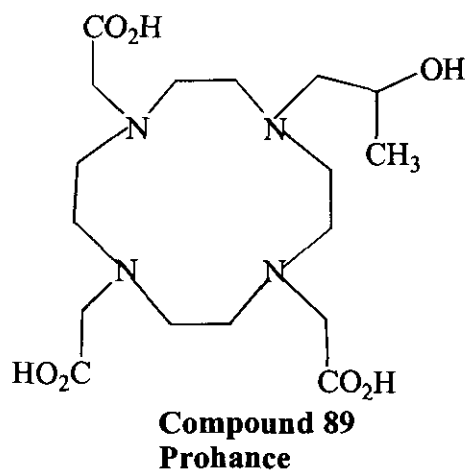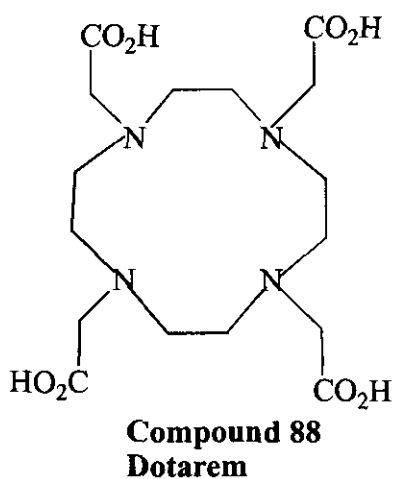
4.4 SYNTHESIS OF POLYETHERS

4.4.1 Synthesis of Crown Ethers

Cyclic polyethers were originally derived from resorcinol[171] and hydroquinones[172]. The cyclic tetramers of ethylene oxide and propylene oxide were first synthesised in the 1950's[147, 149]. However, the real breakthrough came in the early 1960's when Charles Pedersen, of the Du Pont Company, published preparations of over sixty cyclic polyethers[149, 150]. Derived from aromatic vicinal diols, the rings contained up to thirty atoms including up to twenty oxygen atoms. Examples of the compounds prepared are compounds **83, 84 and 85**.

Pedersen was interested in the making bi- and dentate phenolic ligands for copper and vanadium. In an attempt to prepare bis[2-(*o*-hydroxyphenoxy)ethyl)ether][149], compound **90**, an unusual biproduct was seen. Poor yields of seemingly insoluble white crystals resulted in the discovery of the first crown ether. This insoluble compound was in fact dibenzo[18]crown-6, compound **84**. On analysis by UV spectroscopy this compound gave an absorption curve characteristic of a phenolic compound, however, addition of NaOH had no effect on the absorption spectrum. The crystals were also observed to be soluble in methanol in the presence of NaOH.
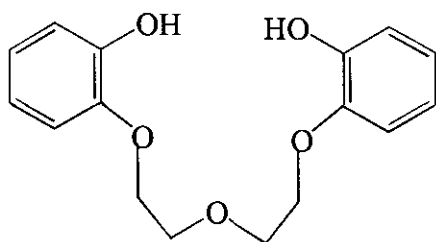
Compound 90
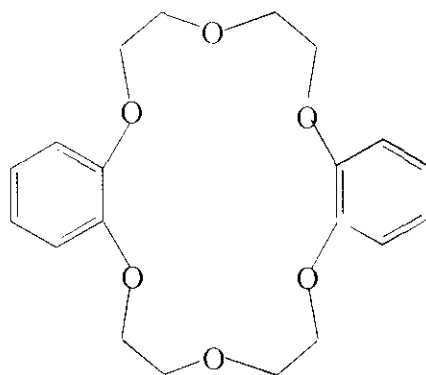
Compound 84:
Dibenzo-18-crown -6
Yield: 0.4%

The sodium ion was shown to been co-ordinated in the hole at the centre of the molecule and was held by electrostatic forces. Further tests showed that other alkali metal ions and ammonium ions also formed stable complexes. This was the first synthetic compound capable of forming stable complexes with sodium and potassium.

Examination of the preparative route led to the discovery of a higher yielding procedure, without resorting to high dilution techniques. Pedersen concluded that the final ring closing step was facilitated by the sodium ion. Utilising ion-dipole interactions, the incomplete ring wraps itself around the sodium ion to form a three-quarter circle, presenting both ends of the chain for cyclisation. The nature of the metal ions used made a significant difference in final yields of crown prepared. Yields were far higher with sodium or potassium hydroxide than with lithium or tetramethylammonium hydroxide.

An extensive program of syntheses followed, with preparation of over sixty macrocyclic polyethers.[147,149,150] A range of compounds with 12 to 60 atoms in the polyether ring were prepared, including those with 4 to 10 oxygen atoms in the ring. Optimum complexing species were recognised as compounds containing 5 to 10 oxygen atoms in a ring. The range of ether linkages investigated identified $-OCH_2CH_2O-$ as the most favourable for

host-guest complexation, –O(CH$_2$)$_3$O- was less efficient with -O(CH$_2$)$_4$O- and beyond becoming completely ineffective. Saturated compounds, obtained by catalytic hydrogenation of their aromatic analogues, were observed as better complexing agents than their corresponding aromatic species.

The complexing affinities of macrocyclic ethers can be placed in order, by measuring the relative distribution of a coloured metal salt, such as picrate, between an immiscible organic solvent and water in the presence of a crown ether. Ineffective complexing agents, will leave the picrate in the water layer, however, a powerful polyether will take the colour into the organic phase. The extent of colour movement between the layer and its dependence on ether concentration was identified as a good indication of an ether's affinity for a cation. Pedersen used this procedure to order a series of polyether compounds with respect to cation complexation.

Frensdorf used potentiometry with cation-selective electrodes to determine the stability constants for 1:1 complexes of macrocylic polyethers[148, 173]. Binding was seen to vary with polyether ring size, the optimum ring size being such that the cation just fits into the cavity. The ideal cavity size for sodium ions was considered to be 15-18 membered rings, with potassium fitting best in an 18 membered ring[149].

4.4.2 Synthesis of Cryptands

Other workers involved in ionophore preparation and analysis, such as Vögtle et al., used a variety of polyether octopus molecules[151]. A number of species were prepared based around 1,11-(bis(8-quinolyloxy)-4,6,9 -trioxaundecane as seen in compounds **91, 92** and **93**[151].
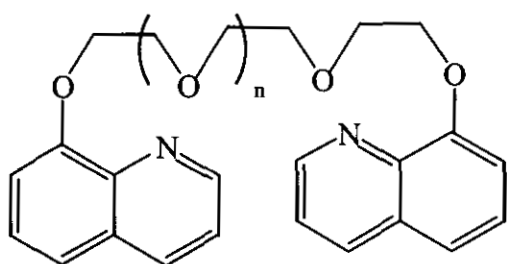
Compound 91
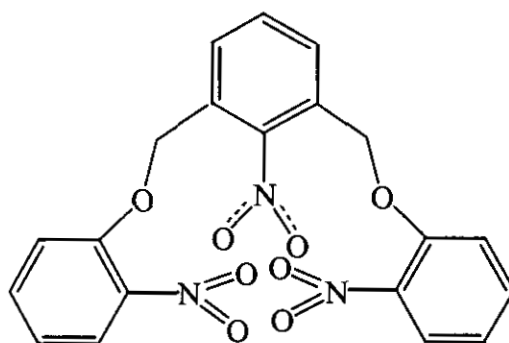
Compound 92
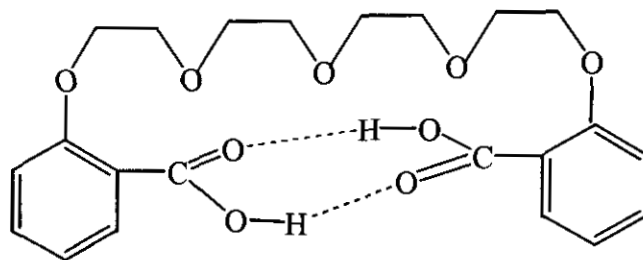
Compound 93

Compound **91** was found to produce a stable neutral ligand with RbI. Seven donor atoms were necessary to form this species, i.e. n was equal to 2. X-ray studies found that heteroatoms, other than those in an ether chain, for example OCH_3, NO_2 etc, can also serve as donor atoms in neutral ligands. However, terminal groups without heteroatoms were incapable of actively participating in complexation. End group donor effects also depend upon geometrical factors, for example, steric crowding and conformational restraints. Compound **92** was considered too sterically hindered for a metal ion to fit into the cavity created by the phenyl rings. Dicarboxylic acids such as compound **93** did complex metal ions, but not by using the acid groups. These hydrogen bond together, drawing the ring closer, forming a crown ether analogue. Ca^{2+} can complex in the centre of the cavity created. This compound will only complex cations of a particular size, for example $Ca(SCN)_2$ was found to react successfully, however KSCN and RbI did not.

Vögtle later published work on polyether octopus molecules with a benzene core.[155] These compounds exhibited unusual complexing properties, with conformational mobility being impeded by spatial crowding. The hexa-polyether compound **94** is one such species which was shown to co-ordinate cations in the dichloromethane-aqueous picrate solution test. A greater affinity for alkali metals over other ions was observed. Complexation was shown to be faster than with known crown ethers, with an efficiency comparable to the cryptands [2,2,2] and [2,2,1].

Compound 94

Represented as

M⁺ → M$^+$
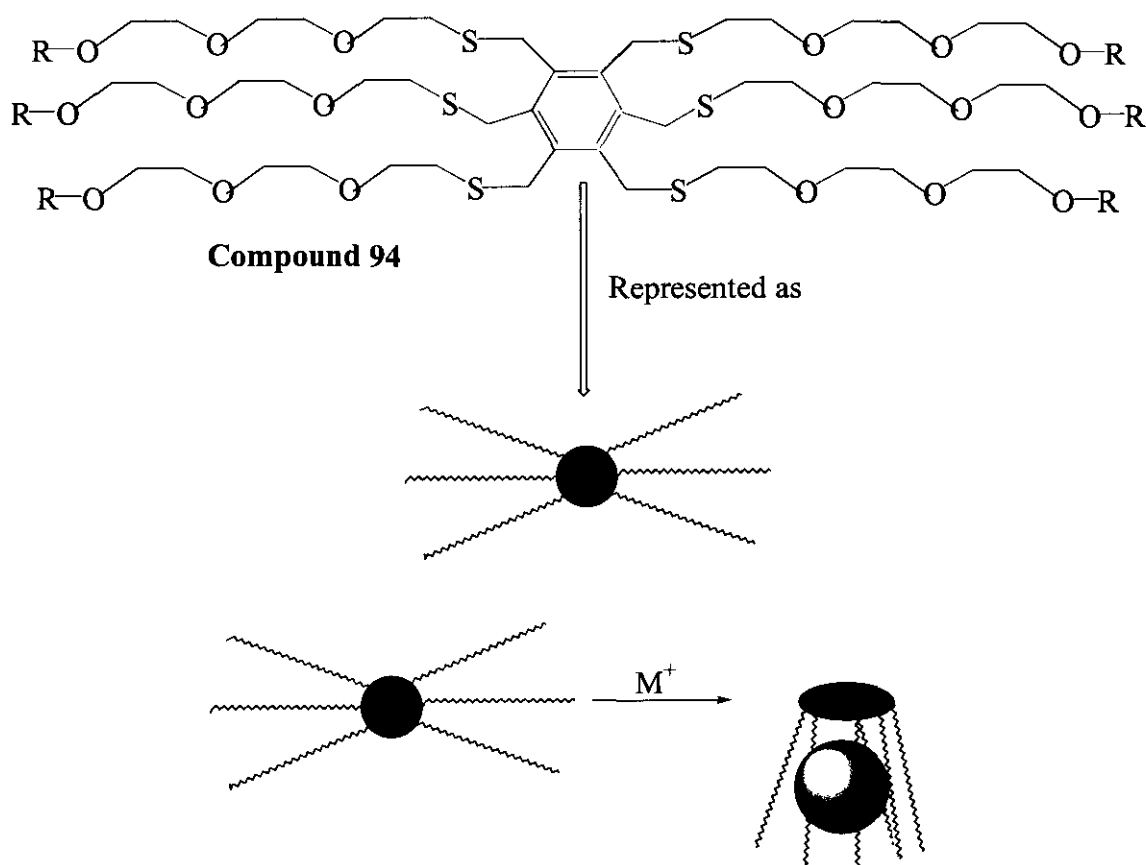
Figure 52: Octopus molecules prepared by Vögtle[155]

Modelling studies indicated a conformational change was necessary to create such extensive complexation. The uncomplexed ligand may be expected to have the six arms radiating away from each other but on complexation all six polyether tentacles need to be orientated on one face of the planar benzene ring, as shown in Figure 52[155]. A distinct

143

decrease in complexation was noticed when the number of donor atoms was reduced, either by shortening the tentacle chain, or reducing the number of substituents on the benzene ring. Phenyl rings substituted in the 1,3,5 and 1,2 positions, as shown in Figure 53, were powerful ligands, with 1,3,4- substitution being better than 1,2,3- substitution due to steric factors[155].
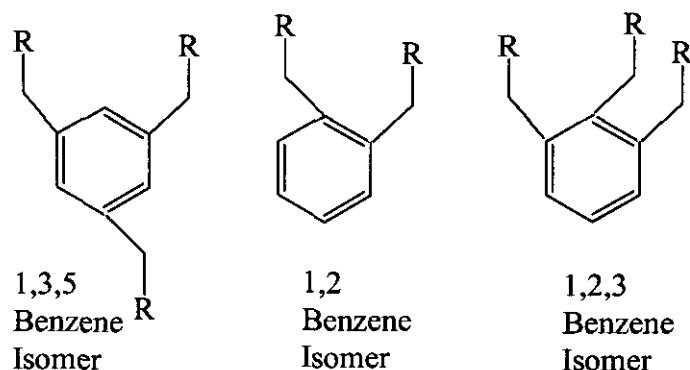
Figure 53: Benzene isomers used in octopus molecules

In light of the unique properties of polyether ionophores we thought that a combination of such species with silsesquioxane cages would produce compounds with very interesting properties. A situation analogous to Vögtles benzene derivatives can be envisaged with a central cage structure and eight radiating arms[155]. A conformational distortion as a consequence of complexation may result in a change in the way the arms align themselves. With this goal in mind, a series of polyether functionalised silsesquioxanes was prepared.

4.5 PREPARATION OF POLYETHER FUNCTIONALISED SILSESQUIOXANES

A series of synthetic routes were devised to prepare polyether functionalised silsesquioxanes. Many routes were considered, with a number of approaches tried prior to successful preparation of the compound.

4.5.1. Route One: Hydrosilylation of a vinyl polyether.

Direct hydrosilylation was attempted using vinylpolyethers and platinum catalysts. As discussed in chapter 3 the coupling of alkenyl species to silsesquioxane cages, occurs in very high yields with few complications. Initially tri(ethyleneglycol)methylvinylether and di(ethyleneglycol)methylvinylether were reacted with both T_8H_8 and $[SiO_{3/2}]_8[OSi(CH_3)_2H]_8$ using Speiers[62] and Karstedts[65] catalysts respectively. Monitoring of the reactions by FTIR indicated that hydrosilylation was progressing, with no SiH stretch visible after 24 hours. For all systems, ^{1}H NMR also suggested complete reaction, with clear and distinct triplets in the region of 0.9-1.2 ppm, typical of $SiCH_2$ groups. However, analysis using ^{29}Si NMR showed multiple peaks in the respective 'T' and 'Q' regions indicating a distribution of products. It was unclear from the ^{1}H and ^{13}C NMR whether these species were a result of α and β addition of the vinyl compound to the silane, or if this mixture was a combination of partially substituted cages. This latter suggestion was thought unlikely because of the lack of a band arising from unreacted SiH in the FTIR spectra. To drive the hydrosilylation to completion the reactions were repeated with an excess of polyether and with higher concentrations of catalyst solution. Unfortunately the same results were obtained suggesting mixtures were formed where purification techniques proved of little use.

In order to eliminate the possibility of α and β addition, a pentenyl derivative was employed, since linear terminal alkenes had been shown to only exhibit β hydrosilylation. Pentenyl(tetraethylene)monomethylglycol, compound **95**, was chosen as our target molecule since 5-bromopentene was readily available from commercial sources. The pentenyl group was considered to be long enough to avoid unwanted side reactions. It was thought that the tetraethylene group would be sufficiently long to possess some complexing ability in a host guest environment. Pentenyl(tetraethylene)monomethylglycol was prepared and coupled to the silsesquioxanes as shown in Reaction Scheme 13.
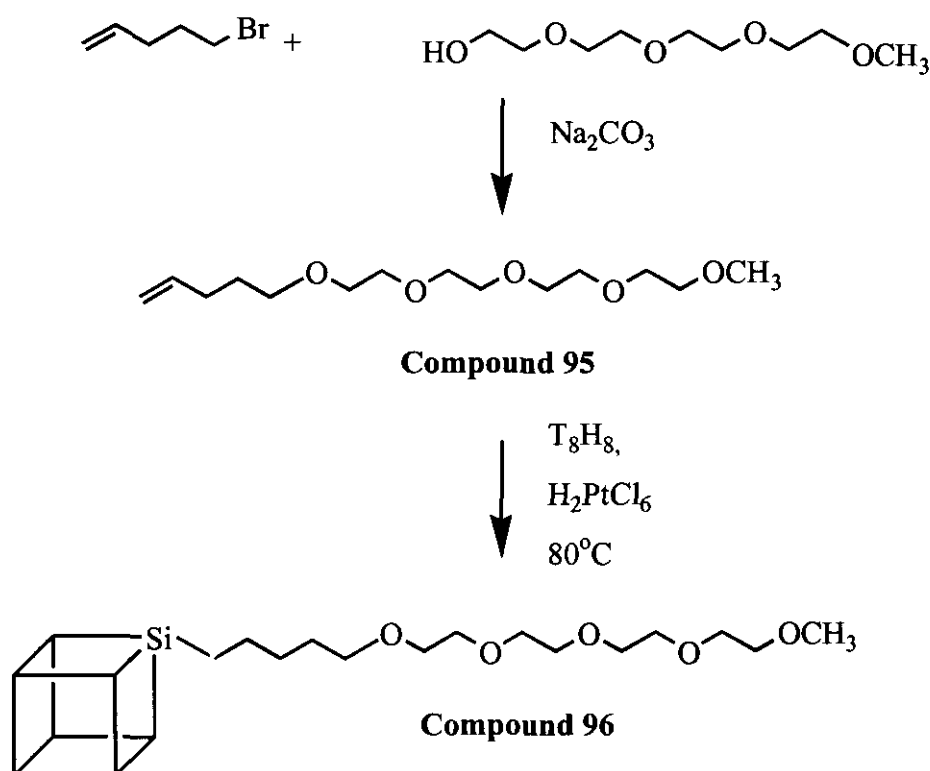
Reaction Scheme 13: Hydrosilylation of an alkenylpolyether.

Purification of compound **96** was carried out using silica column chromatography with dichloromethane and acetone as the eluents.

The outcome of the attempted hydrosilylation with T_8H_8 was unexpected. An eightfold excess of polyether over silsesquioxane failed to produce the desired product. The ^{29}Si

NMR showed the presence of a multi-environment cage species. Typically three peaks were observed in the region of –66ppm, while smaller peaks were also seen on baseline expansion. The distributions of approximately 1:3:4, indicated incomplete cage substitution. The main peak of this distribution at –66.9ppm, being the dominant eight arm species. However, the situation was further complicated by the presence of resonances at – 101ppm. These peaks in the 'Q' region had a similar distribution as those in the 'T' region, as shown in Figure 54. This was found to be in line with earlier work carried out by Gentle[97] where complete cage substitution could not always be achieved by direct coupling reactions. Work carried out by Gentle et al included the attempted hydrosilylation of vinyl alcohols such as allyltetra(ethylene)glycol, with T_8H_8. Mixtures were obtained, assumed to contain both the α and β adducts. In an extension of this work mixed allyl functional polyethers and vinyl functional siloxanes were also hydrosilylated with T_8H_8.
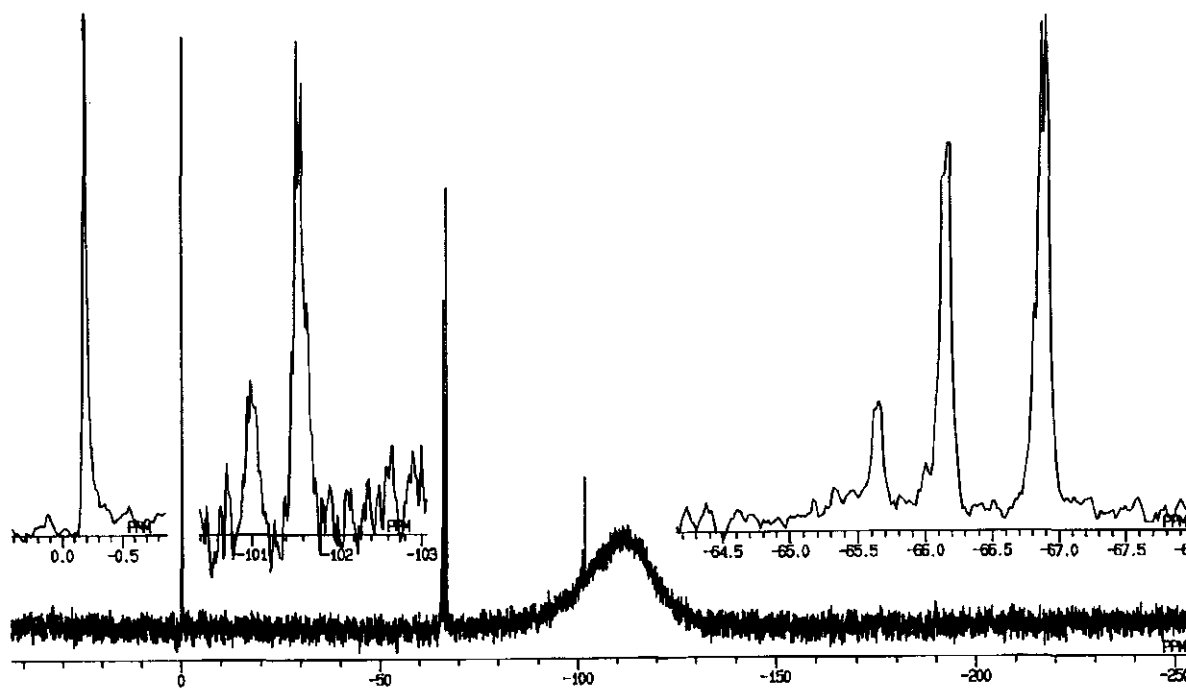
Due to complicated ^{29}Si NMR spectra the products were never fully analysed.

Figure 54: ^{29}Si NMR of the reaction mixture for T_8H_8 with

Pentenyl(tetraethylene)monomethylglycol

To overcome incomplete cage substitution in the preparation of Compound **96**, varying proportions of the two reactants were tried. Ratios of cage to alcohol included 1:8, 1:16 and 1:20 and the catalyst concentrations were also increased. Unfortunately the same multi-peak ^{29}Si NMR spectrum was obtained in each case. The exact nature of this reaction mixture was not discovered. It was not considered to be a combination of 6,7 and 8 substituted cages due to the lack of free SiH, which would be observed at –84ppm.

The presence of the 'Q' compounds were still unaccounted for. The hygroscopic nature of polyethers would mean that water could well be present in the starting materials. This could lead to its catalytic attachment to the cage, producing SiO_4 sites. Modifications to the process included carrying out the reaction with pre-dried pentenylglycol using molecular sieves. Reactions were also carried out in sealed ampules, and under an inert atmosphere, with little difference to the end result. Secondly the alcoholic starting material used to prepare the pentenylglycol could well be present as an impurity leading to competing reactions. Attachment via the OH of the glycol would again produce SiO_4 sites in the product. There would be no control over this reaction and the mode of addition, resulting in a random distribution of cage substitution. Any such impurities however should be negligible following column chromatography purification of compound **96**. There was no evidence for this in the ^{1}H and ^{13}C NMR for the compound prior to hydrosilylation.

One final explanation for attachment via oxygen is the possible decomposition of compound **96** by the platinum catalyst, to give alcoholic sites. As shown in Figure 55, the platinum can co-ordinate to the oxygen of the polyether leading to oxygen coupling to the silicon atom of the cage, in competition with the alkenyl functionality. Such a situation would result in the random attachment of compound **95** via the alkene or ether linkage.
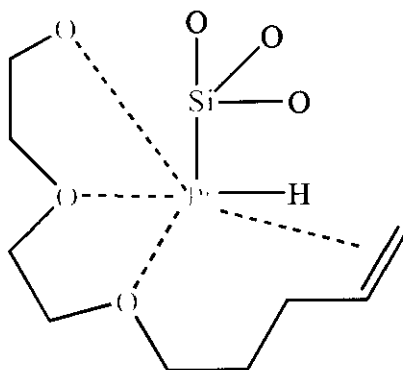
Figure 55: Schematic diagram of catalytic addition to a silsesquioxane.

Attempts to purify the final mixture, using column chromatography, produced little change to the spectra. Co-elution of the individual cage species provided clearer ^{1}H and ^{13}C NMR spectra; however, the pattern of resonances seen in the ^{29}Si NMR remained unchanged.

When $[SiO_{3/2}]_8\{OSi(CH_3)_2H\}_8$ was used as a replacement for T_8H_8, little difference was noticed. These reactions again led to multiple 'Q' environments in the ^{29}Si NMR spectra. Increased amounts of compound **95** and catalyst solution were also investigated, but to no avail. The ratio of peaks in the 'Q' region of the ^{29}Si NMR spectra were typically 1:3:4, with the main peak, at –108ppm, arising from the desired product. As before the ^{1}H and ^{13}C NMR provided no conclusive evidence for the exact composition of the final mixture.

In a final attempt to hydrosilylate alkenylpolyethers, a vinylsilylether was synthesised since it was considered necessary to eliminate all alternatives before abandoning this approach.

Quenching oligoglycols with an alkenylchlorosilane would result in an alkenyl functionalised polyether. This would involve a straightforward nucleophilic substitution and hence should be high yielding. The hydrosilylation of such a compound with a

silsesquioxane cage should then provide the desired product, as shown in Reaction Scheme 14.

HOCH$_2$CH$_2$(OCH$_2$CH$_2$)$_2$OR + ⟋Si(CH$_3$)$_2$Cl

|
| Pyridine
| Dry toluene
↓

⟋Si(CH$_3$)$_2$OCH$_2$CH$_2$(OCH$_2$CH$_2$)$_2$OR

|
| [cube]-Si-O-Si(CH$_3$)$_2$H
↓
Pt catalyst

[cube]-Si-OSi(CH$_3$)$_2$ (CH$_2$)$_2$Si(CH$_3$)$_2$(OCH$_2$CH$_2$)$_3$OR
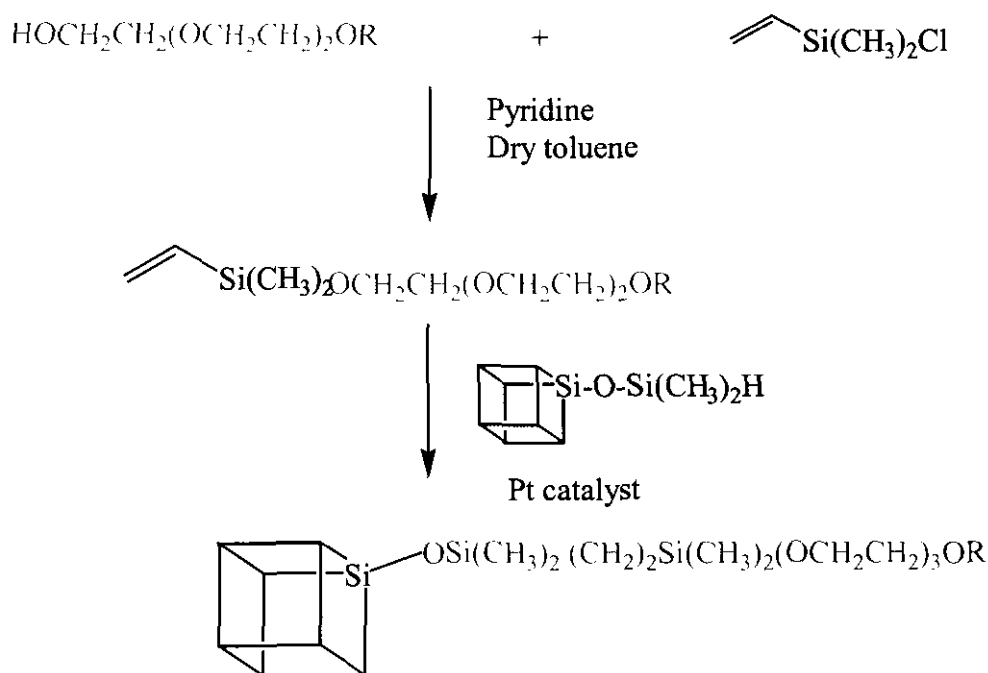
where OR is

Compound 97:   (OCH$_2$CH$_2$)$_2$OC$_6$H$_5$C$_8$H$_{17}$

Compound 98:   OC$_4$H$_9$

Compound 99:   OCH$_3$

Reaction Scheme 14: Silsesquioxane Functionalisation using Route One.

In the light of the oxysilylation by-products seen previously, we expected some problems with this hydrosilylation. However, it was hoped that such problems would not be too significant. Problems concerned with catalyst inhibition were also envisaged in light of earlier findings. Chlorodimethylvinylsilane and allylchlorodimethylsilane were reacted with three oligoglycol species, igepal, compound **100**, tri(ethylene)glycolmonomethylether, compound **101,** and tri(ethylene)glycolmonobutylether, compound **102**. All species were purchased from

150

Aldrich and used without further purification. Compound **100** is actually a mixture of chain lengths ranging from 1 to 5 oxyethyl groups.

Compound 100: Igepal

$HOCH_2CH_2(OCH_2CH_2)_5O$ —⟨benzene ring⟩— C_8H_{17}
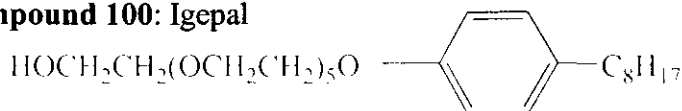
Compound 101: Tri(ethylene)glycolmonomethylether

$HOCH_2CH_2(OCH_2CH_2)_2OCH_3$

Compound 102: Tri(ethylene)glycolmonobutylether

$HOCH_2CH_2(OCH_2CH_2)_2OC_4H_9$
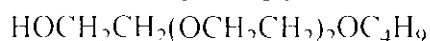
This range of oligoglycol species was selected due to the increasing hydrophobicity of the end groups progressing from compound **102**, to compound **103**, to compound **101**. Initial tests suggested that compound **101** would complex ions, but was not soluble in organic solvents because the CH_3 end group was not hydrophobic enough. Thus the butyl and igepal derivatives were used. The hydrophobic nature of the end group was required to help the complexes dissolve in non-polar solvents. An increase in solubility in non-polar solvents is expected with the order of end groups Me<Bu<Igepal.

The reactions were carried out in dry refluxing toluene to avoid hydrolysis of the chlorosilanes. Solvents and excess chlorosilane were removed, followed by column chromatography using hexane/ethylacetate (1:1) as the eluent. Evidence for the successful nucleophilic substitution was seen in both the FTIR and NMR spectra. The absence of an OH stretch at 3100cm^{-1} in the FTIR, coupled with conclusive ^{29}Si NMR spectra, showing single compounds for all polyethers, at approximately 6.5ppm, confirmed that the required species had been produced cleanly, and in high yields of above 95%. The igepal derivative provided a mixture of compounds, with between 1 and 5 oxyethyl units. These igepal species were combined for use in the next stage. Both T_8 and Q_8 silsesquioxane cages were used, as was the cyclic siloxane tetramethylD_4. The cyclic compound was used to model

the reaction. In this case the hydrosilylation reaction was completed in just 4 hours, compared to the 24 hours necessary for the eightfold functionalisation of the cages.

The hydrosilylation reaction was followed by FTIR, monitoring the decrease in the SiH stretch. Problems were anticipated with α and β addition to both the allyl and vinyl silanes. Reactions were seen to proceed to completion by FTIR, although purification produced poor yields of the desired products. The igepal derivative was the crucial species because it has the most ethylene groups. Attempted purification of the reaction mixture for this species produced many isomers. Igepal itself is a mixture of isomers with varying numbers of ethylene units. Column chromatography performed on the Q_8 derivative separated these individual isomers. Figure 57 shows the ^{29}Si NMR of compound **97**. Problems with α and β addition were not as significant as expected; however, evidence of isomers was observed by the broad peak at -108ppm, labelled D. Peak B is the $OSi(CH_3)_2R$ group attached directly to the cage, the broad nature of this peak indicates more than one cage environment, these are possibly α/β adduct or 6,7,8 substituted cages. Peak C is the result of the silicon attached to the polyether chain as highlighted in Figure 56. The unlabelled peak at -21ppm is the D4 that the Karstedt's catalyst[65] was suspended in. Peak A is the result of unreacted vinylsilylether.
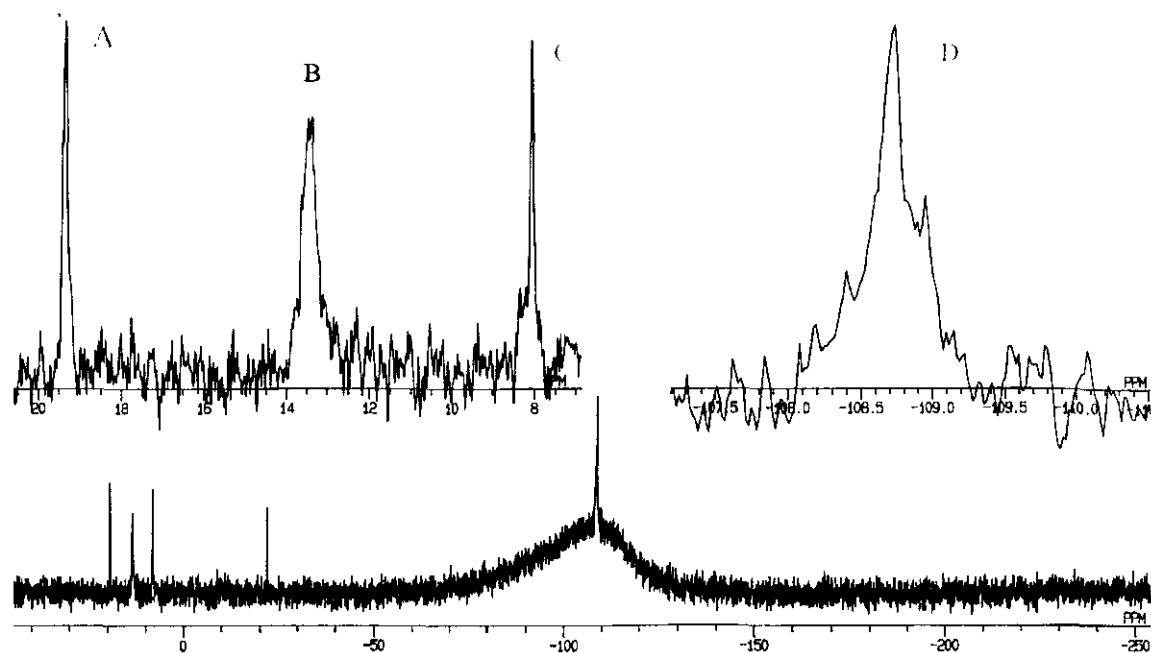
Figure 56: ^{29}Si NMR for Compound 97 (before purification)

Compound 97
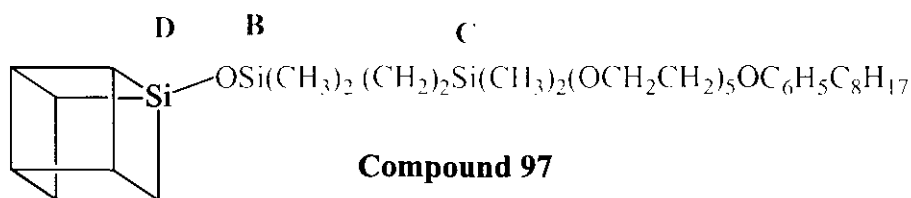
There was no conclusive evidence of oxysilylation, however the broad peak at -108ppm encompasses many products. The ^{1}H and ^{13}C NMR spectra also suggested a mixture of products with some evidence for α and β addition. The allyl derivative was much the same. Spectral detail mirrored that of compound **97**. Both compounds **98** and **99** were seen to be mixtures of the α and β adducts. The reaction between D4 and vinyl-igepal seemed to produce the largest proportion of the desired product, compound **103**. Although impure, this reaction mixture was used for preliminary tests to assess its potassium complexation ability.
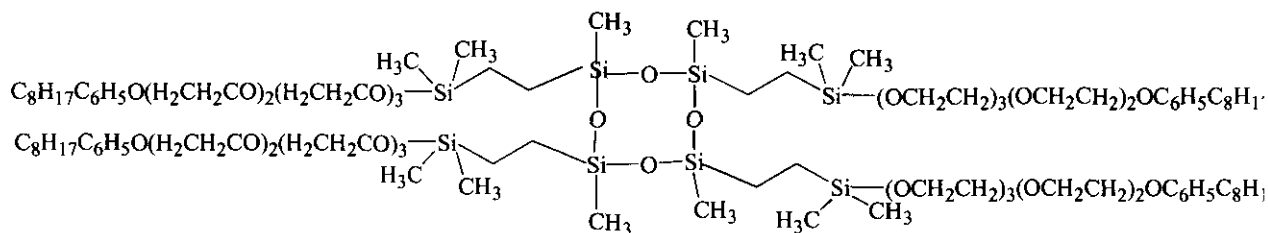
Compound 103: D4 Vinyl Igepal derivative

To overcome the problems associated with α and β addition, an alterative method of alkenylpolyether production was employed. The alcohol compounds **100-102** were reacted with pentenoic acid using trifluoroacetic anhydride in dichloromethane. These simple esterifications produced excellent yields for all compounds following purification by column chromatography with dichloromethane and methanol. Yields of the esters were in excess of 80% for all of the alcohols.

These esters were then hydrosilylated with $[SiO_{3/2}]_8\{OSi(CH_3)_2H\}_8$ using platinum catalysts, as shown in Reaction Scheme 15.

ROH   +   (allyl-CH₂-CH₂-CO-OH structure)

$$ROH \; + \; \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CO}_2\text{H}$$

Trifluoroacetic Acid
DCM
24 hrs

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2R$$

Karstedt's Catalyst
Toluene
O_2
24 hrs

(cube)—Si—OSi(CH$_3$)$_2$(CH$_2$)$_4$CO$_2$R
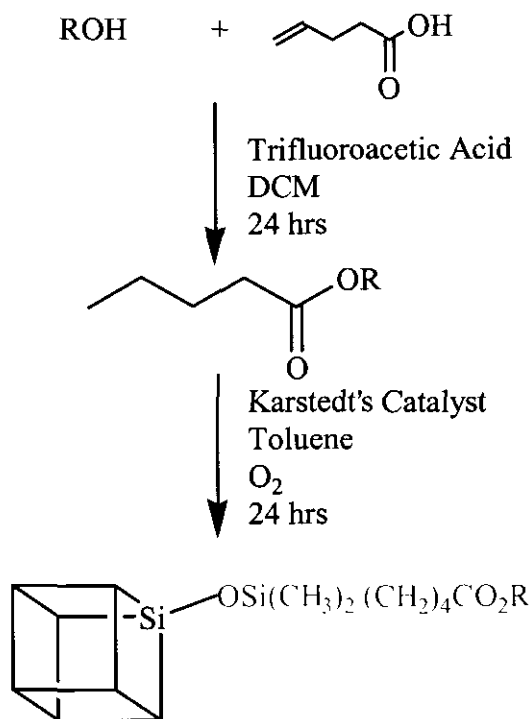
where R is

Compound **104**: $CH_2CH_2(OCH_2CH_2)_4C_6H_5C_8H_{17}$

Compound **105**: $(CH_2CH_2O)_3OC_4H_9$

Compound **106**: $(CH_2CH_2O)_4OCH_3$

Reaction Scheme 15: Polyether silsesquioxanes formed via esters

All three of the ester derivatives were observed to react completely with the cage. The reactions were monitored by ^{1}H NMR observing the gradual development of the SiCH$_2$ peak, and the disappearance of the vinyl peaks at approximately 5.5ppm and 5.9ppm. The integration in the ^{1}H NMR was closely examined, correlating the respective methyl and butyl groups with those of the Si(CH$_3$)$_2$ groups of the cage. ^{29}Si NMR was seen to show clear and distinct resonances from the cages. The ^{1}H NMR spectra of compound **107** is shown in Figure 57.
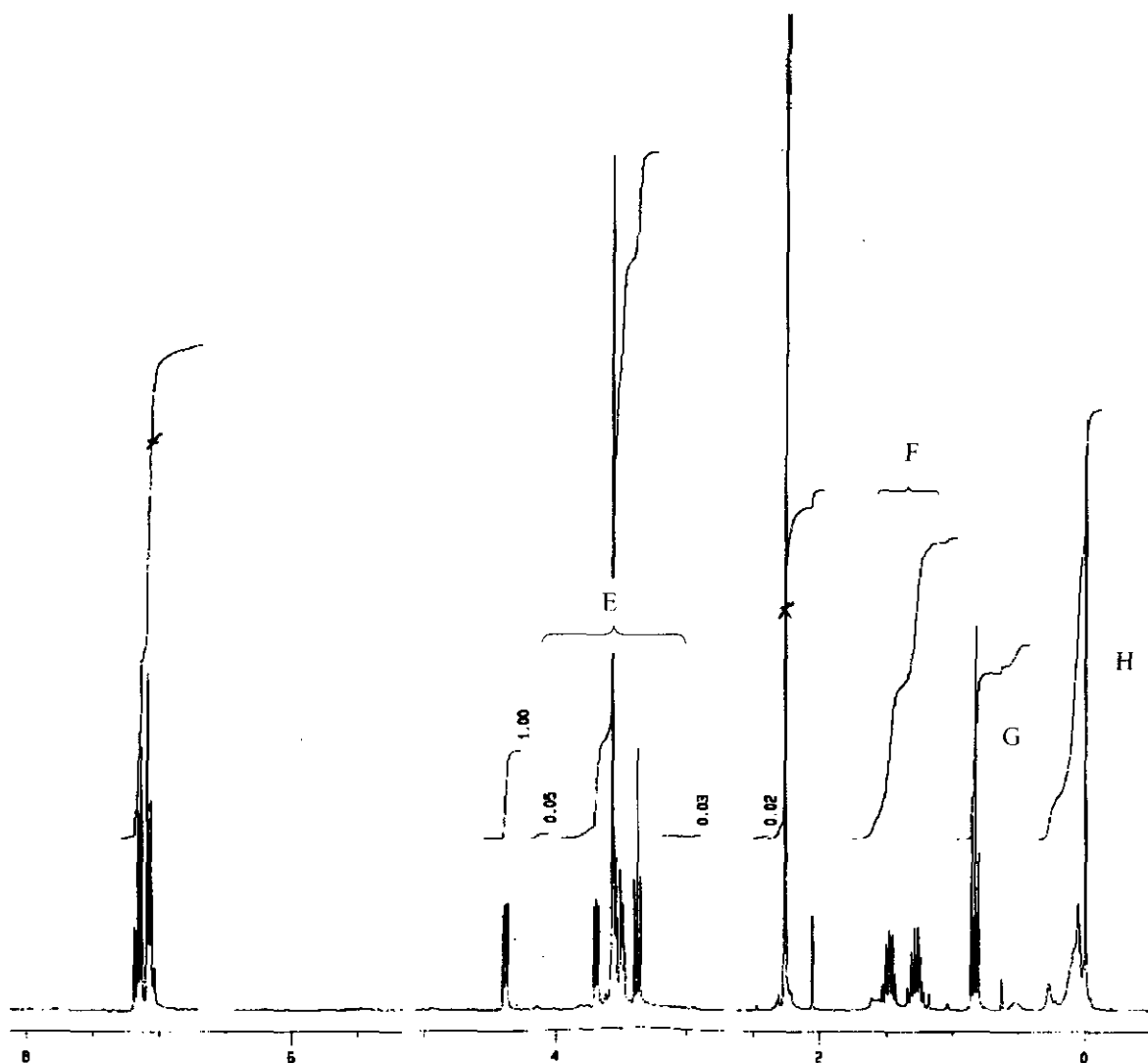
Figure 57: ^{1}H NMR of Compound 105 before purification.
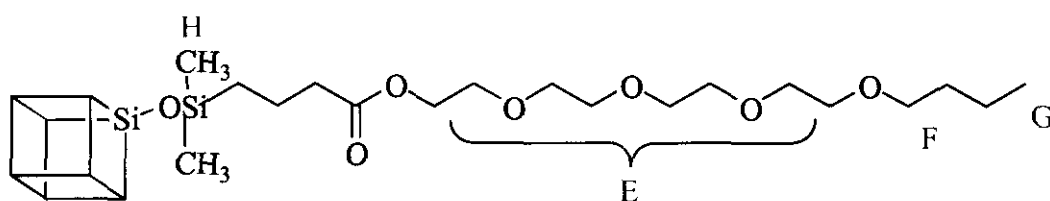
In Figure 57, those peaks crossed out are the remaining toluene present from the hydrosilylation reaction. The polyether region is labelled E. Integration for this section of the spectra accounts for 18 protons. The CH$_2$ furthest downfield is that connecting the ester to the polyether. The alkyl chain of the butyl group is labelled F, with the CH$_3$ labelled G. The singlet resonating at 0.05ppm corresponds to the methyls attached to the cage, labelled

156

H. The SiCH$_2$ is observed at 0.25ppm. The integration on the spectrum in Figure 57 fits well for the assigned peaks.

However, problems were experienced with purification. Purification techniques involving column chromatography were found to cause breakdown of the products. The arms were seen to be cleaved at either the ether or ester linkages, producing a number of fractions with varying degrees of functionalisation of the silsesquioxane.

With the complete substitution of the cage achieved using a 8:1 ratio of the polyether to the cage, the desired products had been prepared although they had not been successfully purified. To assess whether the polyether silsesquioxanes would display any complexing properties, these compounds together with those prepared from chlorodimethylvinylsilane were used in preliminary studies.

4.5.2 Complexation Tests

Preliminary tests were carried out using a sample of solid KMnO$_4$ (0.26g) and a dichloromethane solution of the polyether species, compound **103**, (6×10^{-4}mol dm^{-3}). When no complexing agent was present, the solid did not dissolve in the organic solvent. However, when the polyether derivatives were present as a solution in the dichloromethane the solution became coloured. The coloration was due to K^{+} complexation by the polyether compound which solubilises the purple permanganate ion. A similar result was also achieved with dibenzo-18-Crown-6, which was used as a control. Compounds were used without prior purification. The individual solutions of compounds **97** and **104** were seen to colourise the organic solution immediately they were mixed with the solid. The butyl and methyl derivatives, compounds **98, 99** and compounds **105** and **106**, were also seen to produce a positive result. However, the colouration was paler in these cases. Compound

103, the D4 derivative was seen to produce the strongest coloured solution. Thus we concluded that the degree of colouration and hence the affinity for potassium ion complexation varied in the following manner, derivatised 18-Crown-6> derivatised D_4> derivatised Q_8. Being preliminary studies the degree of complexation was not assessed accurately, merely by the strength of the coloured solutions.

In line with the methodology used by Frensdorf[148] to analyse the complexation of crown ethers, solutions were made of the polyether compounds in chloroform and mixed with sodium and potassium picrate solution in water (prepared using picric acid and sodium or potassium hydroxide). When a 6×10^{-4} mol dm^{-3} solution of compound **103** was used with a 0.01 M KOH 2×10^{-4} mol dm^{-3} solution of picric acid, some of the colour was taken up by the organic layer. Dibenzo-18-Crown-6 was used as a control for these tests. The dibenzo-18-crown-6 solution was prepared as a 2×10^{-4} mol dm^{-3} solution. The picrate uptake for all these tests was measured by UV spectroscopy, based on the maximum absorbance at 350nm, as shown in Figure 58. Levels of absorbance appeared to be greater for the crown ether than the D4 derivative. These studies were repeated using the Q_8 species, compound **104**. In these cases the organic layers were unaffected, with no obvious colour changes being observed.
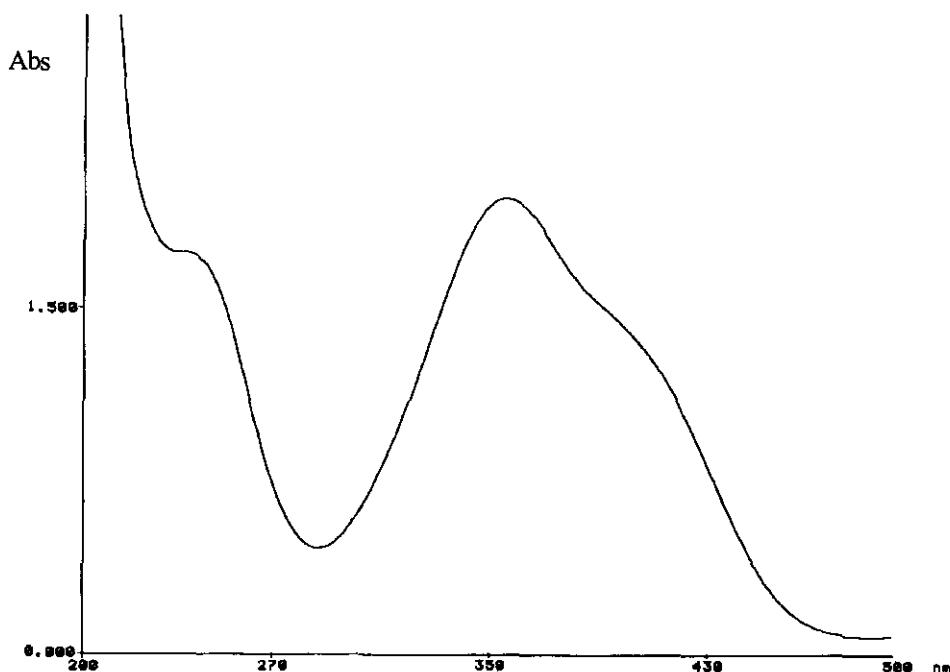
Figure 58: UV Vis absorbance from Dibenzo18-Crown-6 with Picric Acid

Binding constants (K) were calculated for those species tested with picrate solution, as shown in Table 8. The extinction coefficients calculated by Frensdorf were used, with $\varepsilon = 1.8 \times 10^4 \text{cm}^{-1}\text{M}^{-1}$ for λ_{max} at 350nm[148] . Binding constants were determined for dibenzo-18-crown-6 and compound **103** using equation 1.

Equation 1

$$K = \frac{[Complex]}{[Initial\ Polyether]-[Complex]}$$

Table 8: Binding Constants

	[Initial Polyether] mol dm^{-3}	UV absorbance	[Complex] mol dm^{-3}	K
Dibenzo-18-Crown-6	2×10^{-4}	1.8	1.0×10^{-4}	1
Compound 104	6×10^{-4}	1	5.5×10^{-5}	0.10

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It can be clearly seen from Table 8 that the binding constant for dibenzo-18-crown-6 is a magnitude larger than that of compound **103**. In other words more K^+ was transferred from the aqueous layer to the organic layer when the crown ether was present in the organic layer. Whilst dibenzo-18-crown-6 may be a superior complexing agent, this test proves that compounds such as **103** do actively bind the K^+ ion. The presence of more arms may be expected to lead to a larger binding constant; however, the value was much lower.

These results, whilst promising, were not however very reliable. The polyether derivatives used had not been purified and, whilst NMR spectra indicated that the majority of the mixture was the desired species, it is impossible to say which component in the mixture is effecting the metal ion complexation. Brief tests using the glycol starting materials also provided a positive result, albeit with paler colourations and therefore lower binding constants. For this reason, a different strategy was sought, one that yielded pure poly ether species in high quantities.

4.5.3 Route Two: Direct Oxysilylation of an alcohol with a silsesquioxane.

Direct oxysilylation of alcohols with silsesquioxanes using Et_2NOH as a catalyst is a well-known route for functionalising silanes. Previous work carried out by the Bassindale group has shown the reaction to work cleanly and in high yields with T_8H_8[174]. This included attaching alcohols such as pentan-1-ol and hexan-1-ol to the cage. Thus the attachment of polyether chains to a cage in this way should produce the required eightfold functionalised silsesquioxanes.

The cages used were T_8H_8 and $[SiO_{3/2}]_8\{OSi(CH_3)_2H\}_8$ and these were coupled individually with tetra(ethyleneglycol)monomethylether, compound **107**. The glycol was

refluxed separately in acetonitrile or hexane with the silsesquioxanes in the presence of Et$_2$NOH.
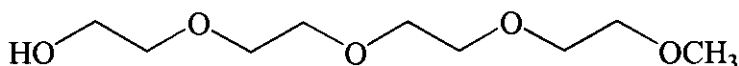
Compound 107: Tetra(ethyleneglycol)monomethylether

The products obtained with T$_8$H$_8$ were sparingly soluble in all common NMR solvents. NMR data suggested that the cage had been decomposed. ^{1}H and ^{13}C NMR were identical to the polyether starting material, with no evidence of the free SiH of the cage. This was confirmed by the ^{29}Si NMR that showed no peaks at all. There was no unreacted cage, nor were there any peaks relating to the expected 'Q' cage. FTIR analysis showed unreacted – OH, with no SiH stretch being seen. It was assumed that the reaction conditions had caused the cage to decompose.

The Q compound was not used because this would probably break down easier than the T compound.

These continued problems and lack of understanding regarding the exact outcome of the reaction resulted in the development of an entirely different synthetic approach.

4.5.4 Route Three: Production of a chlorosilylpolyethyleneglycol, followed by nucleophilic substitution.

Another synthetic route was considered involving the use of tetramethylammonium silicate, compound **108**. This anion is prepared in high yield, as an intermediate in the

synthesis of $[Si_8O_{12}]\{OSi(CH_3)_2H\}_8$, via a reaction of tetramethylammonium hydroxide with silicic acid[89,]
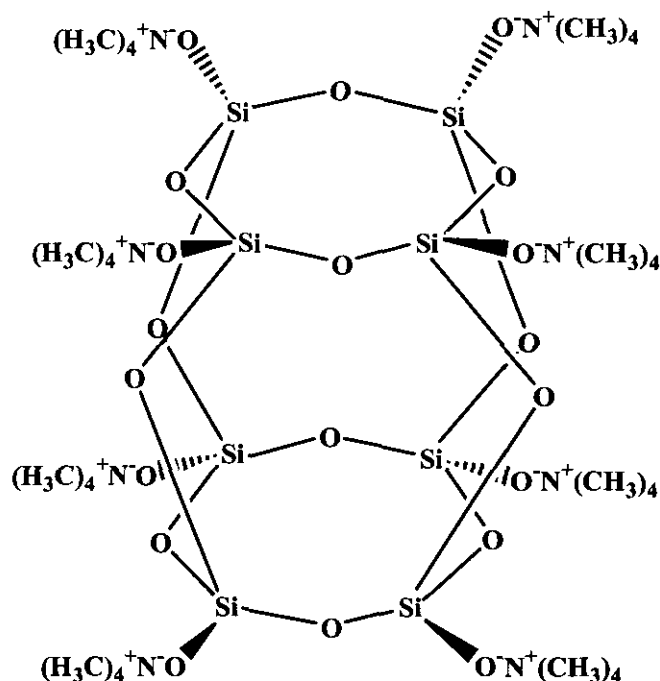
Compound 108: Tetramethylammonium silicate.

Typically this anion is quenched with chlorodimethylsilane in the process of Q_8 silsesquioxane preparation[89,]. It was hoped that this process could be adapted by synthesising a chlorosilane derivative of a suitable polyether. Quenching the anion with this silylpolyether should yield the desired silsesquioxane cage in excellent yield.

The first challenge was to prepare the chlorosilane derivative of the polyether compound. Two approaches were tried, one involving a Grignard reaction[175] the second taking advantage of the hydrosilylation reaction.

The Grignard route is shown in Reaction Scheme 16 and involved a glycol compound undergoing nucleophilic substitution with a dibromoalkane. Successful production of the

bromoether could then lead to the Grignard reagent which could be reacted with dimethylchlorosilane. This silylether, compound **110**, could be chlorinated and reacted with tetramethylammonium silicate to give the silsesquioxane cage.

H_3C—O—…—O—…—O—…—O—…—OH + Br—…—Br

NaH,

THF,

Reflux

H_3C—O—…—O—…—O—…—O—…—O—…—Br

Compound 109

Mg,

$Cl(CH_3)_2SiH$

H_3C—O—…—O—…—O—…—O—…—O—…—$Si(CH_3)_2H$

Compound110

Cl_2,

UV Light

H_3C—O—…—O—…—O—…—O—…—O—…—$Si(CH_3)_2Cl$

1) DMF, Heptane
2)TMAS

H_3C—O—…—O—…—O—…—O—…—O—…—$Si(CH_3)_2$—O—Si
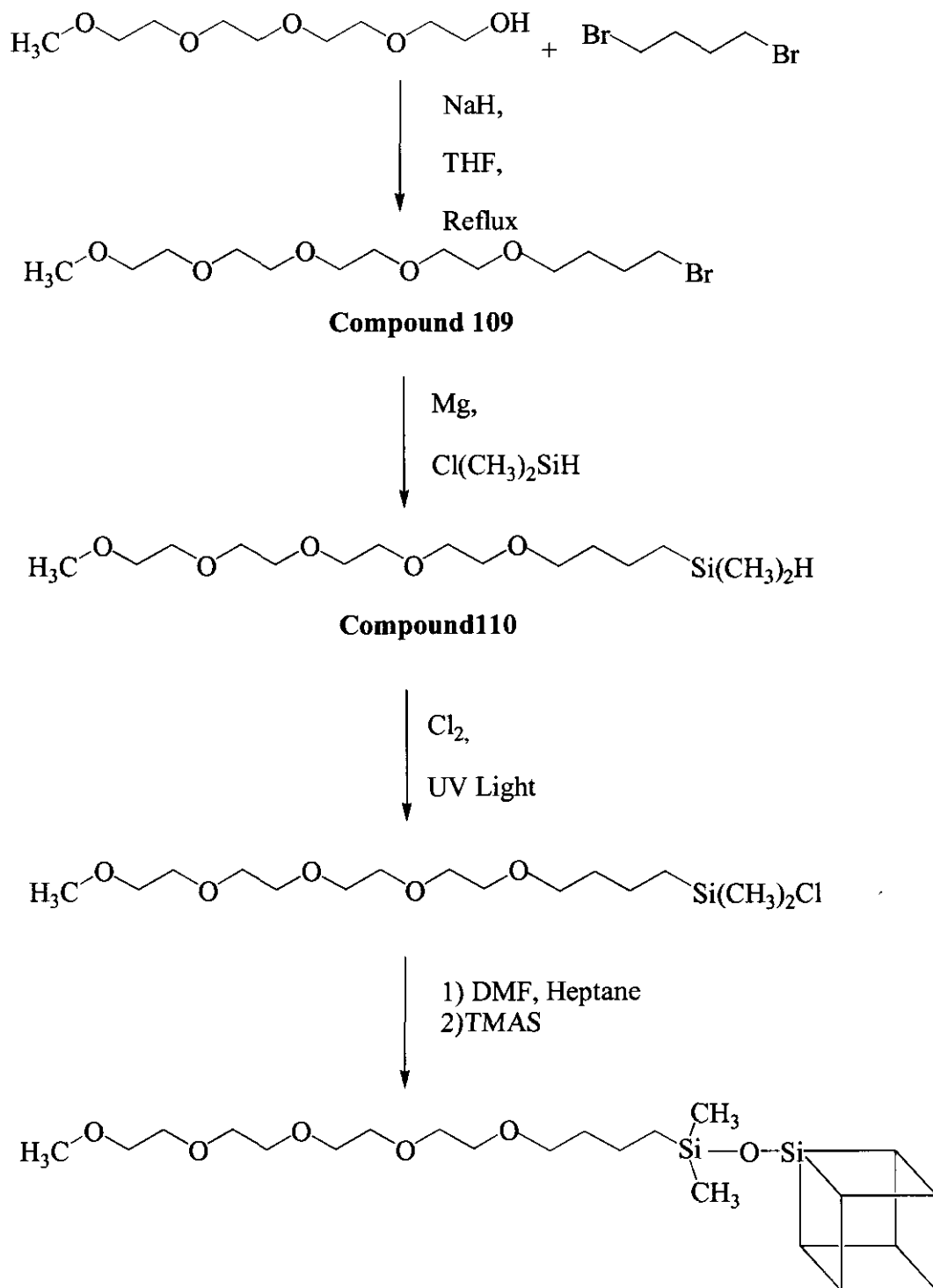
Reaction Scheme 16: Preparation of a silyl ether to react with TMAS

It was anticipated that the production of compound **109** may result in by poor yields, due to nucleophilic attack occurring twice at the dibromobutane. However, since this reaction involves cheap, readily available starting materials low yields would not be a problem. The first stage of the synthesis was carried out in dry THF under reflux and followed by TLC using hexane and ethyl acetate, (1:1). The reaction was monitored by following the disappearance of the dibromobutane in the reaction mixture. Column chromatography with SiO_2 provided the pure bromoether, although final yields were poor. The reaction was repeated using molecular sieves and a variety of bases, such as sodium metal and pyridine, in an attempt to improve the yield. The best final yield of the desired ether was 45% achieved using NaH in THF. With sufficient tetraethylene(monomethyl)bromobutane ether the reaction could be progressed to the next stage, the Grignard reaction.

The Grignard reaction[175] was carried out 'in situ' using solid magnesium and dry THF. After reflux an obvious colour change had occurred within the reaction vessel. Chlorodimethylsilane was added dropwise to the flask as a solution in THF, and after workup the resultant liquid was analysed. ^1H NMR data suggested the desired product had not in fact been produced. Comparison of the integrals resulting from the $Si(CH_3)_2$ groups, with that of the terminal $-OCH_3$ of the ether, indicated a vast excess of the ether. The ^{29}Si NMR showed no peaks at all. Further solvent was removed; however analysis still indicated an excess of the bromopolyether starting material. It appeared that the bromoalkane did not react well with the magnesium, solid particles of Mg remaining in the reaction mixture. It was assumed that the Grignard reagent was formed, however only in low yield. Repetition of the reaction provided no further advances in preparation of the desired dimethylsilylbutylpolyethyleneglycol.

The reasons for this unsuccessful reaction were thus attributed to the lack of formation of the Grignard reagent[175]. In all attempts solid magnesium remained in the final reaction

mixture, despite evidence of an exothermic reaction taking place. Any Grignard reagent formed was in low yield. Furthermore, this species did not react with the cage to produce compound **110**. Possible reasons were that the chlorosilane had undergone hydrolysis, caused by water associated with the polyether material. However, this would produce the silanol which should be evident in the ^{29}Si NMR at approximately 15ppm. Despite efforts to remove any water by the use of molecular sieves, further reaction was not observed. The presence of water in the reaction system would also have resulted in hydrolysis of the Grignard reagent. This would produce the debrominated polyether. A triplet was observed at 0.83ppm, possibly corresponding to this compound, however the integration suggested it was present in very small quantites. It was therefore concluded that the Grignard reagent had formed in very low yields, and under gone hydrolysis.

Continuing with this overall approach, a different method of preparing the silyl ether was sought. This involved the use of the pentenylether from route one. Hydrosilylation of pentenyl(tetraethylene)monomethylether with chlorodimethylsilane leads to a dimethylsilylpentylpolyethyleneglycol suitable for reacting with tetramethylammoniumsilicate via a substitution reaction as shown in Reaction Scheme 17.
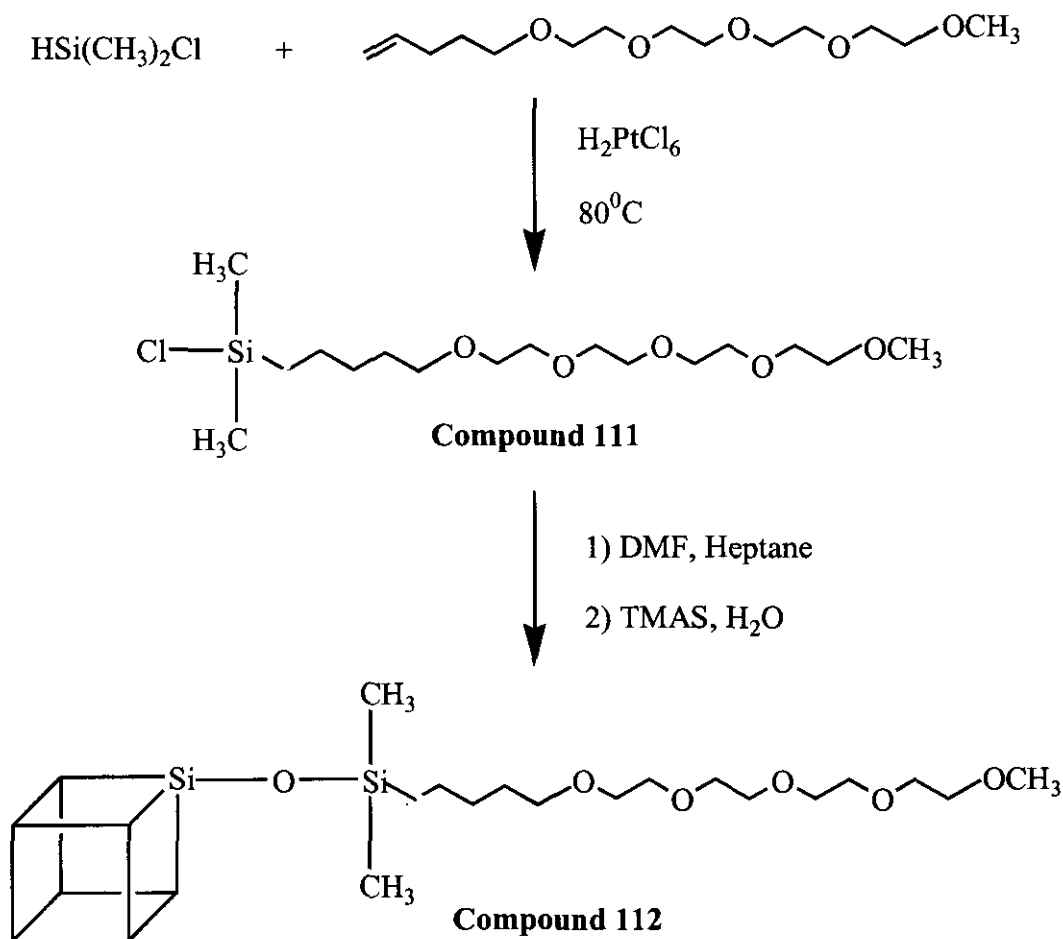
Reaction Scheme 17: Preparation of Polyethersilsesquioxane.

Problems were anticipated with the initial hydrosilylation, similar to those encountered with route one, with oxysilylation competing with hydrolsilylation. In addition hydrolysis of the chlorosilanes would serve to substantially limit the yields of the desired product. To overcome this problem reactions were carried out under a nitrogen atmosphere, at room temperature with a fourfold excess of the chlorosilane.

FTIR and NMR spectra indicated that compound **111** had been made in excellent yields. The remaining chlorodimethylsilane was removed prior to reactions with TMAS. None of the anticipated problems were encountered, with no oxysilylation being observed. The estimated yield for this stage of the reaction was 97%. This compound was not purified prior to further use for fear of hydrolysing the chlorosilane.

The reaction with TMAS was carried out as with the standard preparation of $[Si_8O_{12}]\{OSi(CH_3)_2H\}_8$.[89,] TMAS was added to a stirred solution of the silylether in heptane and DMF. The mixture was washed with water prior to extraction of the product.

Analysis of the final sample by FTIR and NMR indicated an incomplete reaction. ^1H NMR spectra indicated the presence of many $Si(CH_3)_2$ sites, in a range of 0.05-0.1ppm. The presence of the saturated alkyl chain was confirmed by the characteristic $SiCH_2$ resonances in the form of triplets at 0.51ppm. The ^{13}C NMR peaks appeared to be 'doubled up', suggesting two similar compounds, possibly starting material and desired product, or a mixture of multi-functional cages. The ^1H NMR spectrum is shown in Figure 59. Compound 111 appears to remain essentially intact, however the multiplicity observed at 0.05ppm is representative of multiple $SiCH_3$ sites. It was therefore considered that a successful reaction with TMAS had not occurred.
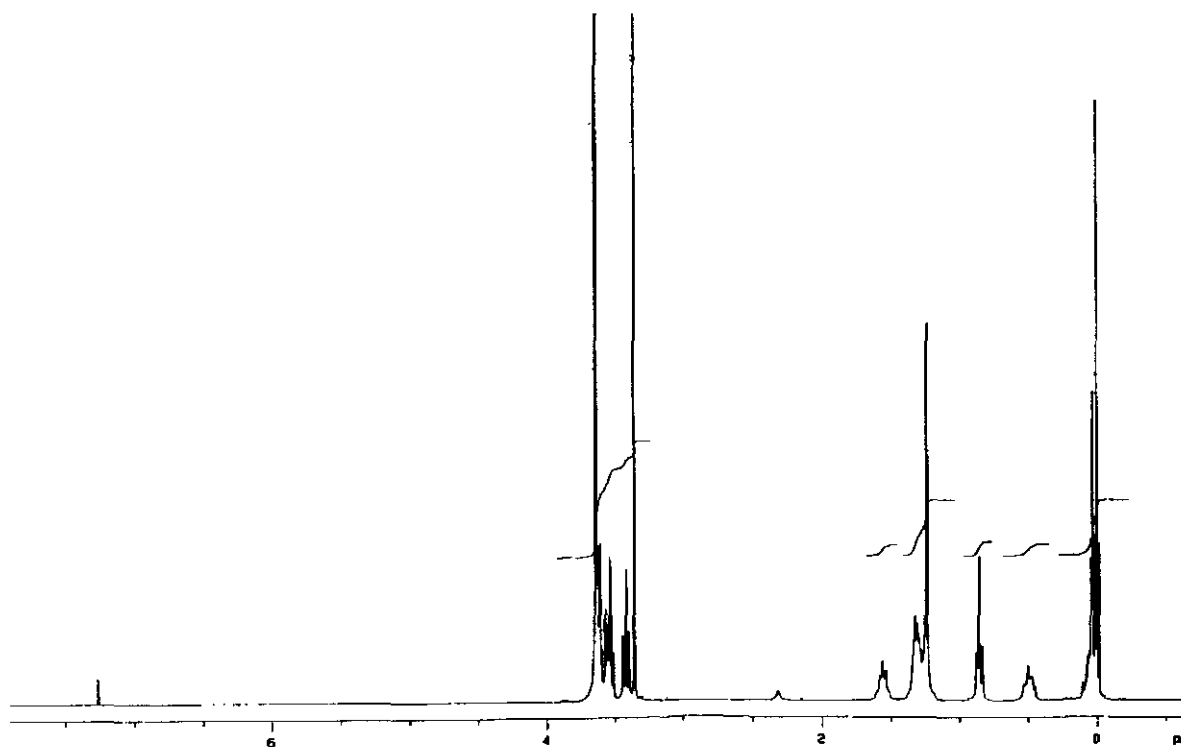
Figure 59: ^1H NMR for the product of Reaction Scheme 5

A peak at 7.28ppm in the ^{29}Si NMR may represent either compound **111** or a disiloxane. As can be seen in Figure 60, there was very little evidence of the cage compound, merely slight indications in the baseline. These did not develop into anything further with increased scans. The resonances for compound **112** had been expected at approximately 12ppm and −108ppm, in line with other 'Q' silsesquioxanes.

Figure 60: ^{29}Si NMR for the product of Reaction Scheme 5

This evidence supports the idea that the mixture contains the silylether starting material, and some broken down cage. FTIR indicated that the polyether chain remained intact and that the cage or some portion of it was present. This was shown by a stretch at 1008cm^{-1}. One of the problems of this route is that TMAS has 21 water molecules associated with it, thus ordinary aqueous hydrolysis would lead to a mixture of compounds **113** and **114**. ^{29}Si NMR peaks representative of compound **113** would be seen at approximately +7ppm, whereas that of compound **114** would be seen at +15ppm, suggesting that the NMR in Figure 60 is that of the disiloxane.

Compound 113

Compound 114

Before eliminating the TMAS route, attempts were made to couple a glycol species with chlorodimethylsilane, in order to prepare compound 115.
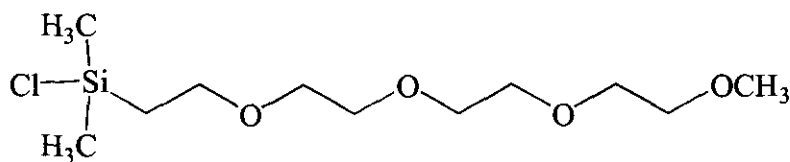
Compound 115.

This coupling was carried out under nitrogen with Et_2NOH as a catalyst. Problems with hydrolysis of the silane were anticipated, in light of previous results. The NMR spectra again showed a mixture of compounds, possibly including starting material, $HSi(CH_3)_2OH$ and a small amount of the desired compound. Approximate yields of the desired product were 20%. This approach was therefore abandoned in favour of higher yielding, more reliable routes.

4.5.5 Route Four: Via an ester substituted silsesquioxane.

The final direction involved preparing an amine-terminated polyether. We had previously observed in dendrimer synthesis that amines will react with methyl esters attached to cages to produce amides[138]. We have shown that methyl 3,3-dimethylpent-4-enoate reacts with silsesquioxanes cages via hydrosilylation in high yields, with easy purification, to provide a suitable ester functionalised cage compound.

Preparation of an amine-terminated polyether was achieved using a three-step process. Two polyethers were used, Igepal, compound 100, and tri(ethyleneglycol)monobutylether, compound 102.

Compounds **100** and **102** have significantly different end groups and ether chain lengths, and it was hoped that this would have a bearing on the results of any complexation tests carried out. A greater number of ether groups should provide a larger host cavity size, hence enabling larger cations to complex. However, the bulky end groups may limit such an outcome due to steric factors.

Preparation of the ester functionalised silsesquioxane was carried out by a hydrosilylation reaction between the cage and methyldimethylpentenoate, as discussed in chapter 3. Isolated yields for both T_8 and Q_8 silsesquioxanes were above 95%.

The synthesis of the amine is shown in Reaction Scheme 18. The polyethyleneglycol compounds were first reacted with tosyl chloride and pyridine, in order to create a good leaving group for nucleophilic substitution. This reaction worked well for both glycols, providing high yields of the tosylates that could be easily purified by SiO_2 column chromatography with dichloromethane, prior to production of the azide. The final yields for these reactions were in excess of 98%.
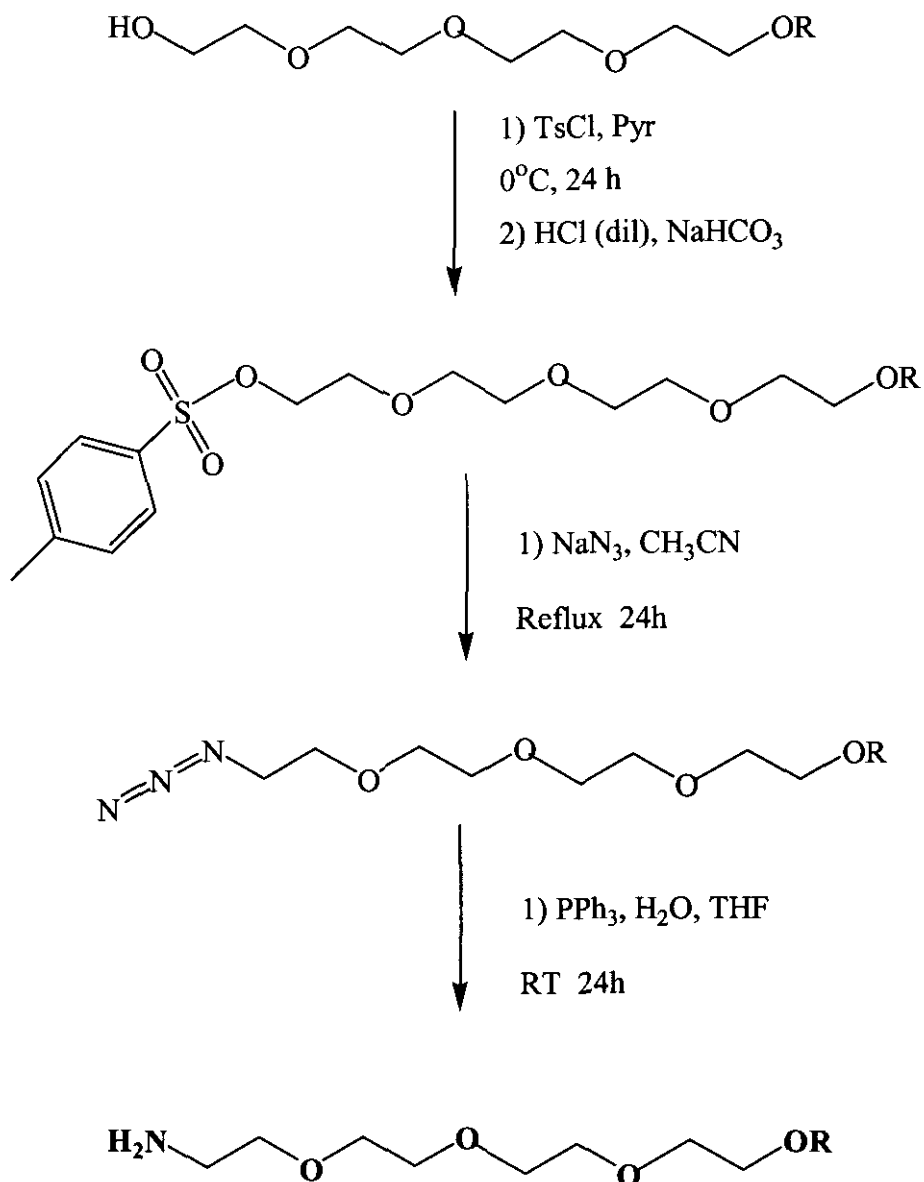
Compound 116 R=$(OCH_2CH_2)_3OC_6H_5C_8H_{17}$

Compound 117 R=C_4H_9

Reaction Scheme 18: Preparation of amine functionalised polyether

Reaction of the tosylethers with sodium azide, in acetonitrile under reflux produced the azide terminated ether compounds. The azide ion is a non-basic, highly reactive nucleophile, capable of displacing good leaving groups such as the tosyl group. Again this reaction was successful for both ethers, providing high yields of the azides that could be easily purified by column chromatography with SiO_2 and ethyl acetate prior to their use in

the production of the final amines. Yields for the azides were again greater than 98%. Reduction of the azides using triphenylphosphine and water in THF yielded the amine ethers in yields of over 84%.

Azides are easily reduced to primary amines by many reducing agents, most typically LiAlH$_4$, NaBH$_4$[176] and PPh$_3$. When the latter of these reagents is used, the process is known as the Staudinger reaction[177]. The nucleophilic attack of the triphenylphosphine followed by the loss of nitrogen and subsequent hydrolysis results in the amine as shown in Reaction Scheme 19.

$$R\text{—}N_3 \xrightarrow{PPh_3} R\text{—}N^-\text{—}N\text{=}N\text{—}P^+Ph_3 \xrightarrow{-N_2} R\text{—}N^-\text{—}P^+Ph_3 \longleftrightarrow R\text{—}N\text{=}PPh_3$$

$$\downarrow H_2O$$

$$RNH_2 \; + \; O\text{=}PPh_3$$
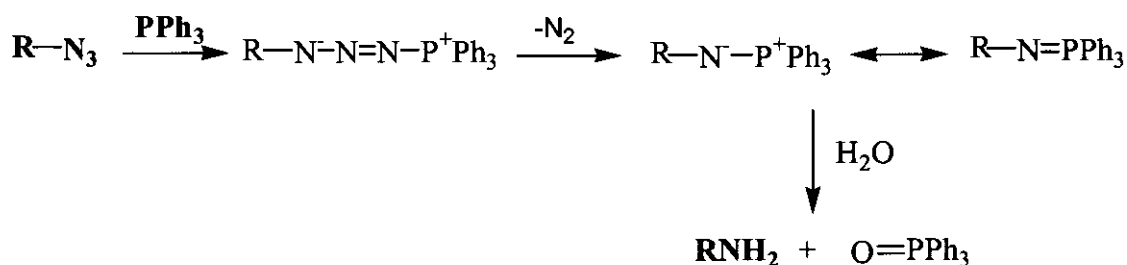
Reaction Scheme 19: General Reaction for reduction of azide with triphenylphosphine

Once prepared the amine ethers were reacted with the silsesquioxane esters. These reactions were carried out at reflux temperature in methanol. The reaction was followed by FTIR and NMR. Evidence that the ester had been removed was provided by the reduction in the FTIR ester stretch at 1706cm^{-1}. Confirmation that the silsesquioxane cages were still complete was provided by the Si-O stretch at 1008cm^{-1}.

This work has been continued within the research group by Zhihua Lui[178]. Repeated attempts to compety react the ester functionalised cage with an amine have proven unsuccessful. Data suggest that the cage has been only partially substituted, and a vast

excess of the amine would be required to force the reaction to completion. Due to the expense of the starting materials and time required to prepare the amine, using such quantites was not considered practical. These ongoing problems have led to a change in approach. In order to provide a more efficient leaving group than the methyl ester, *para*-nitrobenzene derivative was used. This polyfunctional cage, formed from the side arm compound **118**, will hopefully enable complete cage substitution to be achieved. At the time of writing it is believed that the desired product has been prepared, although it has not been purified.
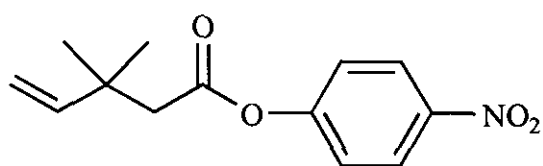
Compound 118: *Para*-nitrobenzene 'arms' used to functionalised silsesquioxane

cages.

4.6 CONCLUSION

Silsesquioxane cages have been successfully substituted with polyether arms. To our knowledge this is the first preparation of such compounds. A number of synthetic routes were examined to achieve the final species. The preferred synthesis involved preparation of an amine functionalised polyether. This was carried out via reduction of an azide compound. Reaction of the amine ether with an ester-substituted cage resulted in the desired products. In total four ether functionalised cages have been made, using ester functionalised cages of both T_8H_8 and $[SiO_{3/2}]_8\{OSi(CH_3)_2H\}_8$ and two different amine polyethers.

4.7 FURTHER WORK

With the successful preparation of polyether functionalised silsesquioxanes complete, it would be interesting to assess the complexing ability of these compounds. Tentative steps have been taken using Frensdorf's method[148] with aqueous picrate solutions and organic solutions of $KMnO_4$. These tests could only be carried out on the product of the allyl and vinyl chlorosilane quenching reactions due to time and cost constraints. The $KMnO_4$ tests proved positive for a number of polyether species, with the compounds seen to colourise a dichloromethane solution of solid $KMnO_4$. The polyether derivatives used were igepal, butyl and methyl terminated chains.

Results of the aqueous picrate solution tests were seen to be positive for the one compound tested. Only the D_4 substituted with a vinyl-igepal-silane $[SiO_{3/2}]_8\{(CH_2)_2Si(CH_3)_2(OCH_2CH_2)_4(OCH_2CH_2)_4OC_6H_5C_8H_{17}\}_8$ was seen to colourise the organic layer in this standard test. The species thought to be the purest, i.e. those prepared via the amine route, should also be tested in this way.

Previously polyether complexing activity has been assessed using du Nuoy ring methods[179] of surface tension measurements. Such analysis of these compounds would be most useful in an interpretation of their physical properties.

Comparisons of the complexation abilities and affinities of these species with crowns and cryptands would also be of interest. It is anticipated that any binding constants measured would be far less than the traditional ionophores. Certainly any complexation of the silsesquioxane polyether would be less than that of the spherands, which are conformationally set up for binding. However, it would be interesting to see how many

silsesquioxane arms would participate in binding, alongside the overall strength of the complexation.

Cation affinity should also be assessed in placing these species in a hierarchy of ionophores. The cavity size created will differ depending upon the number of polyether arms involved in the complexation. The silsesquioxane compounds provide a potential for two to eight arms available for binding. The number of arms involved in binding may have a bearing on the cavity size and stability of the final complex.

4.8 SILSESQUIOXANE COMPLEXATION AGENTS CONTINUED

As an extension to the polyether complexation work, a series of compounds were prepared which should have other chelating properties. Crown ethers are one family of complexing agents[147, 149, 150], however compounds such as *ferrocene*[180], compound **119**, and bis-benzene chromium[181], compound **120**, involve the use of π bonds to chelate metal ions. We wished to chelate metal ions between the arms of a silsesquioxane cage, and thus used these complexes as models, for potential arms.
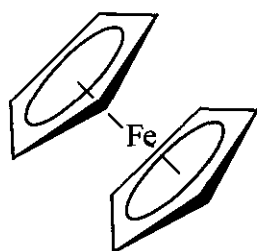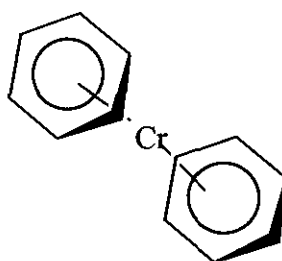
Compound 119   **Compound 120**

In 1948 Miller, Tebboth and Tremaine[182], attempted to prepare amines from olefins and nitrogen in the presence of iron catalysts. They found that with cyclopentadiene, an iron containing compound was formed. This compound was found to be $FeC_{10}H_{10}$. Kealy and Pauson also produced this compound whilst trying to oxidise C_5H_5MgBr with $FeCl_3$[183]. The true nature of the product suggested a sandwich compound with all five carbon atoms of the cyclopentadienyl ligand interacting with the metal centre. This compound was called *ferrocene* as it was recognised that it behaved like a three-dimensional arene compound. *Ferrocene* has since been shown to undergo Friedel-Crafts acylations and many other functionalisations[184-187].

Compounds **119** and **120** are examples of sandwich compounds, others include complexes of cobalt, nickel, titanium and vanadium[188]. The rings are freely rotating in these species. The bonding involves the overlap of the filled bonding orbitals of the rings with the atomic orbitals of the metal atom.

Compound **120** is isoelectronic with *ferrocene* and follows the 18 electron rule. Bonding in this complex resembles that of other metallocenes; however, compared to free benzene the C-C bonds are slightly elongated. There is no electrostatic contribution to the bonding, since the aromatic rings are not charged, hence complexes involving bis-arene ligands are generally less stable than metallocenes and are more easily oxidised. One method of preparation for the $Cr(C_6H_6)_2$ complex is shown in Reaction Scheme 20.

$$3CrCl_3 \; + \; 2Al \; + \; 6C_6H_6 \xrightarrow[\text{2) } H_2O]{\text{1) } AlCl_3}$$
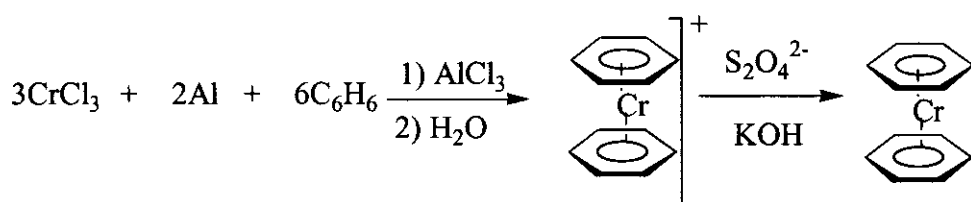
Reaction Scheme 20: Preparation of bis-(benzene)chromium

Ferrocene species have already been attached to silsesquioxane cages. Jutzi was the first to prepare such a species[65]. He synthesised a vinyl functionalised sandwich complex which he then attached to a silsesquioxane via hydrosilylation.

In order to prepare a silsesquioxane analogue of compound **120**, we first considered a route similar to that of Jutzi. Preparation of a divinylbis(benzene)chromium compound could be followed by hydrosilylation with a silsesquioxane cage as shown in Reaction Scheme 21. However, such a hydrosilylation would require reaction at adjacent silicon atoms on the cage, as shown in compound **121.** Previous experience had suggested such hydrosilylation

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was not specific, and may result in cage linking, producing mixtures that would require difficult separations.
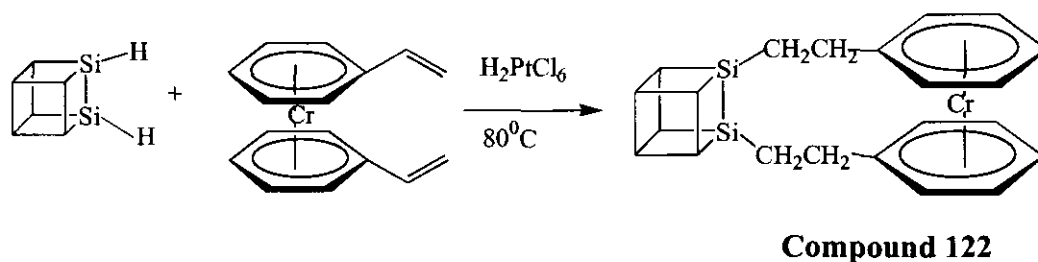
Compound 122

Reaction Scheme 21: Formation of a bis-(benzene)chromium silsesquioxane

We thus decided to use a more linear route, that is prepare an aryl functionalised silsesquioxane and then create the sandwich compound. Our first goal was thus the preparation of a phenyl derivitised silsesquioxane, to be followed by the chromium complexation, in line with the work of Nicholls and Whiting[189].

Such phenyl silsesquioxanes had been successfully prepared previously as discussed in chapter 4.

4.9 PREPARATION OF PHENYL SILSESQUIOXANES

4.9.1: Hydrosilylation

Simple hydrosilylations using styrene and allylbenzene produce eightfold functionalised T and Q silsesquioxane as described in chapter 3.

It was anticipated that the extent of complexation would be identified using NMR techniques. Thus it is important to have a pure functionalised silsesquioxane before beginning such complexation studies. T_8H_8 often produces mixtures of substitution

patterns because of α and β hydrosilylation, whereas such impurities were not observed when $Q_8[OSi(CH_3)_2]_8$ was used. Thus Q_8 species were chosen to provide the backbone for the complexation studies.

The product of the reaction between $Q_8[OSi(CH_3)_2]_8$ and allylbenzene was prepared. The yield for compound **64** was 95.4%.

4.9.2: Reaction of Chlorosilanes with Tetramethylammoniumsilicate

Alternative methods of preparation of the Q_8 species were also considered. In order to probe the effect of the length of the linker between the aryl group and the cage on complexation, $Q_8[SiMePh]_8$ was synthesised. This species contains only the $OSi(CH_3)_2$ link and thus exhibits very poor flexibility. Tetramethylammoniumsilicate was made through hydrolysis of silicic acid and tetramethylammonium hydroxide[89]. The product was then quenched with chlorodimethylphenylsilane. Yields of this reaction were poor, and purification proved difficult. However, a pure sample was prepared and used in complexation studies.

4.9.3: Catechol Derivatives

Preparation of phenyl functionalised cages was also attempted using various catechol derivatives. As shown in Figure 61 catechol, 1,2 benzenedimethanol and benzylalcohol were all reacted with both T_8 and Q_8 silsesquioxanes using Et_2NOH, utilising chemistry described in chapter 3.
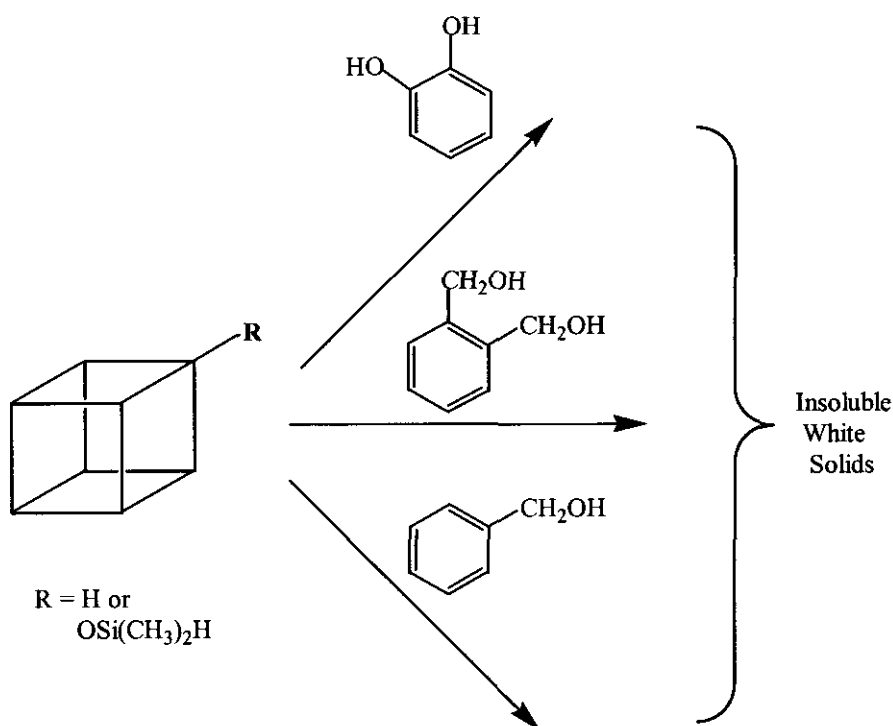
Figure 61: Catechol Reactions with Silsesquioxane

The reactions were effected under a number of conditions, including direct combination at 80°C and 150°C and in refluxing solvents. The solvents tried were toluene, acetonitrile dichloromethane and hexane. We repeatedly obtained white solids insoluble in all common solvents. Solubility tests were carried out in many solvents, all to no avail. FTIR and MAS NMR spectrometry were carried out in an attempt to identify the exact products. The FTIR spectra gave a stretch as 1008cm⁻¹indicating that the SiO framework of the cages remained intact. No other conclusive evidence could be drawn from this data because of solubility

problems. MAS NMR was used in place of traditional solution techniques. Again this technique provided inconclusive data for the successful analysis of these compounds. The spectra obtained were usually similar to that of silica.

4.10 CHROMIUM COMPLEXATION STUDIES

With the successful preparation of phenylsilsesquioxanes via routes 4.9.1 and 4.9.2, the next step was the complexation with Cr. Firstly phenyltrimethylsilane was used as a model by mixing $Cr(CO)_6$ under a number of different reaction conditions. These conditions reflected those of Fischer et al[181], who formed a range of chromium complexes using chromium carbonyl species. It is known that bis-benzene-chromium hydrolyses in air, and thus all reactions were carried out in a nitrogen atmosphere and in dry solvents. Reaction conditions employed involved room temperature stirring and refluxing in both dry toluene and dry THF. The anticipated reaction was a simple metal transfer from the $Cr(CO)_6$ to the aromatic species. Unfortunately this was not achieved. Green fumes were noticeable. The green solids produced from these reactions were found to be only partially soluble in traditional NMR solvents. NMR spectra revealed only phenyltrimethylsilane. It was assumed that the reactions had broken down the $Cr(CO)_6$ complex, however the spectra showed no evidence for transfer to the silane species.

Despite this result, the reaction was repeated using both $T_8[C_6H_5]_8$ and $Q_8[Si(CH_3)_2C_6H_5]_8$. It was hoped that the silsesquioxane species may be more likely to produce complexed species, due to the proximity of the aromatic rings. Silsesquioxanes prepared by both routes 4.9.1 and 4.9.2 were used, $[SiO_{3/2}]_8[C_3H_6C_6H_5]_8$, and $[SiO_{3/2}]_8[OSi(CH_3)_2C_6H_5]_8$, under the same set of conditions as the phenyltrimethylsilane. However, as before, the

products were partially soluble green solids with the NMR showing only the cage starting materials.

4.11 PLATINUM COMPLXEXATION STUDIES

In light of the seemingly unsuccessful reactions using chromium, an alternative approach was sought. The platinum complex of 1,1,2,2 tetramethyldisiloxane, compound **122**, known as Karstedt's catalyst[65] has been studied in great detail by Bassindale et al[190].
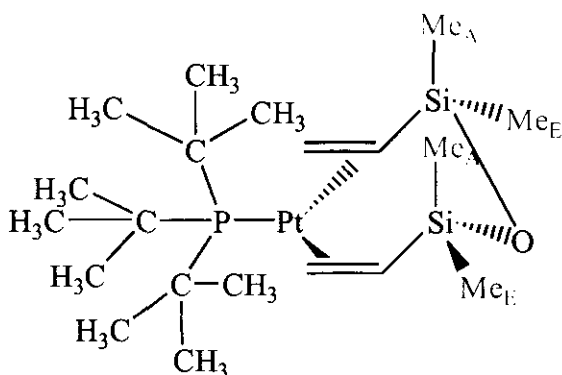
Compound 122: Platinum Complexed 1,1,2,2 tetramethyldisiloxane

The stereochemistry of compound **122** was studied using NMR techniques. Figure 62 shows the ^{1}H NMR spectrum of this species. The vinyl peaks can be clearly seen at 2.5ppm in the form of a complex multiplet, labelled I, intergrating to 6 protons. At 1.47ppm the P(^{t}Bu)$_3$ group integrates to 27 protons in the form of a distinct doublet, labelled J. The methyl groups are also recognisable for the spectrum in the form of two singlets, labelled K and L.
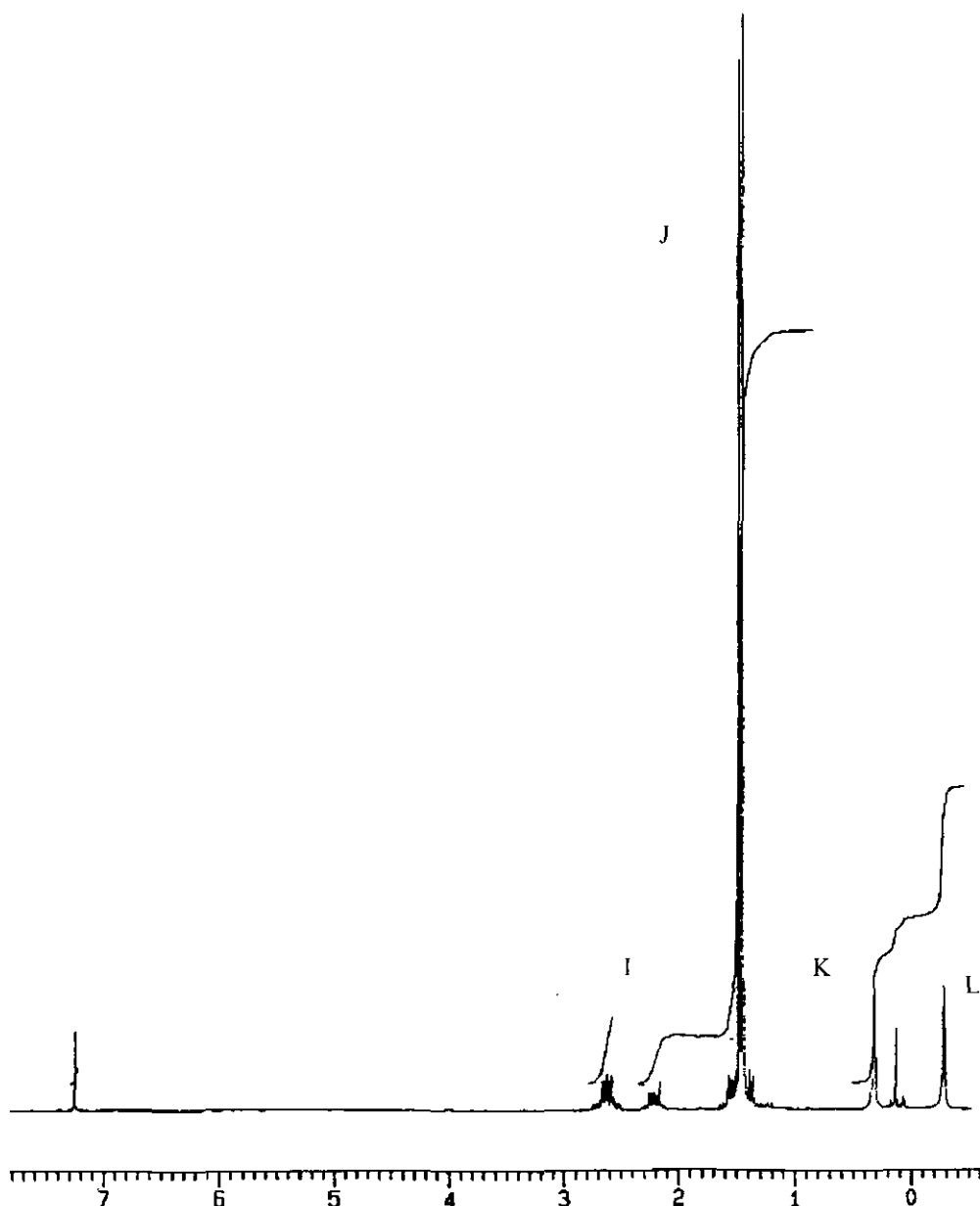
Figure 62: ^{1}H NMR of Compound 123

Bassindale et al observed that when $Si(CH_3)_3$ groups are complexed to a platinum atom two broad singlets at ambient temperature are produced[190]. The resonances were shown to coalesce into a sharp sinlget when heated gently, despite the lack of change in the other peaks. Chandra et al described the structure of compound **122** as a pseudochair, with two pseudoaxial methyl groups and two pseudoequatorial methyl groups[191]. The proton spectra suggested that the resonances at –0.28ppm and 0.33ppm are associated with these psuedo

axial and psuedoequatorial methyl groups respectively. Bassindale recognised that a dynamic process was occurring, whereby the platinum atom undergoes exchange[189]. This intramolecular exchange, which results in only a stereochemical change for the methyl groups, was described as a dissociative-reassociative mechanism, involving a change of co-ordination of the platinum from one face of the vinyl to another.

Based on this simple divinyl system we chose to develop an analogous silsesquioxane species where the transfer of a platinum atom into a polyvinyl-silsesquioxane compound would produce such labile species, with potentially unusual stereochemistry.

4.12 PREPARATION OF A VINYL FUNCTIONALISED SILSESQUIOXANE

4.12.1: Hydrosilylation

Such complexation studies required the preparation of a pure sample of non-isomeric vinyl silsesquioxane. A number of procedures were considered including hydrosilylations involving T_8H_8 and vinyl species such as pent-1,2,3,4-diene. These suggestions were dismissed because of the lack of control over the structure of the final product. Reaction of both vinyl groups with different cages could not be prevented, which would result in a mixture requiring complex purification. Similarly, the problems encountered with α and β addition, together with solubility problems pointed to the need for an alternative route.

4.12.2: Reaction of Tetramethylammoniumsilicate

Preparation of silsesquioxanes using tetramethylammoniumsilicate (TMAS) have been previously described in this thesis. Quenching of TMAS with chlorodimethylvinylsilane results in the production of compound 123[192]. This reaction occurs in excellent yield (85%) and provides a system analogous to compound 122.
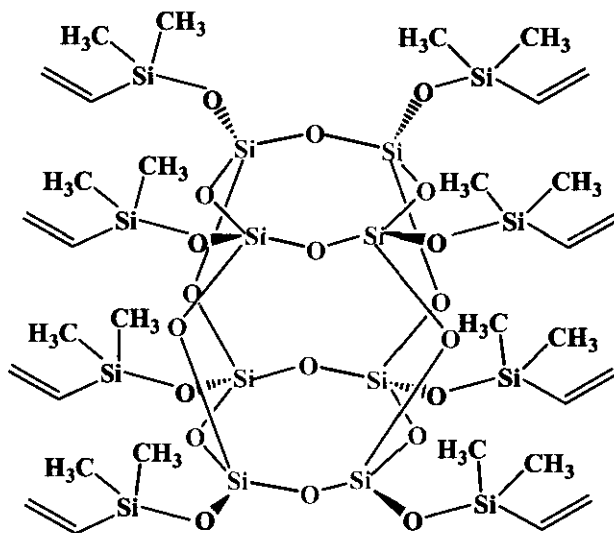
Compound 123: Vinyl Silsesquioxane

Compound 123 was easily purified by recrystallisation in acetone, and could be prepared in sufficient quantity to allow complexation studies. The complexation of platinum with the vinyl group of the silsesquioxane was attempted in number of ways. The intention was to achieve a metal ion transfer from its original environment to the cage.

4.13 PLATINUM COMPLEXATION STUDIES

4.13.1: Reaction of Compound 123 with $H_2PtCl_6 xH_2O$

The reaction between $H_2PtCl_6 xH_2O$, the solid known as Speiers catalyst[62], and compound 123 was carried out as described by Chandra et al[191]. Chandra used this process to prepare a solution containing Pt(0), which was used as a starting point in the synthesis of (i) bis(η-alkyne)platinum (0) complexes and (ii) various (tertiary phoshine)platinum (0) complexes. A catalytic quantity of water was used and then refluxed for 4 hours at 50°C, followed by neutralisation with $NaHCO_3$. Two different ratios were used, firstly the silsesquioxane and H_2PtCl_6 in equal molar quantities and secondly a two fold excess of the platinum species. The aim of this study was to determine the number of arms necessary for platinum complexation.

After reflux a black solution was obtained. NMR and TLC analysis provided little evidence of complexation. The product appeared to be the cage plus decomposed catalyst. However the ^{29}Si NMR spectrum contained 4 peaks. These peaks could correspond to the original cage plus the newly complexed environment, but without further evidence this cannot be verified. Confirmation of the complexation was anticipated in the form of two sets of vinyl peaks in the ^1H and ^{13}C NMR spectra, corresponding to a complexed and uncomplexed environment. The ^1H and ^{13}C NMR showed a mixture being predominantly starting material, with some sign of the complexed species. A complicated pattern was observed in the vinyl region of the ^1H NMR, with four peaks seen in the appropriate region of the ^{13}C NMR. The outcome remained unchanged when the ratio of cage to platinum was increased to 1:2. ^{195}Pt NMR was also employed to see if a species other than the starting materials

was present in the final mixture. These studies proved unhelpful, with no evidence of any other species. In light of this inconclusive evidence, alternative methods were considered.

4.13.2: Platinum transfer using PtCl$_2$

Transfer of platinum to the cage was also attempted using PtCl$_2$. A solution of PtCl$_2$ and compound **123** in butanone was refluxed overnight before removal of solvent under vacuum. Initially both silsesquioxane and platinum were present in equal molar quantities. The results were identical to those achieved using the previous route. A black solution was produced after reflux, that yielded a black gum upon solvent removal. NMR data was again inconclusive, with many peaks unaccounted for. The product seemed to be a mixture of many unidentifiable compounds. The reaction was repeated using a two-fold excess of platinum, producing the same results. No obvious difference was achieved by carrying out the reaction in a nitrogen atmosphere.

4.13.3: Pt Exchange from Karstedt's catalyst

With no evidence for successful platinum transfer from H$_2$PtCl$_6$ and PtCl$_2$ a new approach was considered necessary. The similarity between the vinyl environments in the disiloxane and the silsesquioxane prompted us to attempt to transfer the platinum from compound **122** to the silsesquioxane. Such a reaction should be easy to follow due to their distinctive ^{1}H NMR spectra. Coupling with the phosphorous results in an easily identifiable multiplet due to the P[C(CH$_3$)$_3$]$_3$ group, integrating to 27 protons at 1.47ppm, as shown in Figure **62**. It was therefore anticipated that the transfer of the Pt-P[C(CH$_3$)$_3$]$_3$ from compound **122** to the cage should produce a new unique set of resonances. A new set of vinyl peaks from the disiloxane was also expected, although these may not be so easy to identify.

The silsesquioxane was combined with a four-fold excess of the Karstedts catalyst under argon and heated to 200°C with an airgun. White fumes were observed upon heating, which was assumed to be a result of decomposition of the silsesquioxane. The final solid was found to be insoluble in all common solvents.

The platinum exchange was also attempted in solution. Again a four fold excess of the Karstedts catalyst was used, this time in refluxing chloroform. Removal of the solvent led to a brown gum which was sparingly soluble in most common NMR solvents. This sample had a number of brown particles which were thought to arise from catalyst decomposition. In order to probe this reaction it was monitored by NMR.

The advantage of monitoring this reaction using ^{1}H NMR was the easy observation of product development and loss of starting material. The ^{1}H NMR of compound **122** has already been discussed. The NMR spectrum of compound **123** is very different to that of compound **122**, with vinyl peaks at 6ppm and the singlet of the $Si(CH_3)$ group at 0.2ppm. Any platinum exchange between these two compounds would result in a change in the pattern exhibited by the silsesquioxane.

The experiment was carried out at room temperature with spectra recorded every hour. The two reactants were mixed in $CDCl_3$ immediately prior to the first spectrum being recorded. The results of this stack experiment are shown in Figure 63.
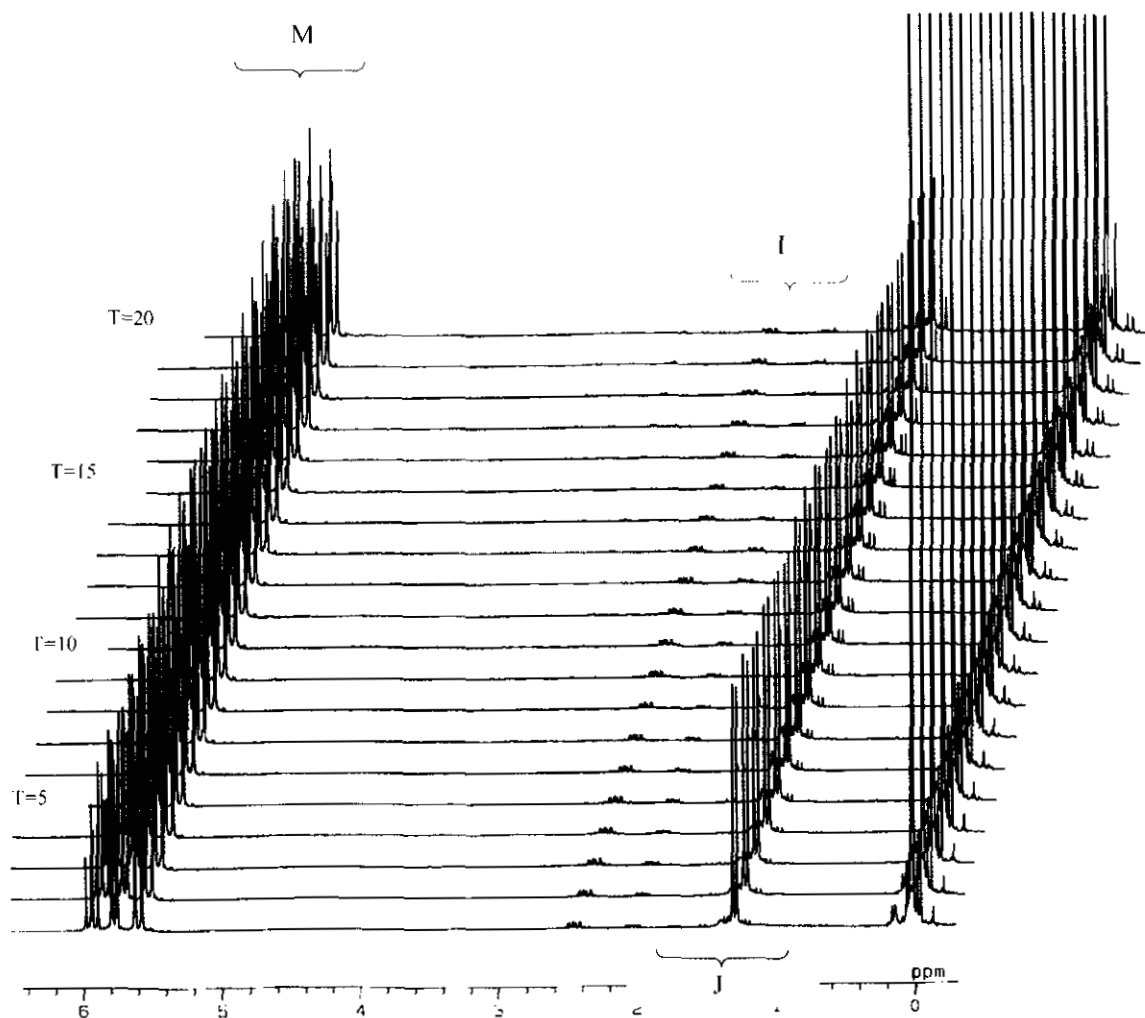
Figure 63: ¹H NMR Stack Experiment, spectra taken every hour for 20 hours.

Figure 63 shows that a change in the ^{1}H NMR spectra occurred over twenty hours. Significant differences can be observed in the region, labelled J away from the PtP^{t}Bu protons. At time T=1 hours, a single doublet is observed which develops into series of doublets by T=20 hours. This can be more clearly seen in the baseline expansion shown in Figure 64. The spectra show more than one type of P^{t}Bu resonance. It appears that the platinum species does exchange environments throughout this experiment; however, transfer is not complete, as more than one set of doublets are observed. This evidence suggests that an equilibrium has been reached in the exchange reaction.
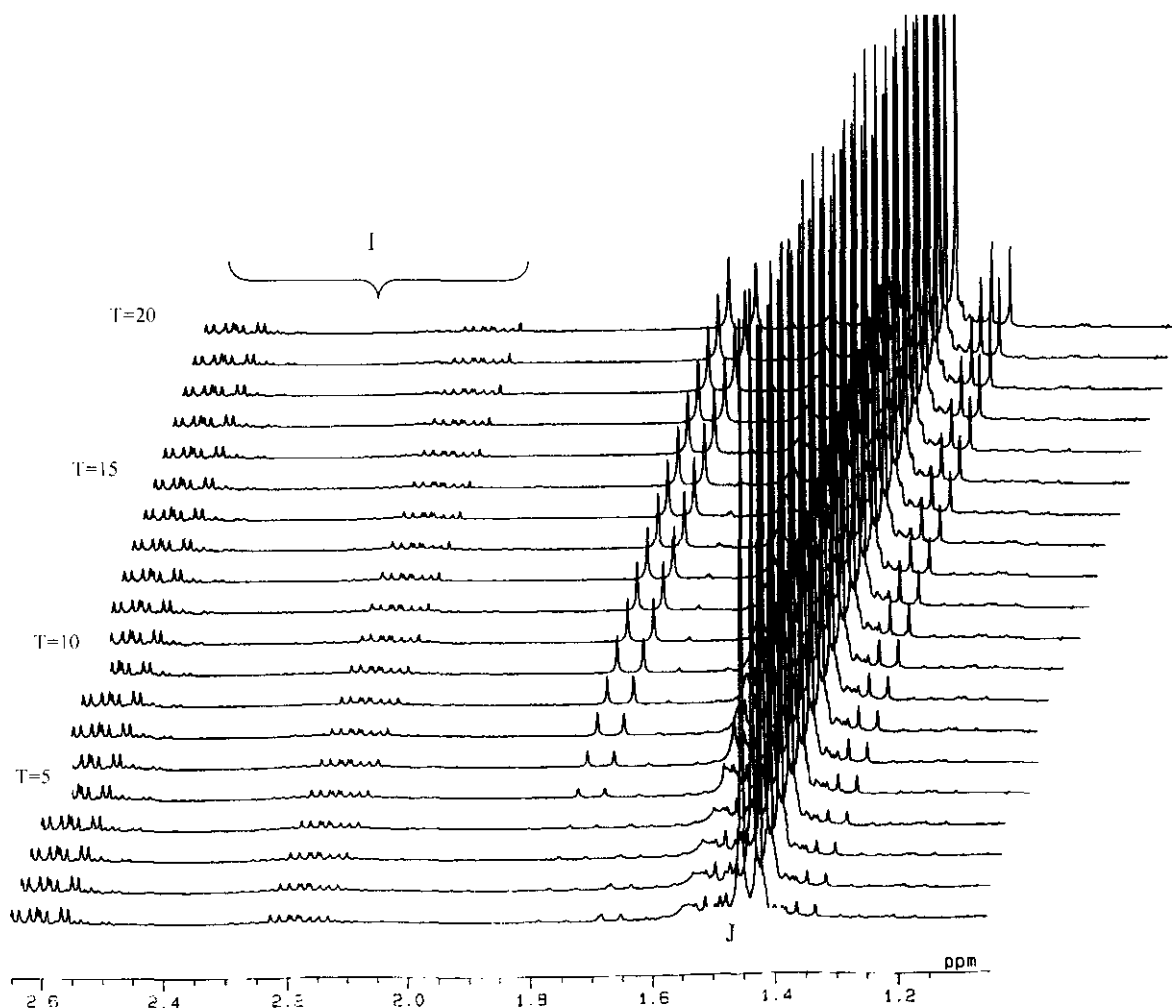
Figure 64: Expansion of ^{1}H NMR for Platinum Exchange Reaction

During the stack experiment there is no obvious reduction in the size of the peaks arising from the vinyls of the compound 4, in the region labelled I. A successful transfer would result in these peaks for the disiloxane being reduced and the vinyls of the newly formed uncomplexed material should be observed at approximately 6ppm. Similarly, the newly complexed vinyl groups of the silsesquioxane cage should be shielded by the platinum. This should give peaks in the same region as those of the original complex **123**. No such peaks were observed, although the peaks may be overlaid by the original resonances.

On examination of the vinyl region of compound **123**, labelled M in Figure 63, it is difficult to determine from the stack experiment if any exchange has occurred. After 20 hours these peaks do appear to be more complicated than in the original spectra. As can be

seen in Figure 63, new peaks have developed making the vinyl pattern more complicated. These are peaks are present at T=1, labelled N in Figure 65, however by T=7 they are far more pronounced and can be clearly seen as part of the vinyl pattern by T=20, labelled O in Figure 65. Owing to the complexity of these resonances with new sets of peaks undoubtedly overlaying the originals, it is difficult to assess the overall multiplicity. It is suggested that these new resonances are a result of the de-complexation of the disiloxane compound **122**.

Figure 65: Expansion of the vinyl region of the ^{1}H NMR in the Platinum Exchange Reaction.

In order to probe the reaction and attempt to drive it to completion, the final reaction mixture after twenty hours was heated to 45°C for 10 hours. The observed spectra showed a further developed situation. This can be seen in Figure 66. The protons of the SiCH$_3$ groups of compound **122** give rise to broad peaks which suggest the presence of more than one complexed species in the reaction mixture.
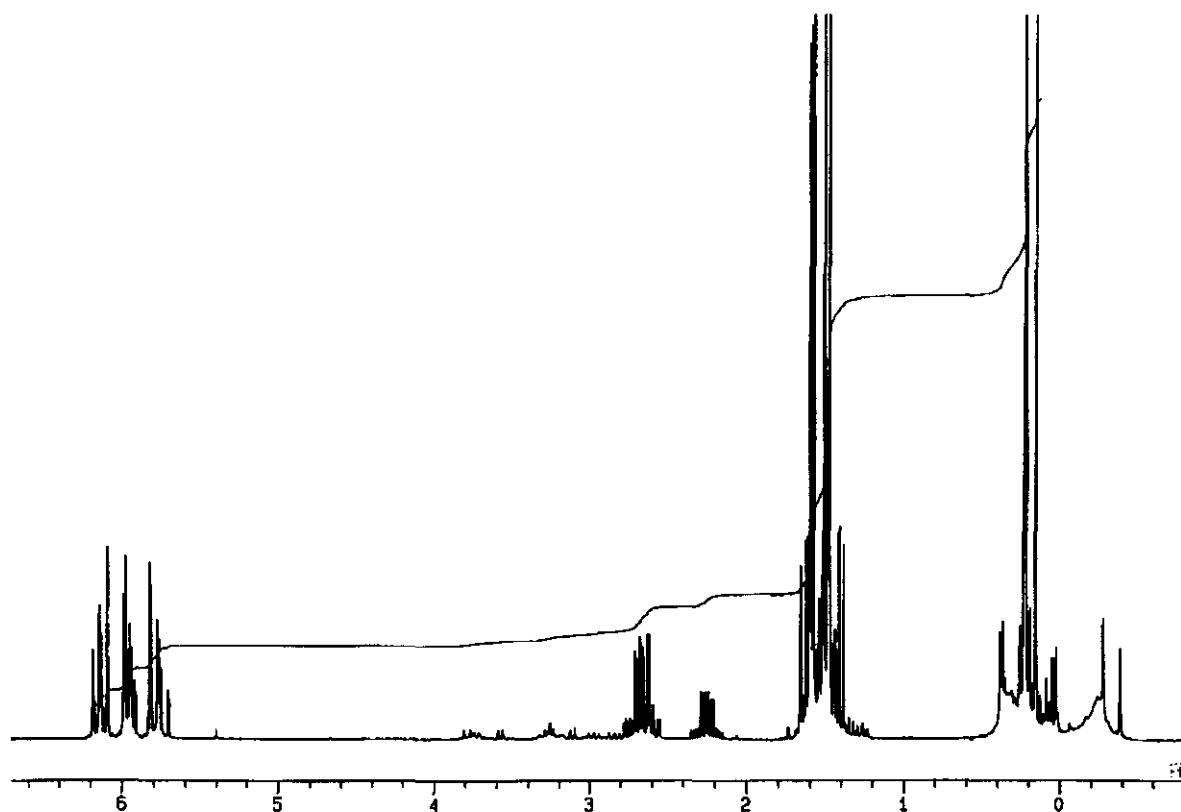
Figure 66: Platinum exchange reaction at 45°C

Based upon this evidence the exchange reaction was again considered to have achieved an equilibrium. There was no conclusive evidence for the de-complexation of Compound **122** nor the total formation of the complexed silsesquioxane species. These data suggest that exchange was occurring, with evidence for the partial formation of a newly complexed species. However the exact stoichiometry of the new complex is unknown.

4.14 CONCLUSIONS

In an attempt to synthesise a metal complexed silsesquioxane cage, a number of routes were considered including preparation of bis-(benzene)chromium and Karstedt's catalyst analogues.

The platinum exchange from Compound **122** to a vinyl silsesquioxane was the most successful route. This was monitored by NMR, however the evidence suggested an equilibrium had been reached for the platinum exchange. The effect of heat went someway to enhancing the exchange, however, the reaction was not driven to completion.

CHAPTER FIVE

Experimental

5.0 GENERAL EXPERIMENTAL DETAILS

A: NMR

All NMR measurements were made either on Jeol JNM LA 300 or Jeol JNM EX400 FT machines fitted with mutlinuclear probes. ^{13}C spectra were broad band decoupled. The pulse delay for ^{29}Si spectra was standardised at 15 seconds. ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY and ^{13}C DEPT were used as necessary to help assign spectra.

All spectra were recorded at room temperature, 20°C, using deuterochloroform (CDCl$_3$) dried over molecular sieves. The internal NMR reference compound for ^{1}H, ^{13}C and ^{29}Si spectra, tetramethylsilane, was present in all samples apart from those where the peaks may interfere with those of the product. In such cases the spectra where referenced using a pre-determined data point for tetramethylsilane.

B: Mass Spectrometry

Low resolution mass spectra were recorded on a VG20-250 mass spectrometer

C: High Resolution mass spectrometry

High resolution mass spectrometry was performed by the National Mass Spectrometry Service Centre, based at the university of Wales, Swansea.

D: MALDI-TOF Mass Spectrometry

This analysis was carried out by the mass spectrometry service at Southampton University on a Tofspec2E instrument.

E: Elemental Analysis

Microanalyses were performed by MEDAC limited.

F: Infra Red Spectrometry

FTIR spectra were carried out using a Perkin-Elmer 1710 infra red fourier transform spectrometer. Unless otherwise stated IR were recorded using NaCl plates.

G: Melting Points

These were determined on an Electrothermal Digital melting point apparatus

H: UV Vis Spectrometry

UV Visible spectra were recorded using Unikon 860 instrument.

I: Differential Scanning Calorimetry

Differential scanning calorimetry was carried out on a Perkin Elmer 7.0 DSC. Samples of approximately 50mg were weighed into aluminium pans and then crimp sealed with lids. The heating cycle used was 2°C per minute from room temperature to 135°C, followed by

a cooling cycle at the same rate. The heating cycle was then repeated. Samples were referenced against an empty aluminium pan.

J: Optical Microscopy

The hot stage optical microscopy analysis was carried out at Dow Corning, Barry.

5.1 EXPERIMENTAL DETAILS

Preparation of [HSiO$_{3/2}$]$_8$

Ferric chloride (anhydrous), (100g) was placed in a round bottomed flask, followed by concentrated hydrochloric acid (40cm^3) and methanol (80cm^3). Hexane (700cm^3) and toluene (100cm^3) were added. The biphasic mixture was stirred and a solution of HSiCl$_3$ (40cm^3, 0.4mol) in hexane (300cm^3) was added dropwise over a period of 6.5 hours. After an additional 30 minutes of stirring, the upper hexane layer was separated together with some of the suspended yellow solid. Sodium carbonate (28g) and calcium chloride (20g) were added to the hexane solution and the contents stirred overnight. The solids were separated by filtration and the organic solvent evaporated under reduced pressure to yield a white powder, which was recrystallised from hexane.

Yield: White crystals 2.03g, (10%); ν_{max} (Nujol mull/cm^{-1}) 2294 (Si-H), 1072 (Si-O); δ_H (400MHz, CDCl$_3$) 4.25 (1H, s, SiH); δ_{Si} (79MHz, CDCl$_3$) –84.7 (SiO); m/z (EI) 422 (M$^+$) (Found: M$^+$ 422.8092, (EI), Si$_8$H$_8$O$_{12}$ requires 422.8089), 377, 289, 211, 49; (Found: H, 1.90%; requires H, 1.90%).

Preparation of $[SiO_{3/2}]_8\{OSi(CH_3)_2H\}_8$

Tetramethylammonium silicate (4.7g, 0.05mol) was slowly added to a mixture of heptane (100cm^3), dimethylformamide (200cm^3) and dimethylchlorosilane (100cm^3) previously stirred for twenty minutes at room temperature. The slightly exothermic reaction was allowed to cool to room temperature and was subsequently cooled to 2°C. Distilled water (500cm^3) was added dropwise. The organic layer was then separated and washed with water until the washings attained pH 7. The organic layer was then reduced under vacuum at 55°C. The reduced organic solvent was then cooled to 4°C and the precipitated solid was recrystallised from acetone.

Yield: White solid 1.4g; ν_{max} (Nujol mull/cm^{-1}) 2960 (C-H), 2142 (Si-H), 1102 (Si-O); δ_H (400MHz, CDCl$_3$) 0.2 (6H, s, SiCH$_3$) 4.72 (1H, s, SiH); δ_C (100MHz, CDCl$_3$) 0.02 (SiCH$_3$); δ_{Si} (79MHz, CDCl$_3$) 12.97 (SiCH$_3$), −108.58(SiO); (Found: C,18.93; H, 5.58%; $Si_{16}C_{16}H_{56}O_{20}$ requires C, 18.90; H, 5.51%); Data as seen in literature[89].

Preparation of Compounds 20-23 $CH_2CH(CH_2)_n$-O-$C_6H_4CO_2C_6H_4OCH_3$

n=2 Preparation of $CH_2CH(CH_2)_2$-O-$C_6H_4CO_2CH_2CH_3$

Bromobutene (4.86g, 3.6×10^{-2}mol) was added to ethyl 4-hydroxybenzoate (5.64g, 3.4×10^{-2}mol) and K$_2$CO$_3$ (18.78g, 0.19 mol) in dry acetone (100 cm^3). The mixture was refluxed for three days and monitored by TLC (hexane:ethylacetate, 1:1) R$_f$ 0.83 (product), 0.68 (bromoalkene). Removal of the solvent under vacuum resulted in a clear liquid. The products were purified by distillation (74°C, 5mm Hg).

Clear liquid 5.20g, (69.5%); v_{max} (film)/cm^{-1} 2878 (C-H), 1718 (C=O), 1643 (C=C), 1585 (C=C), 1474, 1445 (C-C), 1391, 1368 (C-H), 1277 (C-O), 1229 (C-H), 1172 (C-H), 1103; δ_H (400 MHz; CDCl$_3$) 1.25 (3H, t, J 8.0, OCH$_2$CH_3), 2.40 (2H, q, J 6.4, CH_2), 3.89 (2H, t, J 8.0, OCH_2CH$_3$), 4.24 (2H, q, J 6.4, OCH_2CH$_2$), 5.11 (2H, m, CH_2CH), 5.79 (1H, m, J 6.7 cis, 20.0 trans, CH$_2$CH), 6.94 (2H, d, J 11.9, ArH), 7.19 (2H, d, J 11.9, ArH); δ_C (100 MHz; CDCl$_3$) 14.02 (CH_3), 33.30 (CH_2CH$_2$O), 60.68 (OCH_2CH$_3$), 67.06 (OCH_2), 114.58 (CH_2CH), 116.10 (Ar), 119.85 (Ar), 121.62 (Ar), 134.51 (CH$_2$CH), 158.61 (Ar), 166.08 (CO_2); m/z (EI) 220 (M$^+$) (Found: M$^+$, 220.1104 (EI), C$_{13}$H$_{16}$O$_3$ requires 220.1099) 192, 175, 138, 121, 93, 65, 55; (Found C, 70.93; H, 7.32%, requires C, 70.94; H, 7.33%).

Preparation of CH$_2$CH(CH$_2$)$_2$-O-C$_6$H$_4$CO$_2$H

The ester (2.58g, 1.17 × 10^{-2}mol) was added to KOH (1.98g, 3.53 × 10^{-2} mol) in 80% aqueous ethanol (100cm^3). The mixture was refluxed for twelve hours. The reaction was cooled, diluted with water (100cm^3) and acidified with HCl(c). The precipitate was filtered then washed with dilute HCl (50cm^3), followed by cold methylated spirit (20cm^3). The acid was recrystallised from methylated spirit. The product was a white crystalline solid.

White crystals 1.63g (72.4%), m.p.113.6 °C, v_{max} (Nujol mull/cm^{-1}) 2922 (COH), 2677 (C-H), 1693 (C=O), 1643 (C=C), 1602, 1530, 1461 (C-C), 1378, 1312 (C-H), 1243 (C-O), 1159, 1119, 1077; δ_H (400 MHz; CDCl$_3$) 2.57 (2H, m, J 6.5, CH$_2$), 4.09 (2H, t, J 6.5, OCH$_2$), 5.15 (2H, m, CH_2CH), 5.92 (1H, m, J 6.7, cis, 19.9, trans, CH$_2$CH), 6.89 (2H, d, J 12.0, ArH), 7.29 (2H, d, J 12.0, ArH); δ_C (100 MHz; CDCl$_3$), 33.53 (CH_2), 67.45 (OCH_2), 115.15 (CH_2CH), 117.23 (Ar), 120.98 (Ar), 122.68 (Ar), 129.52 (CH$_2$CH), 158.94 (Ar), 171.78 (CO_2); m/z (EI) 192 (M$^+$) (Found 192.0786 C$_{11}$H$_{12}$O$_3$ requires 192.0788) 164, 151, 121, 65, 55, 39; (Found C, 68.79; H, 6.31%; requires C, 68.74; H, 6.29%).

Preparation of Compound 20 CH₂CH(CH₂)₂OC₆H₄CO₂C₆H₄OCH₃

The acid (1.49g, 7.28 × 10⁻³mol) was added to a stirred mixture of 4-methoxyphenol

(0.902g, 7.28 ×10⁻³mol) and trifluoroacetic anhydride (1.39g, 8.5 × 10⁻³) in dry

dichloromethane (150cm³). The mixture was stirred at room temperature for three days.

The solvent was removed under vacuum and the residue purified by column

chromatography. (SiO₂, 3:1, Toluene/Ethylacetate). The powdery white solid was

recrystallised from methylated spirits.

White solid 1.49g, (68.7%); m.p. 73.6°C; v_{max} (Nujol mull/cm⁻¹) 2360 (C-H), 2677 (C-H),

1782 (C=O), 1685 (C=C), 1605, 1578, 1541, 1509, 1462 (C-C), 1377, 1319, 1305 (C-H),

1290 (C-O), 1251 (C-H), 1171, 1127, 1105 (C-O), 1017 (C-O); δ_H (400 MHz; CDCl₃) 2.19

(2H, q, J 7.9, CH_2), 3.38 (2H, s, OCH_3) 3.67 (2H, t, J 7.9, OCH_2), 4.78 (2H, m, CH_2CH),

5.56 (1H, m, J 6.7, cis, 20.0, trans, CH₂CH), 6.46 (2H, d, J 11.7, ArH), 6.56 (2H, d, J 11.7,

ArH), 7.20 (2H, d, J 11.9, ArH), 7.44 (2H, d, J 11.9, ArH); δ_C (100 MHz; CDCl₃) 33.37,

(CH₂), 55.57 (OCH₃), 67.39 (OCH₂), 114.31 (Ar), 114.49 (Ar), 114.80 (CH₂CH), 117.38

(Ar), 122.46 (Ar), 132.29 (CH₂CH), 144.34 (Ar), 149.44 (Ar), 157.18 (Ar), 163.30 (Ar),

165.92 (CO₂); m/z (EI) 298(M⁺) (Found: M⁺, 298.1201 (EI), C₁₈H₁₈O₄ requires 298.1205)

175, 121, 69, 55, 41; (Found: C, 72.48; H, 6.06%; requires C, 72.47; H, 6.08%).

n=3 Preparation of CH₂CH(CH₂)₃-O-C₆H₄CO₂CH₂CH₃

Bromopentene (5.37g, 3.6 × 10⁻²mol) was added to ethyl 4-hydroxybenzoate (5.64g, 3.4 ×

10⁻²mol) and K₂CO₃ (18.78g, 0.19 mol) in dry acetone (100 cm³). The mixture was

refluxed for three days and monitored by TLC (hexane:ethylacetate, 1:1) R_f 0.83 (product),

0.68 (bromoalkene). Removal of the solvent under vacuum resulted in a clear liquid. The products were purified by distillation (86°C, 5mm Hg).

Clear liquid 5.37g, (67.5%); v_{max} (Film)/cm^{-1} 2896 (C-H), 1719 (C=O), 1654 (C=C), 1641, 1603, 1522, 1507, 1474, 1445 (C-C), 1393, 1367 (C-H), 1281 (C-O), 1172, 1102; δ_H (400 MHz; CDCl$_3$) 1.35 (3H, t, J 8.0, OCH$_2$CH_3), 1.80 (2H, m, J 7.6, CH_2), 2.21 (2H, m, J 7.6, CH$_2$), 3.85 (2H, t, J 8.0, OCH_2CH$_3$), 4.31 (2H, q, J 8.0, OCH_2CH$_2$), 4.95 (2H, m, CH_2CH), 6.80 (1H, m, J 6.7, *cis*, 19.9 *trans*, CH$_2$CH), 6.85 (2H, d, J 10.9, ArH), 7.95 (2H, d, J 10.9, ArH); δ_C (100 MHz; CDCl$_3$) 14.33 (CH_3), 27.89 and 29.71 (2×CH_2), 59.72 (OCH$_2$CH$_3$), 66.71 (OCH$_2$), 113.76 (Ar), 114.75 (CH$_2$CH), 121.92 (Ar), 130.95 (Ar), 137.24 (CH$_2$CH), 161.93 (Ar), 165.55 (CO$_2$); *m/z* (EI) 234 (M$^+$) (Found: M$^+$234.1261 (EI), C$_{14}$H$_{18}$O$_3$ requires 234.1256) 231, 166, 138, 121, 69, 55, 41; (Found: C, 71.51; H 7.68%; requires C, 71.77; H 7.74%).

Preparation of CH$_2$CH(CH$_2$)$_3$OC$_6$H$_4$CO$_2$H

The ester (2.74g, 1.17 × 10^{-2}mol) was added to KOH (1.98g, 3.53 × 10^{-2} mol) in 80% aqueous ethanol (100cm^3). The mixture was refluxed for twelve hours. The reaction was cooled, diluted with water (100cm^3) and acidified with HCl(c). The precipitate was filtered then washed with dilute HCl (50cm^3), followed by cold methylated spirit (20cm^3). The acid was recrystallised from methylated spirit. The product was a white crystalline solid. White crystals 1.66 (69%), m.p. 124.3°C; v_{max} (Nujol mull/cm^{-1}) 2922 (C-OH), 2666 (C-H), 1675 (C=O), 1632 (C=C), 1605, 1576, 1514, 1466 (C-C), 1378, 1295 (C-H), 1258 (C-O), 1168, 1128, 1111; δ_H (400 MHz; CDCl$_3$) 1.89, and 2.22 (4H, m, 2×CH$_2$), 4.03 (2H, t, J 6.1, OCH$_2$), 5.01 (2H, m, CH_2CH), 5.85 (1H, m, J 6.7, *cis*, 19.8, *trans*, CH$_2$CH), 6.91 (2H, d, J 11.2, ArH), 8.01 (2H, d, J 11.2, ArH); δ_C (100 MHz; CDCl$_3$), 28.07, and 29.85

(2×*CH₂*), 67.41 (O*CH₂*), 114.43 (*CH₂*CH), 115.42 (Ar), 122.53 (Ar), 132.17 (Ar), 137.62 (CH₂*CH*), 163.26 (Ar), 170.12 (*CO₂*); *m/z* (EI) 206 (M⁺) (Found 206.0942 (EI), $C_{12}H_{14}O_3$ requires 206.0943) 138, 121, 68, 41; (Found C, 69.88; H, 6.84%; requires C, 69.89; H, 6.84%).

Preparation of Compound 21 CH₂CH(CH₂)₃OC₆H₄CO₂C₆H₄OCH₃

The acid (1.18g, 7.28 × 10⁻³mol) was added to a stirred mixture of 4-methoxyphenol (0.902g, 7.28 ×10⁻³mol) and trifluoroacetic anhydride (1.39g, 8.5 × 10⁻³) in dry dichloromethane (150cm³). The mixture was stirred at room temperature for three days. The solvent was removed under vacuum and the residue purified by column chromatography (SiO₂, 3:1, toluene/ethyl acetate). The powdery white solid was recrystallised from methylated spirits.

White solid 1.41g, (61%); m.p. 88.1°C; v_{max} (Nujol mull/cm⁻¹) 2927 (C-H), 1728 (C=O), 1685 (C=C), 1654, 1638, 1607, 1581, 1541, 1466 (C-C), 1423, 1378, 1309 (C-H), 1300, 1258 (C-O), 1199, 1173, 1124; δ_H (400 MHz; CDCl₃) 1.94 and 2.27 (4H, m, 2×CH₂), 3.83 (2H, s, O*CH₃*) 4.06. (2H, t, *J* 6.4, *J* 7.0, O*CH₂*), 5.06 (2H, m, C*H₂*CH), 5.87 (1H, m, *J* 6.8, *cis*, 19.9, *trans*, CH₂C*H*), 6.95 (2H, d, *J* 11.3, Ar*H*), 6.93 (2H, d, *J* 11.3, Ar*H*), 7.11(2H, d, *J* 11.3, Ar*H*), 8.14 (2H, d, *J* 11.3, Ar*H*); δ_C (100 MHz; CDCl₃) 28.35 and 30.10, (2×*CH₂*), 67.43 (O*CH₂*), 114.30 (Ar), 114.52 (Ar), 115.53 (*CH₂*CH), 121.91 (Ar), 122.6 (Ar), 132.29 (Ar), 138.53 (CH₂*CH*), 144.67 (Ar), 157.3 (Ar), 163.49 (Ar), 165.32 (*CO₂*); *m/z* (EI) 312 (M⁺) (Found: M⁺, 312.1362 (EI), $C_{19}H_{20}O_4$ requires 312.1361), 189, 121, 93, 69, 55, 41; (Found: C, 72.03; H, 6.45%; requires C, 72.06; H, 6.45%).

Preparation of $CH_2CH(CH_2)_4$-O-$C_6H_4CO_2CH_2CH_3$

Bromohexene (5.87g, 3.6×10^{-2}mol) was added to ethyl-4-hydroxybenzoate (5.64g, 3.4×10^{-2}mol) and K_2CO_3 (18.78g, 0.19 mol) in dry acetone (100 cm^{-3}). The mixture was refluxed for three days and monitored by TLC (hexane:ethylacetate, 1:1) R_f 0.83 (product), 0.68 (bromoalkene). Removal of the solvent under vacuum resulted in a clear liquid. The products were purified by distillation (89°C, 5mm Hg).

Clear liquid 5.82g (69%); ν_{max} (Film)/cm^{-1} 2912 (C=C), 1715 (C=O), 1641 (C=C), 1607, 1508, 1511, 1466 (C-C), 1421, 1391, 1367 (C-H), 1314, 1272 (C-O), 1168, 1130; δ_H (400 MHz; CDCl$_3$) 1.35 (3H, t, J 8.0, OCH$_2$CH_3), 1.55, 1.78 and 2.10 (6H, m, 3×CH$_2$), 3.95 (2H, t, J 8.0, OCH_2CH$_3$), 4.32 (2H, q, J 8.0, OCH_2CH$_2$), 4.95 (2H, m, CH_2CH), 5.82 (1H, m, J 6.8, cis, 19.9 trans, CH$_2$CH), 6.85 (2H, d, J 14.7, ArH), 8.02 (2H, d, J 14.7, ArH); δ_C (100 MHz; CDCl$_3$) 14.67 (OCH$_2$CH_3), 25.46, 28.56 and 33.41 (3×CH_2), 60.57 (OCH_2CH$_3$), 67.72 (OCH_2), 114.26 (Ar), 115.14 (CH_2CH), 122.82 (Ar), 131.31 (Ar), 138.15 (CH$_2$CH), 162.73 (Ar), 166.37 (CO_2); m/z (EI) 248 (M$^+$) (Found M$^+$ 248.1401 (EI), $C_{15}H_{20}O_3$ requires 248.1412) 166, 138, 121, 93, 82, 67, 55, 41; (Found: C, 72.05; H, 8.41%; requires C, 72.55; H, 8.12%).

Preparation of CH₂CH(CH₂)₄OC₆H₄CO₂H

The ester (2.9g, 1.17×10^{-2} mol) was added to KOH (1.98g, 3.53×10^{-2} mol) in 80% aqueous ethanol (100cm³). The mixture was refluxed for twelve hours. The reaction was cooled, diluted with water (100cm³) and acidified with HCl(c). The precipitate was filtered then washed with dilute HCl (50cm³), followed by cold methylated spirit (20cm³). The acid was recrystallised from methylated spirit. The product was a white crystalline solid.

White crystals 1.62g (63%); m.p. 96.6°C; v_{max} (Nujol mull/cm⁻¹) 2922 (C-OH), 2669 (C-H), 1689 (C=O), 1607 (C-=C), 1578, 1515, 1461 (C-H), 1377, 1308, 1257 (C-O), 1170, 1129, 1108; δ_H (400 MHz; CDCl₃) 1.23, 1.59 and 1.84 (6H, m, 3×CH_2), 4.04 (2H, t, J 6.0, J 7.1, OCH_2), 5.02 (2H, m, CH_2CH), 6.22 (1H, m, J 6.8, *cis*, 19.7, *trans*, CH₂CH), 6.94 (2H, d, J 11.3, ArH), 8.07 (2H, d, J 11.3, ArH); δ_C (100 MHz; CDCl₃) 25.24, 28.51, and 33.38 (3×CH_2), 68.03 (OCH_2), 114.17 (CH_2CH), 114.90 (Ar), 122.38 (Ar), 132.32 (Ar), 138.37 (CH₂CH), 163.59 (Ar), 171.43 (CO_2); m/z (EI) 220 (M⁺) (Found: M⁺ 220.1099 (EI), C₁₃H₁₆O₃ requires 220.1099) 138, 121, 82, 67, 55, 41; (Found C, 70.72; H, 7.39%; requires C, 70.89; H, 7.32%).

Preparation of Compound 22 CH$_2$CH(CH$_2$)$_4$OC$_6$H$_4$CO$_2$C$_6$H$_4$OCH$_3$

The acid (1.60g, 7.28 × 10^{-3}mol) was added to a stirred mixture of 4-methoxyphenol (0.902g, 7.28 ×10^{-3}mol) and trifluoroacetic anhydride (1.39g, 8.5 × 10^{-3}) in dry dichloromethane (150cm^3). The mixture was stirred at room temperature for three days. The solvent was removed under vacuum and the residue purified by column chromatography. (SiO$_2$, 3:1, Toluene/Ethylacetate). The powdery white solid was recrystallised from methylated spirits.

White solid 1.38g, (58%); m.p. 97.2°C; ν$_{max}$ (Nujol mull/cm^{-1}) 2924 (C-H), 1739 (C=O), 1690 (C=C), 1642, 1605, 1586, 1511, 1494, 1461 (C-C), 1398, 1378, 1300 (C-H), 1258 (C-O), 1180, 1159, 1120, 1102; δ$_H$ (400 MHz; CDCl$_3$) 1.68, 1.83 and 2.15 (6H, m, 3×CH$_2$), 3.13 (3H. s, OCH$_3$), 4.05 (2H, s, J 8.0, OCH$_2$), 5.05 (2H, m, CH$_2$CH), 5.83 (1H, m, J 6.8, cis, 19.9, trans, CH$_2$CH), 6.91 (2H, d, J 13.0, ArH), 6.95 (2H, d, J 13.0, ArH), 7.15 (2H, d, J 13.0, ArH), 8.15 (2H, d, J 13.0, ArH); δ$_C$ (100 MHz; CDCl$_3$) 25.23, 28.52 and 33.47, (3×CH$_2$), 55.60 (OCH$_3$) 68.04 (OCH$_2$), 114.22 (Ar), 114.45 (Ar), 114.89 (CH$_2$CH), 121.69 (Ar), 122.52 (Ar), 132.21 (Ar), 138.36 (CH$_2$CH), 144.52 (Ar), 157.18 (Ar), 163.37 (Ar), 165.31 (CO$_2$); m/z (EI) 326 (M$^+$) (Found: M$^+$326.3741 (EI), C$_{20}$H$_{22}$O$_4$ requires 326.3740), 203, 121, 55, 41; (Found: C, 73.64; H, 6.82%; requires C, 73.68; H, 6.79%).

Preparation of CH$_2$CH(CH$_2$)$_6$OC$_6$H$_4$CO$_2$CH$_2$CH$_3$

Bromooctene (6.88g, 3.6 × 10^{-2}mol) was added to ethyl-4-hydroxybenzoate (5.64g, 3.4 × 10^{-2}mol) and K$_2$CO$_3$ (18.78g, 0.19 mol) in dry acetone (100 cm^{-3}). The mixture was refluxed for three days and monitored by TLC (hexane:ethyl acetate, 1:1) R$_f$ 0.83

(product), 0.68 (bromoalkene). Removal of the solvent under vacuum resulted in a clear liquid. The products were purified by distillation (94°C, 5mm Hg).

Clear liquid 6.42g (68.4%); v_{max} (Film)/cm^{-1} 2831 (C-H), 1715 (C=O), 1641 (C=C), 1607, 1580, 1540, 1511, 1472, 1446 (C-C), 1421, 1391, 1367 (C-H), 1314(C-H), 1231 (C-O), 1168, 1104; δ_H (400 MHz; CDCl$_3$) 1.40 (3H, m, J 8.1, OCH$_2$CH$_3$), 1.54 (6H, m, 3×CH$_2$), 1.75 and 2.05 (4H, m, 2×CH$_2$), 3.89 (2H, t, J 8.0, OCH$_2$CH$_3$), 4.29 (2H, q, J 8.0, OCH$_2$CH$_2$), 4.99 (2H, m, CH$_2$CH), 5.81 (1H, m, J 6.7, *cis*, 20.0, *trans*, CH$_2$CH), 6.86 (2H, d, J 15.9, ArH), 7.95 (2H, d, J 15.9, ArH); δ_C (100 MHz; CDCl$_3$) 14.41 (OCH$_2$CH$_3$), 26.23, 28.87, 29.35, 30.28 and 33.39 (5×CH$_2$), 60.48 (OCH$_2$CH$_3$), 67.57 (OCH$_2$), 114.23 (Ar), 115.12 (CH$_2$CH), 122.71 (Ar), 131.53 (Ar), 138.44 (CH$_2$CH), 162.94 (Ar), 166.42 (CO$_2$); m/z (EI) 276 (M$^+$) (Found M$^+$, 276.1712 (EI), C$_{17}$H$_{24}$O$_3$ requires 276.1715) 166,138, 121, 93, 81, 69, 55, 41; (Found: C, 73.33; H, 8.89%; requires C, 73.88; H, 8.75%).

Preparation of CH$_2$CH(CH$_2$)$_6$OC$_6$H$_4$CO$_2$H

The ester (3.23g, 1.17×10^{-2}mol) was added to KOH (1.98g, 3.53×10^{-2} mol) in 80% aqueous ethanol (100cm^3). The mixture was refluxed for twelve hours. The reaction was cooled, diluted with water (100cm^3) and acidified with HCl(c). The precipitate was filtered then washed with dilute HCl (50cm^3), followed by cold methylated spirit (20cm^3). The acid was recrystallised from methylated spirit. The product was a white crystalline solid.

White crystals 1.71g (59%), m.p. 98.2°C; v_{max} (Nujol mull/cm^{-1}) 2923 (C-OH), 2854 (C-H), 2665 (C=C), 1727 (C=O), 1672, 1641 (C=C), 1579, 1554, 1464 (C-C), 1434, 1378, 1308 (C-H), 1258 (C-H), 1232 (C-O), 1170, 1065, 1027; δ_H (400 MHz; CDCl$_3$) 1.36, (6H, m, 3×CH$_2$), 1.75 and 1.98 (4H, m, 2×CH$_2$), 3.96 (2H, t, J 8.1, OCH$_2$), 4.95 (2H, m,

CH_2CH), 5.72 (1H, m, J 6.8, *cis*, 19.9, *trans*, CH$_2$CH), 6.86 (2H, d, J 13.9, ArH), 7.98 (2H, d, J 13.9, ArH); δ_C (100 MHz; CDCl$_3$) 25.78, 28.74, 28.99, 29.73 and 33.63 (5 × CH$_2$), 68.18 (OCH$_2$), 114.42 (Ar), 114.69 (CH$_2$CH), 121.58 (Ar), 132.32 (Ar), 138.88 (CH$_2$$C$H), 157.14 (Ar), 165.34 (CO$_2$); *m/z* (EI) 248(M$^+$) (Found: M$^+$, 248.1414 (EI),C$_{15}$H$_{20}$O$_3$ requires 248.1412) 138, 121, 69, 55, 41; (Found: C, 72.26; H, 8.23%; requires C, 72.55; H, 8.12%).

Preparation of Compound 23 CH$_2$CH(CH$_2$)$_6$OC$_6$H$_4$CO$_2$C$_6$H$_4$OCH$_3$

The acid (1.81g, 7.28 × 10^{-3}mol) was added to a stirred mixture of 4-methoxyphenol (0.902g, 7.28 ×10^{-3}mol) and trifluoroacetic anhydride (1.39g, 8.5 × 10^{-3}mol) in dry dichloromethane (150cm^3). The mixture was stirred at room temperature for three days. The solvent was removed under vacuum and the residue purified by column chromatography (SiO$_2$, 3:1, toluene/ethyl acetate). The powdery white solid was recrystallised from methylated spirits.

White solid 1.55g, (60%); m.p. 60.9°C; v_{max} (Nujol mull/cm^{-1}) 2924(C-H), 1734 (C=O), 1643 (C=C), 1607, 1582, 1511, 1462 (C-C), 1378, 1315 (C-H), 1301, 1250 (C-O), 1195, 1166, 1104 1074, 1009; δ_H (400 MHz; CDCl$_3$) 1.48 (6H, m, 3×CH$_2$), 1.85 and 2.11 (4H, m, 2×CH_2), 3.82 (3H. s, OCH_3), 4.05 (2H, s, J 7.9, OCH_2), 5.01 (2H, m, CH_2CH), 5.85 (1H, m, J 6.8, *cis*, 19.9, *trans*, CH$_2$CH), 6.93 (2H, d, J 9.5, ArH), 6.99 (2H, d, J 9.5, ArH), 7.15 (2H, d, J 12.5, ArH), 8.15 (2H, d, J 12.5, ArH); δ_C (100 MHz; CDCl$_3$) 21.44, 25.81, 28.78, 29.03 and 33.68, (5×CH$_2$), 55.56 (OCH$_3$) 68.02 (OCH$_2$), 114.22 (Ar), 114.45 (CH$_2$CH), 122.52 (Ar), 125.28 (Ar), 129.01 (Ar), 132.19 (Ar), 138.94 (CH$_2$$C$H), 144.54 (Ar), 157.16 (Ar), 163.41 (Ar), 165.29 (CO$_2$); *m/z* (EI) 354 (M$^+$) (Found: M$^+$, 354.4212 (EI), C$_{22}$H$_{26}$O$_4$ requires 354.4196), 231, 121, 69, 55, 41; (Found: C, 74.72; H, 7.37%; requires C, 74.55; H, 7.39%).

Hydrosilylation of compounds 20-23 with [SiO₃/₂]₈{OSi(CH₃)₂H}₈

The appropriate alkenic ester (compounds **20-23**) (2.18×10^{-3} mol), was added to a solution of [SiO₃/₂]₈{OSi(CH₃)₂H}₈ (0.26g, 2.64×10^{-4} mol) in toluene (25cm³). Karstedts catalyst[65] as a 3% solution in toluene (0.5cm³) was added and the mixture refluxed for two days. Solvent was removed under vacuum and the solid purified by column chromatography (SiO₂, 10:1 dichloromethane/acetone).

Compound 27 n=2. [SiO₃/₂]₈[OSi(CH₃)₂(CH₂)₄OC₆H₄CO₂C₆H₄OCH₃]₈

White solid 0.78g, (82.4%), m.p.98.6°C, ν_{max} (Nujol mull/cm⁻¹) 2943 (C-H), 1742 (C=O), 1610 (C=C), 1585, 1520, 1505, 1450 (C-C), 1375, 1320 (C-H), 1249 (C-O), 1164, 1132, 1080 (Si-O); δ_H (400 MHz; CDCl₃) 0.05 (6H, s, 2×Si(CH₃)₂), 0.53 (2H, t, J 7.8, SiCH₂), 1.35 (2H, t, J 7.8, CH₂CH₂), 1.60 (2H, m, CH₂), 3.65 (3H. s, OCH₃), 3.85 (2H, s, J 8.3, OCH₂), 6.70 (2H, d, J 11.9, ArH), 6.80 (2H, d, J 11.9, ArH), 6.95 (2H, d, ArH), 7.95 (2H, d, J 11.9, ArH); δ_C (100 MHz; CDCl₃) 0.32 (2×SiCH₃), 17.90 (SiCH₂) 23.10 and 29.90, (2×CH₂), 55.70 (OCH₃) 68.45 (OCH₂), 114.25 (Ar), 114.90 (Ar), 121.96 (Ar), 122.73 (Ar), 132.15 (Ar), 144.85 (Ar), 157.46 (Ar), 163.66 (Ar), 165.50 (CO₂); δ_{Si} (79MHz, CDCl₃) 12.53 (SiCH₃), -108.83 (SiO); m/z (MALDI-TOF) 3583.16 (M+Na); (Found: C, 53.83; H, 5.68%; Si₁₆O₆₂C₁₆₀H₂₀₀ requires C, 53.92; H, 5.66%).

Compound 28 n=3. [SiO₃/₂]₈[OSi(CH₃)₂(CH₂)₅OC₆H₄CO₂C₆H₄OCH₃]₈

White solid 0.79g, (85.2%); m.p.104.3°C; ν_{max} (Nujol mull/cm⁻¹) 2925 (C-H), 1721 (C=O), 1606 (C=C), 1580, 1511, 1503, 1462 (C-C), 1377, 1315 (C-H), 1246 (C-O), 1196, 1165, 1070 (Si-O); δ_H (400 MHz; CDCl₃) 0.05 (6H, s, 2×Si(CH₃)₂), 0.48 (2H, t, J 7.0, SiCH₂),

1.31 (4H, m, 2×CH_2), 1.65 (2H, m, CH_2), 3.60 (3H. s, OCH_3), 3.81 (2H, s, J 8.2, OCH_2, 6.68 (2H, d, J 12.2, ArH), 6.75 (2H, d, J 12.2, ArH), 6.92 (2H, d, ArH), 7.92 (2H, d, J 12.2, ArH); δ_C (100 MHz; CDCl$_3$) 0.29 (2×SiCH_3), 17.87 (SiCH_2) 23.08, 25.84 and 29.92, (3×CH_2), 55.79 (OCH_3) 68.43 (OCH_2), 114.19 (Ar), 114.98 (Ar), 121.91 (Ar), 122.78 (Ar), 132.144(Ar), 144.73 (Ar), 157.40 (Ar), 163.60 (Ar), 165.47 (CO_2); δ_{Si} (79MHz, CDCl$_3$) 12.91 (SiCH_3), -108.73 (SiO); m/z (MALDI-TOF) 3535.59 (M+Na), 3460.4; (Found: C, 57.72; H, 6.17%; Si$_{16}$O$_{52}$C$_{168}$H$_{216}$ requires C, 57.38; H, 6.19%).

Compound 29 n=4. [SiO$_{3/2}$]$_8$[OSi(CH$_3$)$_2$(CH$_2$)$_6$OC$_6$H$_4$CO$_2$C$_6$H$_4$OCH$_3$]$_8$

White solid 0.81g, (84.7%); m.p. 84.3°C; ν_{max} (Nujol mull/cm^{-1}) 2943 (C-H), 1729 (C=O), 1610 (C=C), 1581, 1531, 1465 (C-C), 1423, 1377, 1318 (C-H), 1278 (C-O), 1202, 1171, 1072 (Si-O); δ_H (400 MHz; CDCl$_3$) 0.03 (6H, s, Si(CH$_3$)$_2$), 0.48 (2H, t, J 7.9, SiCH_2), 1.21 (4H, m, 2×CH_2), 1.32 (2H, m, CH_2), 1.68 (2H, m, CH_2), 3.65 (3H. s, OCH_3), 3.87 (2H, s, J 8.2, OCH_2), 6.77 (2H, d, J 11.9, ArH), 6.79 (2H, d, J 11.9, ArH), 6.98 (2H, d, J 11.9, ArH), 7.96 (2H, d, J 11.9, ArH); δ_C (100 MHz; CDCl$_3$) 1.29 (Si(CH_3)$_2$), 17.89 (SiCH_2) 23.26, 26.35, 29.72 and 33.69 (4×CH_2), 55.87 (OCH_3) 68.54 (OCH_2), 114.48 (Ar), 114.74 (Ar), 121.93 (Ar), 122.80 (Ar), 132.48(Ar), 144.78 (Ar), 157.46 (Ar), 163.69 (Ar), 165.56 (CO_2); δ_{Si} (79MHz, CDCl$_3$) 12.73 (SiCH_3), -108.84 (SiO); m/z (MALDI-TOF) 3656.61 (M+Na), 3633.63; (Found: C, 56.62; H, 6.94%; Si$_{16}$O$_{52}$C$_{176}$H$_{232}$ requires C, 56.44; H, 6.59%).

Compound 30 n=6. [SiO$_{3/2}$]$_8$[OSi(CH$_3$)$_2$(CH$_2$)$_8$OC$_6$H$_4$CO$_2$C$_6$H$_4$OCH$_3$]$_8$

White solid 0.85g, (83.7%); m.p.98.5°C; ν_{max} (Nujol mull/cm^{-1}) 2912 (C-H), 1723 (C=O), 1607 (C=C), 1581, 1531, 1464 (C-C), 1321 (C-H), 1285, 1249 (C-O), 1201, 1171, 1074

(Si-O); δ_H (400 MHz; CDCl$_3$) 0.04 (6H, s, Si(CH$_3$)$_2$), 0.45 (2H, t, J 7.8, SiCH$_2$), 1.18 (8H, m, 4×CH$_2$), 1.31 (2H, m, CH$_2$), 1.67 (2H, m, CH$_2$), 3.63 (3H. s, OCH$_3$), 3.88 (2H, s, J 8.2, OCH$_2$), 6.76 (2H, d, J 11.9, ArH), 6.79 (2H, d, J 11.9, ArH), 6.97 (2H, d, J 11.9, ArH), 7.98 (2H, d, J 11.9, ArH); δ_C (100 MHz; CDCl$_3$) 1.27 (Si(CH$_3$)$_2$), 17.96 (SiCH$_2$) 23.26, 26.35, 29.44, 29.63, 29.72 and 33.71 (6×CH$_2$), 55.87 (OCH$_3$) 68.54 (OCH$_2$), 114.67 (Ar), 114.72 (Ar), 121.91 (Ar), 122.80 (Ar), 132.48(Ar), 144.77 (Ar), 157.44 (Ar), 163.68 (Ar), 165.56 (CO$_2$); δ_{Si} (79MHz, CDCl$_3$) 12.75 (SiCH$_3$), -108.77 (SiO), m/z (MALDI-TOF) 3871.75 (M+Na), 3642.8, 3521.7, 3462.8; (Found: C, 59.47; H, 6.86%; Si$_{16}$O$_{52}$C$_{192}$H$_{264}$ requires C, 59.88; H, 6.86%).

Preparation of Compound 49 [CH$_3$CH$_2$]$_3$Si{(CH$_2$)$_5$CH$_3$}

Triethylsilane (1g, 8.60×10^{-3}mol) was placed in a small vial with hex-1-ene (0.72g, 8.60×10^{-3}mol) and H$_2$PtCl$_6$ (5μl of a 0.02mol dm^{-3} solution in isopropyl alcohol). The vial was incubated at 80°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear liquid [117].

Yield: (1.64g, 95.4%); ν_{max} (film/cm^{-3}) 2955 (C-H), 2920, 1458 (C-C), 1417, 1378 (C-H), 1239, 1180, 1073 (Si-O); δ_H (300MHz, CDCl$_3$) 0.51 (6H, q, J 7.3, SiCH$_2$CH$_3$), 0.56 (2H, t, J 7.5, SiCH$_2$CH$_2$R), 0.89 (3H, t, J 7.5, CH$_2$CH$_2$CH$_2$CH$_3$), 0.93 (9H, t, J 7.3, SiCH$_2$CH$_3$), 1.30 (8H, m, CH$_2$CH$_2$CH$_2$CH$_2$); δ_C (100MHz, CDCl$_3$) 3.50 (SiCH$_2$CH$_3$)$_3$), 6.70 (SiCH$_2$R), 11.30 (SiCH$_2$CH$_3$), 14.06 (CH$_3$R), 22.63, 23.79, 31.58 and 33.64 (4×CH$_2$); δ_{Si} (79MHz, CDCl$_3$) 6.65; m/z (EI) 201 (MH$^+$) (Found M$^+$, 200.1962 (EI), SiC$_{12}$H$_{28}$ requires 200.1960) 170, 44; (Found: C, 71.41; H, 14.58%; requires C, 71.91; H, 14.08%).

Preparation of Compound 50 [CH$_3$CH$_2$O]$_3$Si{(CH$_2$)$_5$CH$_3$}

Triethoxysilane (1g, 6.09×10^{-3}mol) was placed in a small vial with hex-1-ene (0.5g, 6.09×10^{-3}mol) and H$_2$PtCl$_6$ (10µl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for 24 hours. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear liquid [117].

Yield: 1.49g, (98.7%); ν$_{max}$ (film/cm^{-3}) 2972, 2927 (C-H), 2736, 1391, 13669 (C-C), 1296, 1168, 1105 (Si-O); δ$_H$ (300MHz, CDCl$_3$) 0.56 (2H, t, J 7.1, SiCH_2R), 0.83 (3H, t, J 6.4, SiOCH$_2$CH_3), 1.15, (17H, m, CH$_2$CH$_2$CH$_2$CH$_2$ and SiOCH$_2$CH_3), 3.79 (6H, q, J 7.1, SiOCH_2); δ$_C$ (100MHz, CDCl$_3$) 10.30 (SiCH$_2$), 13.94 (CH$_2$CH$_3$), 18.15(OCH$_2$CH$_3$), 22.47, 22.72, 31.51 and 32.77 (4×CH$_2$), 58.94 (OCH$_2$); δ$_{Si}$ (79MHz, CDCl$_3$) -44.65; m/z (FAB) 266 (MNH$_4$$^+$), 249 (MH$^+$) (Found MH$^+$ 249.1888 (EI), SiC$_{12}$H$_{29}$O$_3$ requires 249.1886), 220, 180; (Found: C, 58.22; H, 11.21%; requires C, 58.02; H, 11.36%).

Preparation of Compound 51 [SiO$_{3/2}$]$_8${(CH$_2$)$_5$CH$_3$}$_8$.

Octahydridosilsesquioxane (0.20g, 4.73×10^{-4}mol), 1-hexene (0.38g, 4.56×10^{-3}mol) and 10µl of a 0.02mol dm^{-3} solution of H$_2$PtCl$_6$ in isopropyl alcohol were placed in a small vial. The vial was capped and placed in an oil bath and maintained at 60°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear liquid. (0.50g 96%).

When Karstedts catalyst was used the same procedure was followed except that 400µl of a 3% solution of Karstedts catalyst in xylene was added instead of chloroplatinic acid. The

reaction mixture was aerated for two minutes prior to incubation. The resultant gel was decolourised using activated charcoal in chloroform. The product was a clear gel.

Yield: (0.48g, 92%); ν_{max} (film/cm^{-3}) 1378 (C-C), 1288 (C-H), 1256, 1230, 1193, 1124, 1008 (Si-O); δ_H (400MHz, CDCl$_3$) 0.54 (2H, t, J 7.7, SiCH_2), 0.86 (3H, t, J 7.7, CH$_2$CH_3), 1.22 (8H, m, 4×CH$_2$); δ_C (100MHz, CDCl$_3$) 12.29 (SiCH$_2$), 14.42 (CH$_3$), 22.92, 23.09, 31.94, 32.69 (4×CH$_2$); δ_{Si} (79MHz, CDCl$_3$) –66.56 (SiO); m/z (EI) 1097 (MH$^+$), 1067, 925, 857, 422; (Found: C, 52.45; H, 9.24%; requires C, 52.55; H, 9.49%).

Preparation of Compound 52 [SiO$_{3/2}$]$_8$\{OSi(CH$_3$)$_2$(CH$_2$)$_5$CH$_3$\}$_8$

Si$_8$O$_{12}$[OSi(CH$_3$)$_2$H]$_8$ (0.2g, 1.97×10^{-4}mol) was dissolved in toluene (25cm^3). To this was added 1-hexene (0.143g, 1.67×10^{-3}mol) and 400µl of a 3% solution of Karstedt's catalyst in xylene. The mixture was refluxed for 24 hours. The solvent was removed under vacuum. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a gum.

Yield: 0.33g, (98%); ν_{max} (film/cm^{-3}) 1377 (C-C), 1284 (C-H), 1253, 1231, 1194, 1123, 1102 (Si-O); δ_H (400MHz, CDCl$_3$) 0.01 (6H, s, Si(CH$_3$)$_2$), 0.24, (2H, t, J 6.7, SiCH$_2$), 0.81 (3H, t, J 6.7, CH$_2$CH_3), 1.34 (8H, m, 4×CH$_2$); δ_C (100MHz, CDCl$_3$) 1.34 (Si(CH$_3$)$_2$) 14.48 (SiCH$_2$), 18.02 (CH$_3$), 22.97, 30.05, 31.94, 33.40 (4×CH$_2$); δ_{Si} (79MHz, CDCl$_3$) 12.34 (Si(CH$_3$)$_2$, -108.67 (SiO); m/z (EI) 1689 (MH$^+$) 1605, 1520, 1450, 1375; (Found: C, 45.45; H, 9.05%; requires C, 44.92; H, 8.89%).

Preparation of Compound 53 [CH₃CH₂]₃Si{(CH₂)₂C(CH₃)₂CH₂CO₂CH₃}.

Triethylsilane (1g, 8.60×10^{-3}mol) was placed in a small vial with methyl 3,3-dimethylpent-4-enaote (1.22g, 8.60×10^{-3}mol) and H_2PtCl_6 (5μl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for one day. Filtering a $CHCl_3$ solution through activated charcoal afforded the product as a clear liquid.

Yield: (2.2g, 99.2%); v_{max} (film/cm^{-3}) 2953 (C-H), 2912, 2875, 2360, 1740 (C=O), 1467, 1436 (C-C), 1417, 1388, 1344 (C-H), 1282 (C-O), 1230 (C-H), 1148, 1098 (Si-O); δ_H (300MHz, CDCl₃) 0.42 (2H, t, J 7.4, SiCH_2), 0.46 (6H, q, J 7.3, SiCH_2CH₃), 0.84 (9H, t, J 7.3, SiCH₂CH_3), 0.88 (6H, s, C(CH_3)₂), 1.21 (2H, t, J 7.4, SiCH₂CH_2C) 2.09 (2H, s, CH_2CO₂CH₃), 3.53 (3H, s, COCH_3); δ_C (100MHz, CDCl₃) 3.28 (Si(CH_2)₃), 4.51 (SiCH_2), 7.89 (SiCH₂(CH₃)₂), 26.47 C(CH_3)₂), 33.85 (CH₂CH₂), 35.84 (C(CH₃)₂), 44.64 (CH₂CO₂), 50.63 (OCH₃), 172.47 (CO₂); δ_{Si} (79MHz, CDCl₃) 7.46; m/z (EI) 259 (MH⁺), 229, 132, (Found: C, 64.72; H, 11.12%; requires C, 65.01; H, 10.93%).

Preparation of Compound 54 [CH₃CH₂O]₃Si{(CH₂)₂C(CH₃)₂CH₂CO₂CH₃}

Triethoxysilane (1g, 6.09×10^{-3}mol) was placed in a small vial with methyl 3,3-dimethylpent-4-anoate (0.87g, 6.09×10^{-3}mol) and H_2PtCl_6 (10μl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for one day. Filtering a $CHCl_3$ solution through activated charcoal afforded the product as a clear liquid

Yield: 1.75g, (97.8%); v_{max} (film/cm^{-3}) 2974 (C-H), 2929, 2736, 1740 (C=O), 1642, 1439 (C-C), 1390, 1367 (C-H), 1347, 1310, 1168 (C-O), 1080, 1021 (Si-O); δ_H (300MHz, CDCl₃) 0.47 (2H, t, J 7.4, SiCH_2), 0.50 (6H, s, (CH₃)₂, 0.74 (9H, t, J 7.2, SiOCH₂CH_3),

1.38 (2H, t, J 7.4, SiCH$_2$CH_2), 2.19 (2H, s, CH$_2$CO$_2$), 3.68 (3H, s, OCH$_3$), 3.73 (6H, q, J 7.2, OCH_2CH$_3$); δ_C (100MHz, CDCl$_3$) 4.62 (SiCH$_2$), 17.85 (OCH$_2$CH$_3$), 26.37 (CH$_2$), 26.91 (C(CH$_3$)$_2$), 33.67 (C(CH$_3$)$_2$), 34.65 (CH$_2$CO$_2$), 50.72 (CO$_2$CH$_3$), 172.42 (CO$_2$); δ_{Si} (79MHz, CDCl$_3$) -45.94; m/z (EI) 307 (MH$^+$), 276, 178. %); (Found: C, 54.32; H, 9.86%; requires C, 54.87; H, 9.87%).

Preparation of Compound 55 [SiO$_{3/2}$]$_8${(CH$_2$)$_2$C(CH$_3$)$_2$CH$_2$CO$_2$CH$_3$}$_8$

[HSiO$_{3/2}$]$_8$ (1.00g, 2.35×10^{-3}mol), methyl 3,3-dimethylpent-4-enoate (5.03g, 3.53×10^{-2}mol) and 50µl of a 0.02mol dm^{-3} solution of H$_2$PtCl$_6$ in isopropyl alcohol were placed in a small vial. The vial was capped and placed in an oil bath at 80°C for one day. The gel was purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$/acetone). The product was a clear viscous liquid.

Yield: 3.77g, (95%); ν_{max} (film/cm^{-3}) 2955 (C-H), 2871, 1735 (C=O), 1468, 1438(C-C), 1338, 1354 (C-H) 1313, 1225, 1114, 1037, 1017 (Si-O); δ_H (400MHz, CDCl$_3$) 0.52 (2H, t, J 7.4, SiCH$_2$), 0.92, (6H, s, C(CH$_3$)$_2$, 1.38 (2H, t, J 7.4, CH$_2$), 2.25 (2H, s, CH$_2$CO$_2$), 3.60 (3H, s, OCH$_3$); δ_C (100MHz, CDCl$_3$) 6.06 (SiCH$_2$), 26.49 (2×CH$_3$), 33.82, 35.32, (2×CH$_2$), 44.94 (C(CH$_3$)$_2$), 51.09 (OCH$_3$), 172.92 (CO$_2$); δ_{Si} (79MHz, CDCl$_3$), -66.07 (SiO); m/z (CI)1578 (M$^+$NH$_4$), 1560 (M$^+$) (Found M$^+$, 1560.6122 (EI) Si$_8$C$_{64}$H$_{120}$O$_{28}$ requires 1560.6120) 1534, 1391, 144, 63, 59, 31; (Found: C, 49.46; H, 7.23%; requires C, 49.21; H, 7.73%).

Preparation of Compound 56 [SiO$_{3/2}$]$_8${OSi(CH$_3$)$_2$(CH$_2$)$_2$C(CH$_3$)$_2$CH$_2$CO$_2$CH$_3$}$_8$

Si$_8$O$_{12}$[OSi(CH$_3$)$_2$H]$_8$ (1g, 9.84×10^{-4}mol) was dissolved in toluene (25cm^3). To this was added methyl 3,3-dimethylpent-4-enoate (1.19g, 8.36×10^{-3}mol) and 800µl of a 3% solution of Karstedt's catalyst in xylene. The mixture was refluxed for one day. The solvent was removed under vacuum and the gum was purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$). The product was a clear gum.

Yield: 2.10g, (99%); ν$_{max}$ (film/cm^{-3}); 2959 (C-H), 1739 (C=O), 1549 (C-H), 1513, 1470 (C-C), 1389 (C-H), 1347, 1311, 1255, 1088 (Si-O); δ$_H$ (400MHz, CDCl$_3$) 0.25 (6H, s, Si(CH$_3$)$_2$), 0.43 (2H, t, J 7.3, SiCH$_2$), 0.83, (6H, s, C(CH$_3$)$_2$, 1.15 (2H, t, J 7.3, CH$_2$), 2.13 (2H, s, CH$_2$), 3.49 (3H, s, OCH$_3$); δ$_C$ (100MHz, CDCl$_3$) 0.22 (Si(CH$_3$)$_2$), 11.76 (SiCH$_2$), 27.25 (2×CH$_3$), 34.42, 35.62, (2×CH$_2$), 45.67 (C(CH$_3$)$_2$), 51.55 (OCH$_3$), 173.32 (CO$_2$); δ$_{Si}$ (79MHz, CDCl$_3$), 13.61 (Si(CH$_3$)$_2$), -108.89 (SiO); m/z (CI) 2171 (MNH$_4^+$,), 2154 (MH$^+$) 2125, 1982, 144, 63, 59, 31; (Found, C, 44.62; H, 7.86%; requires C, 44.65; H, 7.74%).

Preparation of Compound 57 [CH$_3$CH$_2$]$_3$Si{(CH$_2$)$_3$O(CH$_2$)$_3$CH$_3$}

Triethylsilane (1g, 8.60×10^{-3}mol) was placed in a small vial with allyl butyl ether (0.98g, 8.60×10^{-3}mol) and H$_2$PtCl$_6$ (5µl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear liquid. (95% by NMR).

Yield: 1.85g, (86.8%); ν$_{max}$ (film/cm^{-3}) 2935 (C-H), 2912, 2875, 1735, 1654, 1559 (C-C), 1378, 1238 (C-H), 1185 (C-O), 1115, 1016 (Si-O); δ$_H$ (300MHz, CDCl$_3$) 0.44 (2H, t, J 7.5, SiCH$_2$), 0.47 (6H, q, J 7.3, SiCH$_2$CH$_3$), 0.89 (3H, t, J 7.5, CH$_2$CH$_2$CH$_2$CH$_3$), 0.90 (9H, t, J

7.3, SiCH$_2$CH_3), 1.34 (2H, q, J 7.5, SiCH$_2$CH_2CH$_2$O), 1.53 (4H, m, OCH$_2$CH_2CH_2CH$_3$),

3.32 (2H, t, J 7.5, OCH_2), 3.37 (2H, t, J 7.5, OCH_2); δ$_C$ (100MHz, CDCl$_3$) 3.18

(SiCH$_2$(CH$_3$)$_3$), 7.28 (SiCH$_2$R), 7.46 (SiCH$_2$CH$_3$), 13.81 (CH$_3$CH$_2$CH$_2$), 19.34, 23.23 and

31.87 (3×CH$_2$), 70.50 and 74.02 (OCH$_2$); δ$_{Si}$ (79MHz, CDCl$_3$) 7.15; m/z (EI) 230 (M$^+$)

(Found: M$^+$ 230.2070 (EI), SiC$_{13}$H$_{30}$O requires 230.2066), 229, 201, 173, 132, 72, 58;

(Found: C, 67.32; H, 12.87%; requires C, 67.75; H, 13.12%).

Preparation of Compound 58 [CH$_3$CH$_2$O]$_3$Si{(CH$_2$)$_3$O(CH$_2$)$_3$CH$_3$}

Triethoxysilane (1.06g, 6.4×10^{-3}mol) was placed in a small vial with allyl butyl ether

(0.74g, 6.4×10^{-3}mol) and H$_2$PtCl$_6$ (10µl of a 0.02mol dm^{-3}). The vial was incubated at

80°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the

product as a clear liquid. The reaction was seen to proceed with α and β addition giving

[CH$_3$CH$_2$O]$_3$Si{(CH$_2$)$_3$O(CH$_2$)$_3$CH$_3$} (90% by NMR),

[CH$_3$CH$_2$O]$_3$Si{CHC(CH$_3$)O(CH$_2$)$_3$CH$_3$} (<10%by NMR);

Yield: 1.70g, (95.2%) (mixture); ν$_{max}$ (film/cm^{-3}) (mixture) 2973, 2930 (C-H), 2875, 1737,

1442 (C-C), 1391, 1296 (C-O) 1195 (C-H), 1168, 1106 (Si-O);

[CH$_3$CH$_2$O]$_3$Si{CH$_2$)$_3$O(CH$_2$)$_3$CH$_3$} (90% by NMR): δ$_H$ (300MHz, CDCl$_3$) 0.61 (2H, t, J

7.3, SiCH_2R), 0.86 (3H, s, RCH_3), 1.13, (9H, t, J 7.2, SiOCH$_2$CH_3), 1.31 (2H, m, J 7.3,

CH$_2$CH_2CH$_2$), 1.47 (2H, m, J 7.3, CH$_2$CH_2), 1.63 (2H, m, J 7.3, CH$_2$CH_2), 3.32 (4H, m, J

7.3, 2×OCH_2), 3.75 (6H, q, J 7.2, OCH_2CH$_3$); δ$_C$ (100MHz, CDCl$_3$) 6.84 (SiCH$_2$R), 13.77

(CH$_2$CH$_3$), 17.86 (RCH$_3$), 18.78 (SiOCH$_2$CH$_3$), 22.93 (CH$_2$), 31.79 (2×CH$_2$), 58.97

(OCH$_2$CH$_3$), 72.39 and 72.96 (2×OCH$_2$); δ$_{Si}$ (79MHz, CDCl$_3$) -45.94;

[CH$_3$CH$_2$O]$_3$Si{CH(CH$_3$)CH$_2$O(CH$_2$)$_3$CH$_3$} (10% by NMR): δ$_H$ (300MHz, CDCl$_3$) 0.54

(1H, m, J 7.1, SiCHR), 0.90 (3H, s, RCH$_3$), 1.10 (3H, d, J 7.1, SiCHCH_3), 1.15 (3H, t, J

7.3, SiOCH$_2$CH$_3$), 1.41 (2H, m, J 7.4, CH$_2$CH_2), 1.53 (4H, m, J 7.4, CH$_2$CH$_2$CH_2), 3.42

(2H, m, J 7.1, OCH_2CH$_2$), 3.74 (6H, q, J 7.1, SiOCH_2CH$_3$), 3.98 (2H, d, J 7.1, CHCH_2O);

δ_C (100MHz, CDCl$_3$) 6.62 (SiCHR), 12.43 (SiCHCH$_3$), 13.53 (OCH$_2$$CH_3$), 17.90 (R$CH_3$), 18.82 (SiOCH$_2$$CH_3$), 22.21 ($CH_2$), 31.53 ($CH_2$), 58.80 (O$CH_2CH_3$), 72.54 and 73.54 (2×O$CH_2$); δ_{Si} (79MHz, CDCl$_3$) -46.29; m/z (EI) (mixture) 278 (M$^+$) (Found M$^+$, 278.1917 (EI), SiC$_{13}$H$_{30}$O$_4$ requires 278.1913) 233, 222, 205, 191, 73, 58; (Found C, 56.12; H, 11.01%; requires C, 56.08; H, 10.86%).

Preparation of Compound 59 [SiO$_{3/2}$]$_8${(CH$_2$)$_3$O(CH$_2$)$_3$CH$_3$}$_8$

[HSiO$_{3/2}$]$_8$ (0.2g, 4.7×10^{-4}mol), allyl butyl ether (0.46g, 4.0×10^{-3}mol) and 10µl of a 0.02mol dm^{-3} solution of H$_2$PtCl$_6$ in isopropyl alcohol were placed in a small vial. The vial was capped and placed in an oil bath at 80°C for one day. The reaction was seen to proceed with α and β addition. Filtering a CHCl$_3$ solution through activated charcoal afforded a clear gum. The products were identified by NMR techniques, ^{1}H/^{13}C COSY and DEPT.

Yield: 0.42g (67.5%) (mixture); ν_{max} (film/cm^{-3})(mixture); 2895 (C-H), 2875, 1721, 1659, 1394 (C-C), 1259 (C-O), 1239 (C-H) 1148, 1089, 1017 (Si-O);

[SiO$_{3/2}$]$_8${(CH$_2$)$_3$O(CH$_2$)$_3$CH$_3$}$_8$ (70% by NMR). δ_H (400MHz, CDCl$_3$) 0.61 (2H, t, J 6.3, SiCH$_2$), 0.85 (3H, t, J 7.1, CH$_3$), 1.26 (2H, t, J 6.3 CH$_2$), 1.53 (2H, m, CH$_2$), 1.71 (2H, m, CH$_2$), 3.58 (4H, m, 2×OCH$_2$); δ_C (100MHz, CDCl$_3$) 8.02 (SiCH$_2$), 13.39 (CH$_3$), 19.36, 22.88, 31.88 (3×CH$_2$), 70.53 (OCH$_2$), 72.76 (OCH$_2$); δ_{Si} (79MHz, CDCl$_3$) -66.95 (SiO);

[SiO$_{3/2}$]$_8${CH(CH$_3$)CH$_2$O(CH$_2$)$_3$CH$_3$}$_8$ (30% by NMR). δ_H (400MHz, CDCl$_3$) 0.62 (2H, sextet, J 6.4, SiCH), 0.85 (3H, t, J 7.1, CH$_3$), 1.08 (3H, d, SiCCH$_3$), 1.26 (2H, t, J 6.4, CH$_2$), 1.53 (2H, m, CH$_2$), 3.70 (4H, m, 2×OCH$_2$); δ_C (100MHz, CDCl$_3$) 11.4 (SiCH), 13.39 (CH$_3$), 13.74 (SiCCH$_3$), 18.77, 25.01 (2×CH$_2$), 69.43 (OCH$_2$), 73.41 (OCH$_2$); δ_{Si} (79MHz,

CDCl$_3$) -66.95 (SiO); m/z (mixture) (EI) 1338 (M$^+$), 1279, 1221, 115, 73, 57; (Found C, 50.32; H, 9.01%; requires C, 50.26; H, 9.04%).

Preparation of Compound 60 {Si$_8$O$_{12}$}[OSi(CH$_3$)$_2$(CH$_2$)$_3$O(CH$_2$)$_3$CH$_3$]$_8$

Si$_8$O$_{12}$[OSi(CH$_3$)$_2$H]$_8$ (1g, 9.84×10^{-4}mol) was dissolved in toluene (25cm^3). To this was added allyl butyl ether (0.96g, 8.36×10^{-3}mol) and 800µl of a 3% solution of Karstedt's catalyst in xylene. The mixture was refluxed for one day. The solvent was removed under vacuum. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear gel.

Yield: 1.85g, (97.5%); ν_{max} (film/cm^{-3}) 2896 (C-H), 2734, 1734, 1649, 1503, 1498 (C-C), 1398 (C-H), 1287 (C-O), 1164, 1087 (Si-O); δ_H (400MHz, CDCl$_3$) 0.25 (6H, s, Si(CH$_3$)$_2$), 0.54 (2H, t, J 7.2, SiCH$_2$R), 0.89, (3H, t, J 7.2, RCH$_3$), 1.28 (2H, m, OCH$_2$CH$_2$CH_2CH$_3$), 1.54 (2H, m, CH$_2$), 1.78 (2H, m, CH$_2$), 3.62 (4H, m, 2×OCH$_2$); δ_C (100MHz, CDCl$_3$) 0.35 (Si(CH$_3$)$_2$), 11.61 (SiCH$_2$R), 13.54 (RCH$_3$), 19.42, 21.81 and 26.41 (3×CH$_2$), 71.42 and 72.18 (2×OCH$_3$); δ_{Si} (79MHz, CDCl$_3$) 12.01 (Si(CH$_3$)$_2$), -108.41 (SiO); m/z (EI) 1928 (M$^+$), 1876, 1859, 1845, 1831, 1816, 115, 73, 57; (Found, C, 44.47; H, 8.57%; requires C, 44.78; H, 8.77%).

Preparation of Compound 61 [CH$_3$CH$_2$]$_3$Si{(CH$_2$)$_3$C$_6$H$_5$}

Triethylsilane (1g, 8.60×10^{-3}mol) was placed in a small vial with allylbenzene (1.02g, 8.60×10^{-3}mol) and H$_2$PtCl$_6$ (5µl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a

clear liquid. The reaction was seen to proceed with α and β addition, in a ratio of 5:95, determined by NMR.

Yield: 1.88g, (93.2%) (mixture); v_{max} (film/cm^{-3}) (mixture) 2897 (C-H), 2438, 1543 (C=C), 1497, 1375, 1275 (C-H), 1209, 1106, 1049 (Si-O);

[CH$_3$CH$_2$]$_3$Si{(CH$_2$)$_3$(C$_6$H$_5$}: δ_H (300MHz, CDCl$_3$) 0.57 (2H, t, J 7.3, SiCH_2R), 0.83 (6H, q, J 7.0, SiCH_2CH$_3$), 1.06 (3H, t, J 7.0, SiCH$_2$CH_3), 1.46 (2H, m, CH$_2$CH_2CH$_2$), 2.84 (2H, t, J 7.3, CH$_2$CH$_2$CH_2Ph), 6.93-7.01 (5H, m, Ph); δ_C (100MHz, CDCl$_3$) 2.96 (SiCH$_2$R), 6.78 (SiCH$_2$CH$_3$), 13.78 (SiCH$_2$CH$_3$), 24.56 (SiCH$_2$CH$_2$CH$_2$), 38.07 (SiCH$_2$CH$_2$CH$_2$Ph), 125.44, 126.36, 128.17, 142.64 (4×Ar); δ_{Si} (79MHz CDCl$_3$) 6.81; m/z (EI) (mixture) 234 (M$^+$) 128, 105, 76; (Found: C, 77.28; H, 10.67%; requires C, 77.18; H, 10.79%).

Preparation of Compound 62 [CH$_3$CH$_2$O]$_3$Si{(CH$_2$)$_3$C$_6$H$_5$}

Triethoxysilane (1g, 6.09×10^{-3}mol) was placed in a small vial with allylbenzene (0.72g, 6.09×10^{-3}mol) and H$_2$PtCl$_6$ (10µl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear liquid. The reaction was seen to proceed with α and β addition giving [CH$_3$CH$_2$O]$_3$Si{(CH$_2$)$_3$C$_6$H$_5$} (90% by NMR), [CH$_3$CH$_2$O]$_3$Si{CHC(CH$_3$)CH$_2$C$_6$H$_5$} (<10%by NMR);

Yield: 1.47g, (85.4%) (mixture); v_{max} (film/cm^{-3}) (mixture) 2974 (C-H), 2928, 2887 (C=C), 2735, 1643 (C=C), 1497, 1454 (C-C), 1391, 1295, 1234 (C-H), 1168, 1082 (Si-O);

[CH$_3$CH$_2$O]$_3$Si{(CH$_2$)$_3$C$_6$H$_5$}: δ_H (300MHz, CDCl$_3$) 0.56 (2H, t, J 7.7, SiCH$_2$), 1.10 (9H, t, J 6.8, OCH$_2$CH$_3$), 1.68 (2H, m, J 7.7, CH$_2$CH_2CH$_2$), 2.50 (2H, t, J 7.7, CH$_2$CH$_2$CH_2Ph),

3.53 (6H, q, *J* 6.8, OC*H₂*CH₃), 6.98-7.12 (5H, m, Ar); δ_C (100MHz, CDCl₃) 10.63
(SiCH₂), 18.18 (SiOCH₂*C*H₃), 25.27 (CH₂), 39.19 (*C*H₂Ph), 58.27 (O*C*H₂CH₃), 125.31
(Ar), 126.09 (Ar), 127.77 (Ar), 142.22 (Ar); δ_{Si} (79MHz, CDCl₃) -45.18;

[CH₃CH₂OSi]₃{CH(CH₃)CH₂C₆H₅}: δ_H (300MHz, CDCl₃) 0.82 (1H, m, *J* 7.2, SiCH), 0.91
(3H, m, CHC*H₃*), 1.13 (3H, m, *J* 7.2, OCH₂C*H₃*), 1.75 (2H, dd, *J* 6.9, *J* 7.2, CH₂Ph), 6.74-
6.85 (5H, m, Ar); δ_C (100MHz, CDCl₃) 10.63 (SiCH), 18.18 (SiOCH₂*C*H₃), 25.27 (CH₃),
39.19 (*C*H₂Ph), 58.27 (O*C*H₂CH₃), 125.52 (Ar), 126.23 (Ar), 127.91 (Ar), 137.63 (Ar); δ_{Si}
(79MHz, CDCl₃) -46.21; *m/z* (EI) (mixture) 282 (M⁺) (Found: M⁺ 282.1651(EI),
SiC₁₅H₂₆O₃ requires 282.1655) 238, 193, 176, 107, 76, 45; (Found: C, 63.41; H, 9.12%;
SiC₁₅H₂₆O₃ requires C, 63.79; H, 9.28%).

Preparation of Compound 63 [SiO₃/₂]₈{(CH₂)₃C₆H₅}₈

[HSiO₃/₂]₈ (0.20g, 4.62×10⁻⁴mol), allylbenzene (0.52g, 4.4×10⁻³mol) and 10μl of a 0.02mol
dm⁻³ solution of H₂PtCl₆ in isopropyl alcohol were placed in a small vial. The vial was
capped and placed in an oil bath at 80°C for one day. Filtering a CHCl₃ solution through
activated charcoal afforded the product as a viscous liquid. (0.50g, 86.87%).

When Karstedts catalyst was used the same procedure was followed execpt the reaction
mixture was aerated for two minutes prior to incubation. The resultant gel was
decolourised using activated charcoal in chloroform. The product was a clear viscous
liquid.

Allylbenzene was shown to isomerise in the presence of both catalysts producing a mixture
of octa(3-phenylpropyl)silsesquioxane (70% by NMR) and octa(1-methyl-2-phenyl-
ethyl)silsesquioxane (30% by NMR).

Yield: (0.50g, 85.05%) (mixture); v_{max} (film/cm^{-3}) (mixture) 3062, 3026 (C=C), 1943 (C-H), 1869, 1803, 1745, 1706, 1663 (C=C), 1603, 1496, 1454, 1407, 1377 (C-H), 1045, 1008 (Si-O);

$[SiO_{3/2}]_8\{(CH_2)_3C_6H_5\}_8$ (70% by NMR): δ_H (400MHz, CDCl$_3$) 0.64 (2H, t, J 8.4, SiCH_2), 1.68 (2H, m, J 8.4, SiCH$_2$CH_2), 2.59 (2H, t, J 8.4 PhCH_2), 6.96 – 7.09 (5H, m, Ar); δ_C (100MHz, CDCl$_3$) 11.54 (SiCH$_2$), 24.76 (CH$_2$CH$_2$CH$_2$Ph), 38.79 (CH$_2$Ph), 125.79 (Ar), 128.24 (Ar), 128.42 (Ar), 142.21 (Ar); δ_{Si} (79MHz, CDCl$_3$) –66.81 (SiO);

$[SiO_{3/2}]_8\{CH(CH_3)CH_2C_6H_5\}_8$ (30% by NMR): δ_H (400MHz, CDCl$_3$) 0.86 (1H, sextet, J 7.5, SiCHCH$_3$) 1.07 (3H, d, J 7.5, SiCHCH_3), 1.80 (2H, d, J 7.5, SiCHCH_2), 6.32 – 6.35 (5H, m, Ar); δ_C (100MHz, CDCl$_3$) 13.84 (SiCH), 18.49 (SiCHCH$_3$), 38.06 (CH$_2$Ph), 125.62 (Ar), 128.24 (Ar), 128.42 (Ar), 142.26 (Ar); δ_{Si} (79MHz, CDCl$_3$) –66.78 (SiO);

m/z (mixture) (EI) 1369 (MH$^+$) (Found: MH$^+$ 1368.4431 (EI), Si$_8$C$_{72}$H$_{88}$O$_{12}$ requires 1368.4429) 1250, 424, 119, 78.); (Found C, 63.64; H, 6.37%; requires C, 63.16; H, 6.43%).

Preparation of Compound 64 {Si$_8$O$_{12}$}[OSi(CH$_3$)$_2$(CH$_2$)$_3$C$_6$H$_5$]$_8$

Si$_8$O$_{12}$[OSi(CH$_3$)$_2$H]$_8$ (1g, 9.84×10^{-4}mol) was dissolved in toluene (25cm^3). To this was added allylbenzene (0.99g, 8.36×10^{-3}mol) and 800μl of a 3% solution of Karstedt's catalyst in xylene. The mixture was refluxed for one day. The solvent was removed under vacuum. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear gum.

Yield: 1.84g, (95.4%); v_{max} (film/cm^{-3}) 3149 (C=C), 2987, 2831, 1694 (C-H), 1501 (C=C), 1431 (C-H), 1210 (C-O), 1181 (C-H), 1094, 1081 (Si-O); δ_H (400MHz, CDCl$_3$) 0.28 (6H, s, Si(CH_3)$_2$), 0.61 (2H, t, J 8.1, SiCH_2R), 1.84 (2H, m J 8.1, SiCH$_2$CH_2R), 2.63 (2H, t, J

8.1, SiCH$_2$CH$_2$CH_2R), 7.04-7.13 (5H, m, Ar); δ_C (100MHz, CDCl$_3$) 0.64 (Si(CH$_3$)$_2$), 10.79

(SiCH$_2$R), 25.32 (SiCH$_2$CH$_2$R), 37.64 (SiCH$_2$CH$_2$CH$_2$R), 124.81, 126.71, 128.31 and

128.48 (4×Ar); δ_{Si} (79MHz, CDCl$_3$), 12.04 (Si(CH$_3$)$_2$), -108.27 (SiO); m/z (EI) 1964 (M$^+$)

(Found M$^+$ 1963.3171 (EI), Si$_{16}$C$_{88}$H$_{136}$O$_{20}$ requires 1963.3184) 1845, 1016, 119, 78;

(Found, C, 53.63; H, 6.94%; requires C, 53.84; H, 6.98%).

Preparation of Compound 65 [CH$_3$CH$_2$]$_3$Si{(CH$_2$)$_2$C$_6$H$_5$}

Triethylsilane (1g, 8.60×10^{-3}mol) was placed in a small vial with styrene (0.90g, 8.60×10^{-3}mol) and H$_2$PtCl$_6$ (5μl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for one day.

Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear liquid.

Yield: 1.40g, (73.9%); ν_{max} (film/cm^{-3}) (mixture) 2897 (C-H), 2594, 2435, 1432 (C=C),

1321 (C-C), 1232, 1198, 1078 (Si-O);

[CH$_3$CH$_2$]$_3$Si{(CH$_2$)$_2$C$_6$H$_5$}: δ_H (300MHz, CDCl$_3$) 0.53 (6H, q, J 7.4, SiCH_2CH$_3$), 0.59

(2H, t, J 7.0, SiCH_2R), 0.95 (9H, t, J 7.4, SiCH$_2$CH_3), 2.48 (2H, t, J 7.0, SiCH$_2$CH_2R),

6.95-7.18 (5H, m, Ph); δ_C (100MHz, CDCl$_3$) 3.12 (SiCH$_2$CH$_3$), 6.24 (SiCH$_2$CH$_3$), 16.58

(SiCH_2R), 38.54 (SiCH$_2$CH$_2$R), 125.84, 127.42, 129.85 and 139.87 (4×CH$_2$); δ_{Si} (79MHz

CDCl$_3$) 6.87; m/z (EI) (mixture) 221 (MH$^+$), 206, 192, 135, 85, 77; (Found: C, 76.49; H,

10.57%; requires C, 76.28; H, 10.97%).

Preparation of Compound 66 [CH$_3$CH$_2$OSi]$_3${(CH$_2$)$_2$C$_6$H$_5$}

Triethoxysilane (1g, 6.09×10^{-3}mol) was placed in a small vial with styrene (0.63g, 6.09×10^{-3}mol) and H$_2$PtCl$_6$ (10µl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear liquid. The reaction was seen to proceed with α and β addition giving (CH$_3$CH$_2$O)$_3$Si{(CH$_2$)$_2$C$_6$H$_5$} (60% by NMR), and (CH$_3$CH$_2$O)$_3$Si{CH(CH$_3$)C$_6$H$_5$} (40% by NMR);

Yield: 1.49g, (90.0%) (mixture); ν_{max} (film/cm^{-3}) (mixture) 2974 (C-H), 2927 (C=C), 2736, 1603 (C=C), 1496, 1454 (C-C), 1390, 1366, 1295, 1167, 1105 (Si-O);

[CH$_3$CH$_2$O]$_3$Si{(CH$_2$)$_2$C$_6$H$_5$}: δ_H (300MHz, CDCl$_3$) 0.86 (2H, t, J 7.15, SiCH$_2$), 1.01 (9H, t, J 7.0, OCH$_2$CH$_3$), 2.52 (2H, t, J 7.1, CH$_2$CH_2Ph), 3.69 (2H, m, J 7.0, SiOCH_2), 7.03 (5H, m, Ar); δ_C (100MHz, CDCl$_3$) 12.46 (SiCH$_2$), 18.19 (SiOCH$_2$$CH_3$), 28.91 (CH$_2$Ph), 58.67 (OCH$_2CH_3$), 125.81 (Ar), 126.08 (Ar), 127.72 (Ar), 128.19 (Ar); δ_{Si} (79MHz, CDCl$_3$) -45.93;

[CH$_3$CH$_2$OSi]$_3${CH(CH$_3$)C$_6$H$_5$}: δ_H (300MHz, CDCl$_3$) 1.00 (9H, t, J 7.0, OCH$_2$CH$_3$), 1.28 (3H, d, J 7.5, CCH_3), 1.30 (1H, m, J 7.5, CCH), 3.61 (2H, t, J 6.96, OCH$_2$CH$_3$), 7.03 (5H, m, Ar); δ_C (100MHz, CDCl$_3$) 15.50 (SiCH), 17.81 (SiCCH$_3$), 18.09 (OCH$_2$CH$_3$), 58.27 (OCH$_2$CH$_3$), 125.51 (Ar), 126.68 (Ar), 127.78 (Ar), 143.93 (Ar); δ_{Si} (79MHz, CDCl$_3$) -46.47; m/z (EI) (mixture) 286 (MNH$_4^+$), 269 (M$^+$H), 226, 182, 91, 76, 58, 44; (Found C, 62.8; H, 8.79%; requires C, 62.6; H, 9.00%).

Preparation of Compound 67 [SiO$_{3/2}$]$_8${(CH$_2$)$_2$C$_6$H$_5$}$_8$.

[HSiO$_{3/2}$]$_8$ (0.1g, 2.37×10^{-4}mol), styrene (0.21g, 2.01×10^{-3}mol) and 20µl of a 0.02 moldm^{-3} solution of H$_2$PtCl$_6$ were placed in a vial. The vial was capped and incubated in an oil bath

at 80°C for 3 days. The reaction was followed by FTIR. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a highly viscous gum. Both α and β addition were observed by NMR.

Yield: 0.21%, (72.1%) (mixture); ν$_{max}$ (film/cm^{-3}) (mixture) 3054, 2925 (C=C), 1943 (C-H), 1874, 1697 (C=C), 1589, 1498, 1472 (C-H), 1108 (Si-O);

[SiO$_{3/2}$]$_8${(CH$_2$)$_2$C$_6$H$_5$}$_8$ (60% by NMR): δ$_H$ (400MHz, CDCl$_3$) 0.85 (2H, t, J 7.4, SiCH_2), 2.56 (2H, t, J 7.4, CH_2Ph),7.0 (5H, m, broad, C$_6$H$_5$); δ$_C$ (100MHz, CDCl$_3$) 13.68 (SiCH$_2$), 28.85 (CH$_2$$CH_2$Ph), 125.72 (Ar), 127.82 (Ar), 129.87 (Ar), 137.73 (Ar); δ$_{Si}$ (79MHz, CDCl$_3$) –66.94 (SiO);

[SiO$_{3/2}$]$_8${(CH(CH$_3$)C$_6$H$_5$}$_8$ (40% by NMR): δ$_H$ (400MHz, CDCl$_3$) 1.1 (1H, t, J 7.3, SiCH), 1.5 (3H, m, CHCH_3), 7.0 (5H, m, broad, C$_6$H$_5$); δ$_C$ (100MHz, CDCl$_3$) 14.86 (SiCH), 15.61 (CHCH$_3$), 125.13 (Ar), 127.64 (Ar), 128.15 (Ar), 144.06 (Ar); δ$_{Si}$ (79MHz, CDCl$_3$) –66.70 (SiO); m/z (EI) (mixture) 1258 (M$^+$), 153, 424, 105, 76; (Found C, 60.98; H, 5.61%; requires C, 61.11; H, 5.77%).

Preparation of Compound 68 Si$_8$O$_{12}$[OSi(CH$_3$)$_2$(CH$_2$)$_2$C$_6$H$_5$]$_8$

Si$_8$O$_{12}$[OSi(CH$_3$)$_2$H]$_8$ (1g, 9.84×10^{-4}mol) was dissolved in toluene (25cm^3). To this was added styrene (0.86g, 8.36×10^{-3}mol) and 800μl of a 3% solution of Karstedt's catalyst in xylene. The mixture was refluxed for 24 hours. The solvent was removed under vacuum. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a gum.

Yield: 1.18g, (64.9%); ν$_{max}$ (film/cm^{-3}) 2986 (C-H), 2300 (C=C) 2248, 2137 (C-H), 2098, 1876, 1654 (C=C), 1498, 1432 (C-C), 1414, 1386, 1178, 1088 (Si-O); δ$_H$ (400MHz, CDCl$_3$) 0.05 (6H, s, Si(CH$_3$)$_2$) 0.51 (2H, t, J 6.1, SiCH_2), 2.48 (2H, t, J 6.1, CH_2Ph), 6.87

(2H, m, Ar), 7.05 (2H, m, Ar), 7.16 (1H, m, Ar); δ_C (100MHz, CDCl$_3$) 0.29 (SiCH$_3$), 17.59

(SiCH$_2$), 21.42(CH$_2$$CH_2$), 39.83 ($CH_2$Ph), 126.33 (Ar), 126.70 (Ar), 131.36 (Ar), 142.76

(Ar); δ_{Si} (79MHz, CDCl$_3$) 12.99 (Si(CH$_3$)$_2$), –108.58 (SiO); m/z (EI) 1852 (M$^+$) (Found:

M$^+$ 1851.4680 (EI), Si$_{16}$C$_{80}$H$_{120}$O$_{20}$ requires 1851.4681) 1747, 105, 77; (Found: C, 51.67;

H, 6.43%; requires C, 51.91; H, 6.53%).

Preparation of Compound 69 [CH$_3$CH$_2$]$_3$Si{CH$_2$CH(CH$_3$)C$_6$H$_5$}

Triethylsilane (1g, 8.60×10^{-3}mol) was placed in a small vial with α-methylstyrene (1.02g,

8.60×10^{-3}mol) and H$_2$PtCl$_6$ (5μl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for

one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a

clear liquid.

Yield: 1.68g, (83.1%); ν_{max} (film/cm^{-3}) (mixture) 2897 (C-H), 2695, 1529 (C=C), 1492,

1463 (C-C), 1398, 1279 (C-H), 1105, 1067 (Si-O);

[CH$_3$CH$_2$]$_3$Si{CH$_2$CH(CH$_3$)C$_6$H$_5$}: δ_H (300MHz, CDCl$_3$) 0.32 (2H, d, J 7.2,

SiCH_2CHCH$_3$), 0.64 (6H, q, J 7.5, SiCH_2CH$_3$), 0.73 (9H, t, J 7.5, SiCH$_2$$CH_3$), 1.36 (3H, d,

J 6.8, CCH$_3$), 3.05 (1H, sextet, J 7.2, CHCH$_3$), 7.11-7.19 (5H, m, Ph); δ_C (100MHz, CDCl$_3$

) 3.69 (SiCH$_2$CH$_3$), 7.39 (SiCH$_2$$CCH_3$), 8.43 (SiCH$_2$$CH_3$), 25.56 (SiCH$_2CHCH_3$), 26.48

(SiCH$_2$$CHCH_3$), 125.71 (Ar), 126.56 (Ar), 128.23 (Ar), 130.45 (Ar); δ_{Si} (79MHz CDCl$_3$)

7.02; m/z (EI) (mixture) 234 (M$^+$) (Found: M$^+$234.1804 (EI), SiC$_{15}$H$_{26}$ requires 234.1804)

131, 105, 76; (Found: C, 76.50; H, 11.24%; requires C, 76.84; H, 11.18%).

Preparation of Compound 70 [CH₃CH₂O]₃Si{CH₂CH(CH₃)C₆H₅}

Preparation of Compound 70 $[CH_3CH_2O]_3Si\{CH_2CH(CH_3)C_6H_5\}$

Triethoxysilane (1g, 6.09×10^{-3}mol) was placed in a small vial with α-methylstyrene (0.72, 6.09×10^{-3}mol) and H_2PtCl_6 (5μl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for one day. Filtering a $CHCl_3$ solution through activated charcoal afforded the product as a clear liquid.

$[CH_3CH_2O]_3Si\{CHC(CH_3)C_6H_5\}$ was the major product in more than 95% yield, by NMR.

Yield: 1.46g (84.6%); v_{max} (film/cm^{-3}) (mixture) 2968 (C-H), 2746 (C=C), 2391, 1730 (C=C), 1504, 1492 (C-C), 1321, 1314, 1242, 1209, 1109, 1005 (Si-O);

$[CH_3CH_2O]_3Si\{CH_2CH(CH_3)C_6H_5\}$: δ_H (300MHz, CD_3OD) 1.13 (2H, d, J 7.1, SiCH_2R), 1.15 (9H, t, J 7.5, SiOCH₂CH_3), 1.60 (3H, d, J 7.0, CHCH_3), 3.14 (1H, d, J 7.0, CHCH₃), 3.64 (6H, q, J 7.5, SiOCH_2CH₃), 6.84 (5H, m, Ar); δ_C (100MHz, CD_3OD) 18.40 (SiCH₂R), 20.45 (SiOCH₂CH₃), 25.13 (CCH₃), 26.56 (CHCH₃), 58.45 (SiOCH₂CH₃), 127.45 (Ar), 128.10 (Ar), 128.54 (Ar), 133.08 (Ar); δ_{Si} (79MHz, CD_3OD) -44.67; m/z (EI) 282 (M$^+$), 224, 179, 119, 76, 45; (Found: C, 63.72; H, 9.16%; requires C, 63.78; H, 9.28%).

Preparation of Compound 72 $Si_8O_{12}[OSi(CH_3)_2CH_2CH(CH_3)(C_6H_5)]_8$

$Si_8O_{12}[OSi(CH_3)_2H]_8$ (1g, 9.84×10^{-4}mol) was dissolved in toluene (25cm³). To this was added α-methylstyrene (0.99g, 8.36×10^{-3}mol) and 800μl of a 3% solution of Karstedt's catalyst in xylene. The mixture was refluxed for one day. Solvent was removed under vacuum. Filtering a $CHCl_3$ solution through activated charcoal afforded the product as a clear gum.

Yield: 1.93g, (100%); v_{max} (film/cm^{-3});3062 (C=C), 2959, 2871 (C-H), 1943, 1605 (C=C), 1494, 1453 (C-H), 1408, 1373, 1353, 1255, 1088 (Si-O); δ_H (300MHz, CDCl$_3$) 0.05 (3H, s, SiCH$_3$), 0.07 (3H, s, SiCH$_3$), 1.01, (2H, d, J 7.53, SiCH$_2$), 1.24 (3H, d, J 7.14, CCH$_3$), 2.92 (1H, m, CHCH$_3$), 7.19 (5H, m, Ar); δ_C (100MHz, CDCl$_3$) 0.62 (Si(CH$_3$)$_2$), 25.80 (SiCH$_2$), 26.80 (CHCH$_3$), 27.79 (C(CH$_3$)H), 125.66 (Ar), 126.47 (Ar), 128.19 (Ar), 149.32 (Ar); δ_{Si} (79MHz, CDCl$_3$), 11.88 (Si(CH$_3$)$_2$), -109.08 (SiO); m/z (EI) 1964 (M$^+$), 1859, 1016, 119, 78; (Found: C,54.2; H, 6.85%; requires C, 53.8; H, 7.0%).

Preparation of Compound 73 [CH$_3$CH$_2$]$_3$Si{(CH$_2$)$_3$CO$_2$H}

Triethylsilane (1g, 8.60×10^{-3}mol) was placed in a small vial with but-3-enoic acid (0.74g, 8.60×10^{-3}mol) and H$_2$PtCl$_6$ (5µl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear liquid. [CH$_3$CH$_2$]$_3$Si{(CH$_2$)$_3$CO$_2$H}and the product of oxysilylation of this compound, [CH$_3$CH$_2$]$_3$Si{(CH$_2$)$_3$CO$_2$Si(CH$_2$CH$_3$)$_3$} were observed by NMR in 95% and 5% yield respectively.

v_{max} (film/cm^{-3}) (mixture) 2958 (C-OH), 2914, 2878 (C-H), 2736, 1718 (C=O), 1459, 1415, 1381 (C-H), 1350, 1289, 1266, 1241 (C-H), 1193, 1093, 1043 (Si-O); [CH$_3$CH$_2$]$_3$Si{(CH$_2$)$_3$CO$_2$H}: δ_H (300MHz, CDCl$_3$) 0.47 (2H, t, J 7.3, SiCH_2R), 0.70 (6H, q, J 7.5, SiCH_2CH$_3$), 0.87 (9H, t, J 7.5, SiCH$_2$CH_3), 1.54 (2H, quintet, J 7.5, SiCH$_2$CH_2CH$_2$), 2.21 (2H, t, J 7.5, SiCH$_2$CH$_2$CH_2CO$_2$); δ_C (100MHz, CDCl$_3$) 3.00 (SiCH$_2$R), 4.22 (SiCH$_2$CH$_3$), 5.75 (SiCH$_2$CH$_3$), 18.30 (SiCH$_2$CH$_2$CH$_2$), 35.69 (SiCH$_2$CH$_2$CH$_2$CO$_2$), 173.97 (CO$_2$); δ_{Si} (79MHz, CDCl$_3$) 6.58; (Found: C, 58.94; H, 10.44%; requires C, 59.35; H, 10.96%).

[CH$_3$CH$_2$]$_3$Si{(CH$_2$)$_3$CO$_2$Si(CH$_2$CH$_3$)$_3$}: 0.50 (6H, t, J 7.2, SiCH_2R), 0.83 (12H, q, J 7.8, SiCH_2CH$_3$ ×2), 0.90 (18H, t, J 7.8, SiCH$_2$CH$_3$ ×2), 1.63 (2H, q, J 7.2, SiCH$_2$CH_2CH$_2$CH$_2$), 2.51 (2H, t, J 7.2, SiCH$_2$CH$_2$CH_2CO$_2$); δ_C (100MHz, CDCl$_3$) 3.64 (SiCH_2CH$_3$), 4.85 (SiCH_2R), 5.20 (CO$_2$SiCH_2CH$_3$), 5.79 (SiCH$_2$CH_3), 14.62 (CO$_2$SiCH$_2$CH_3), 18.80 (SiCH$_2$CH_2CH$_2$), 36.81 (SiCH$_2$CH$_2$CH_2CO$_2$), 171.70 (CO$_2$); δ_{Si} (79MHz, CDCl$_3$) 6.65, 24.72; m/z (EI) (mixture) 334 (MNH$_4^+$) 317 (MH$^+$) (Found: MH$^+$ 316.2255(EI), Si$_2$O$_2$C$_{16}$H$_{36}$ requires 316.2254), 287, 203 (MH$^+$) (Found: M$^+$ 202.1383(EI), SiC$_{10}$H$_{22}$O$_2$ requires 202.1389) 173, 132; (Found: C, 61.05; H, 11.53%; requires C, 60.70; H, 11.46%).

Preparation of Compound 74 [CH$_3$CH$_2$O]$_3$Si{(CH$_2$)$_3$CO$_2$H}

Triethoxysilane (1g, 6.09×10^{-3}mol) was placed in a small vial with but-3-enoic acid (0.52g, 6.09×10^{-3}mol) and H$_2$PtCl$_6$ (5μl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear liquid. The reaction was seen to proceed via β addition and oxysilylation giving [CH$_3$CH$_2$O]$_3$Si{(CH$_2$)$_3$CO$_2$H} (80% by NMR), [CH$_3$CH$_2$O]$_3$Si{(CH$_2$)$_3$CO$_2$Si(OCH$_2$CH$_3$)$_3$} (20% by NMR);

v_{max} (film/cm^{-3}) (mixture); 3447 (C-OH), 2978 (C-H), 2934, 2741, 1735 (C=O), 1684, 1457, 1447 (C-C), 1393, 1349, 1260 (C-H), 1080 (Si-O);

[CH$_3$CH$_2$O]$_3$Si{(CH$_2$)$_3$CO$_2$H} (80% by NMR): δ_H (300MHz, CDCl$_3$) 0.83 (2H, t, J 7.3, SiCH$_2$), 1.09 (9H, t, J 7.0, OCH$_2$CH$_3$), 1.55 (2H, quin, J 7.3, CH$_2$) 2.15 (2H, q, J 7.3, CH$_2$CH$_2$CH_2), 4.04 (6H, q, J 7.0, SiOCH_2); δ_C (100MHz, CDCl$_3$) 8.32 (OSiCH_2R), 17.61 (CH_3CH$_2$OSi), 17.93 (CH$_2$CH_2CH$_2$), 36.83 (CH_2CO$_2$), 59.86 (SiOCH_2CH$_3$), 173.50 (CO_2); δ_{Si} (79MHz, CDCl$_3$) -46.47;

[CH$_3$CH$_2$O]$_3$Si{(CH$_2$)$_3$CO$_2$Si(OCH$_2$CH$_3$)$_3$} (20% by NMR): δ$_H$ (300MHz, CDCl$_3$) 0.85 (2H, t, J 7.4, SiCH$_2$R), 1.12 (18H, t, J 7.1, SiOCH$_2$CH$_3$), 1.59 (2H, quin, J 7.4, CH$_2$CH$_2$CH$_2$), 2.21 (2H, t, J 7.4, CH$_2$CO$_2$), 3.73 (6H, m, J 7.1, SiOCH$_2$CH$_3$), 3.81 (6H, J 7.1, SiOCH$_2$CH$_3$); δ$_C$ (100MHz, CDCl$_3$) 8.32 (OSiCH$_2$R), 17.61 (CH$_3$CH$_2$OSi), 17.93 (CH$_2$CH$_2$CH$_2$), 18.15 (CO$_2$SiOCH$_2$CH$_3$), 38.89 (CH$_2$CO$_2$), 59.86 (SiOCH$_2$CH$_3$), 60.36 (CO$_2$SiOCH$_2$CH$_3$), 171.34 (CO$_2$); δ$_{Si}$ (79MHz, CDCl$_3$) -46.47 (SiO$_3$), -88.12 (SiO$_4$); m/z (EI) (mixture) 429 (M$^+$) 413, 398 235, 162, 87, 45.

Preparation of Compound 75 Si$_8$O$_{12}$[(CH$_2$)$_3$CO$_2$H]$_8$

[HSiO$_{3/2}$]$_8$ (0.20g, 4.62×10^{-4}mol), vinyl acetic acid (0.34g, 4.0×10^{-3}mol) and 10µl of a 0.02mol dm^{-3} solution of H$_2$PtCl$_6$ in isopropyl alcohol were placed in a small vial. The vial was capped and placed in an oil bath at 80°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a viscous liquid. The reaction was seen to proceed with α and β addition producing Si$_8$O$_{12}$[(CH$_2$)$_3$CO$_2$H]$_8$ (75% by NMR), and Si$_8$O$_{12}$[CH(CH$_3$)CH$_2$CO$_2$H]$_8$ (25% by NMR);

Yield: 0.31g (61.1%) (mixture); ν$_{max}$ (film/cm^{-3}) (mixture) 2987 (C-OH), 2941, 2731, 1735 (C=O), 1681 (C-C), 1491, 1381 (C-H), 1214, 1178, 1054 (Si-O);

Si$_8$O$_{12}$[(CH$_2$)$_3$CO$_2$H]$_8$: δ$_H$ (300MHz, CDCl$_3$) 0.91 (2H, t, J 7.3, SiCH$_2$) 1.61 (2H, m, J 7.3, CH$_2$CH$_2$), 2.29 (2H, t, J 7.3 CH$_2$CO$_2$); δ$_C$ (100MHz, CDCl$_3$) 13.94 (SiCH$_2$), 19.44, (CH$_2$CH$_2$), 36.83 (CH$_2$CO$_2$), 175.37 (CO$_2$H); δ$_{Si}$ (79MHz, CDCl$_3$) –66.72 (SiO);

Si$_8$O$_{12}$[CH(CH$_3$)CH$_2$CO$_2$H]$_8$: δ$_H$ (300MHz, CDCl$_3$) 0.91 (1H, m, SiCH) 1.14 (3H, d, J 7.71, SiCH$_3$), 1.84 (2H, m, CH$_2$CH$_2$); δ$_C$ (100MHz, CDCl$_3$) 11.34 (SiCH), 17.64 (SiCH$_3$), 37.35 (CH$_2$CO$_2$), 179.31 (CO$_2$H) δ$_{Si}$ (79MHz, CDCl$_3$) –66.72 (SiO); m/z (EI) (mixture)

1130 (MNH$_4^+$), 1113 (MH$^+$) (Found MH$^+$ 1113.3124 (EI), Si$_8$C$_{32}$H$_{57}$O$_{28}$ requires 1113.3124), 1026, 424, 87, 45; (Found: C, 34.13; H, 5.10%; requires C, 34.52; H, 5.07%).

Preparation of Compound 76 Si$_8$O$_{12}$[OSi(CH$_3$)$_2$(CH$_2$)$_3$CO$_2$H]$_8$

Si$_8$O$_{12}$ [OSi(CH$_3$)$_2$H]$_8$ (1g, 9.84×10^{-4}mol) was dissolved in toluene (25cm^3). To this was added vinyl acetic acid (0.72g, 8.36×10^{-3}mol) and 800μl of a 3% solution of Karstedt's catalyst in xylene. The mixture was refluxed for one day. The solvent was removed under vacuum. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear gum.

Yield: 1.60g, (95.4%); ν_{max} (film/cm^{-3}) 2951 (C-OH), 2841 (C-H), 2735, 754 (C=O), 1674, 1549, 1481 (C-C), 1373, 1215, 1183, 1084 (Si-O); δ_H (400MHz, CDCl$_3$) 0.08 (6H, s, Si(CH$_3$)$_2$), 0.99 (2H, t, J 7.2, SiCH$_2$R), 1.58 (2H, m, J 7.2, SiCH$_2$CH$_2$R), 2.34 (2H, t, J 7.2, SiCH$_2$CH$_2$CH$_2$R); δ_C (100MHz, CDCl$_3$) 0.85 (Si(CH$_3$)$_2$), 12.45 (SiCH$_2$R), 20.94 (SiCH$_2$CH$_2$R), 35.84 (SiCH$_2$CH$_2$CH$_2$R), 175.98 (CO$_2$); δ_{Si} (79MHz, CDCl$_3$) 12.04 (Si(CH$_3$)$_2$), -108.27 (SiO); m/z (EI) 1724 (MNH$_4^+$), 1707 (M$^+$), 1620, 1546, 161, 87, 45; (Found: C, 33.51; H, 6.02%; requires C, 33.78; H, 6.14%).

Preparation of Compound 77 [CH$_3$CH$_2$]$_3$Si{(CH$_2$)$_2$CO$_2$(CH$_2$)$_5$CH$_3$}

Triethylsilane (1g, 8.60×10^{-3}mol) was placed in a small vial with hexyl acrylate (1.34g, 8.60×10^{-3}mol) and H$_2$PtCl$_6$ (5μl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear liquid. The reaction was seen to proceed with α and β addition, in a ratio of 5:95, determined by NMR.

Yield: 1.73g, (73.9%) (mixture); v_{max} (film/cm^{-3}) (mixture) 2987 (C-H), 2784, 2479, 1758 (C=O), 1429 (C-C), 1319 (C-H), 1289 (C-O), 1190, 1078 (Si-O);

$[CH_3CH_2]_3Si\{(CH_2)_2CO_2(CH_2)_5CH_3\}$: δ_H (300MHz, CDCl$_3$) 0.56 (6H, q, J 7.3, SiCH$_2$CH_3), 0.59 (2H, t, J 6.9, SiCH_2CH$_2$R), 0.98 (9H, t, J 7.3, SiCH$_2$CH_3), 1.03-1.12 (8H, m, CH_2CH_2CH_2CH_2), 1.50 (3H, t, J 7.3, RCH_3), 2.04 (2H, t, J 6.9, SiCH$_2$CH_2CO$_2$), 3.97 (2H, t, J 7.3, CO$_2$CH_2); δ_C (100MHz, CDCl$_3$) 2.65 (SiCH$_2$R), 3.04 (SiCH$_2$CH$_3$), 6.39 (SiCH$_2$$CH_3$), 16.88 (R$CH_3$), 22.38, 25.39, 28.53 and 29.52 (4×CH$_2$), 38.69 (SiCH$_2$$CH_2CO_2$), 62.82 (CO$_2$$CH_2$), 173.00 ($CO_2$); δ_{Si} (79MHz CDCl$_3$) 7.31; m/z (EI) 273 (MH$^+$), 258, 244, 188; (Found: C, 66.42; H, 11.82%; requires C, 66.12; H, 11.84%).

Preparation of Compound 78 $[CH_3CH_2O]_3Si\{(CH_2)_2CO_2(CH_2)_5CH_3\}$

Triethoxysilane (1g, 6.09×10^{-3}mol) was placed in a small vial with hexyl acrylate (0.95, 6.09×10^{-3}mol) and H$_2$PtCl$_6$ (5μl of a 0.02mol dm^{-3}). The vial was incubated at 80°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear liquid.

$[CH_3CH_2O]_3Si\{(CH_2)_2CO_2(CH_2)_5CH_3\}$ was the major product in more than 95% yield, by NMR.

Yield: 1.64g, (84.1%); v_{max} (film/cm^{-3}) (mixture) 2941 (C-H), 2902, 2781, 1721 (C=O), 1634, 1497, 1415 (C-C), 1378 (C-H), 1264 (C-O), 1081 (Si-O); δ_H (300MHz, CDCl$_3$) 0.56 (2H, t, J 7.2, SiCH_2CH$_2$), 0.96-1.14 (8H, m, CH$_2$CH$_2$CH$_2$CH$_2$), 1.15 (9H, t, J 7.0, SiOCH$_2$CH_3), 1.84 (3H, t, J 7.4, RCH_3), 2.31 (2H, t, J 7.2, CH_2CH$_2$CO$_2$), 4.02 (6H, q, J 7.0, SiOCH_2CH$_3$), 4.46 (2H, t, J 7.4, OCH_2); δ_C (100MHz, CD$_3$OD) 9.05 (SiCH$_2$R), 16.98 (SiOCH$_2$$CH_3$), 18.00 (R$CH_3$), 22.44, 25.12, 26.96, 28.53 (4×CH$_2$), 32.23 (SiOCH$_2$CH$_2$CO$_2$), 58.38 (SiOCH$_2$CH$_3$), 63.45 (CO$_2$$CH_2$), 173.63 ($CO_2$); δ_{Si} (79MHz,

CDCl$_3$) -44.83; m/z (EI) (mixture) 320 (M$^+$) (Found: M$^+$ 320.2021 (EI) SiC$_{15}$H$_{32}$O$_5$ requires 320.2019), 303, 218, 85, 46; (Found: C, 56.19; H, 10.31%; requires C, 56.21; H, 10.06%).

Preparation of Compound 79 Si$_8$O$_{12}$[(CH$_2$)$_2$CO$_2$(CH$_2$)$_5$CH$_3$]$_8$

[HSiO$_{3/2}$]$_8$ (0.20g, 4.62×10^{-4}mol), hexyl acrylate (0.62g, 4.0×10^{-3}mol) and 10µl of a 0.02mol dm^{-3} solution of H$_2$PtCl$_6$ in isopropyl alcohol were placed in a small vial. The vial was capped and placed in an oil bath at 80°C for one day. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a viscous liquid. The reaction was seen to proceed with α and β addition, producing Si$_8$O$_{12}$[(CH$_2$)$_2$CO$_2$(CH$_2$)$_5$CH$_3$]$_8$ (90% by NMR), and Si$_8$O$_{12}$[CHCH$_3$CO$_2$(CH$_2$)$_5$CH$_3$]$_8$ (10% by NMR);

Yield: 0.63g, (76.3%) (mixture); ν_{max} (film/cm^{-3}) (mixture) 2958 (C-H), 2861, 1943, 1858, 1729 (C=O), 1637, 1621, 1605, 1496 (C-C), 1466, 1408, 1380 (C-H), 1296 (C-O), 1265 (C-H), 1191, 1065(Si-O);

Si$_8$O$_{12}$[(CH$_2$)$_2$CO$_2$(CH$_2$)$_5$CH$_3$]$_8$ (90% by NMR): δ_H (300MHz, CDCl$_3$) 0.83 (2H, t, J 7.2, SiCH_2) 1.20-1.26 (11H, m, (CH$_2$)$_4$CH$_3$), 2.29 (2H, t, J 7.2 CH$_2$CO$_2$), 4.02 (2H, t, J 6.8, OCH$_2$); δ_C (100MHz, CDCl$_3$) 10.44 (SiCH$_2$), 13.93 (CH$_3$), 24.95, 25.54, 27.26, 28.55, 29.41 (5×CH$_2$), 64.72 (OCH$_2$), 174.55 (CO$_2$); δ_{Si} (79MHz, CDCl$_3$) –66.72 (SiO);

Si$_8$O$_{12}$[CHCH$_3$CO$_2$(CH$_2$)$_5$CH$_3$]$_8$ (10% by NMR): δ_H (300MHz, CDCl$_3$) 1.08 (1H, m, SiCH) 1.20 (3H, d, J 6.2, SiCH_3), 1.20-1.26 (11H, m, (CH$_2$)$_4$CH$_3$), 4.21 (2H, t, J 6.8, OCH$_2$); δ_C (100MHz, CDCl$_3$) 9.11 (SiCH), 11.31 (SiCH$_3$), 13.93 (CH$_3$), 24.95, 25.54, 27.26, 28.55, 29.61 (5×CH$_2$), 66.95 (OCH$_2$), 172.31 (CO$_2$); δ_{Si} (79MHz, CDCl$_3$) –66.72 (SiO);

m/z (EI) (mixture) 1803 (MNH$_4$$^+$) 1786 (M$^+$), 1615, 1556, 171, 85; (Found: C, 54.01; H, 8.44%; requires C, 53.78; H, 8.57%).

Preparation of Compound 80 Si$_8$O$_{12}$[OSi(CH$_3$)$_2$(CH$_2$)$_2$CO$_2$(CH$_2$)$_5$CH$_3$]$_8$

Si$_8$O$_{12}$[OSi(CH$_3$)$_2$H]$_8$ (1g, 9.84×10^{-4}mol) was dissolved in toluene (25cm^3). To this was added hexyl acrylate (1.31g, 8.36×10^{-3}mol) and 800μl of a 3% solution of Karstedt's catalyst in xylene. The mixture was refluxed for one day. The solvent was removed under vacuum. Filtering a CHCl$_3$ solution through activated charcoal afforded the product as a clear gum.

Yield: 2.31g (98.2%); ν$_{max}$ (film/cm^{-3}) 2958 (C-H), 2932, 2861, 1943, 1858, 1729 (C=O), 1637, 1621, 1605, 1496 (C-C), 1408, 1380 (C-H), 1296, 1265 (C-O), 1191, 1065 (Si-O); δ$_H$ (300MHz, CDCl$_3$) 0.09 (6H, s, Si(CH_3)$_2$), 0.75 (2H, t, J 8.1, SiCH_2R), 1.40-1.51 (11H, m (CH_2)$_4$CH_3), 2.15 (2H, t, J 8.1, SiCH$_2$CH_2R), 4.18 (2H, t, J 7.3, OCH_2); δ$_C$ (100MHz, CDCl$_3$) 0.79 (Si(CH_3)$_2$), 11.84 (SiCH_2R), 13.41 (RCH_3), 25.81, 26.81, 27.41 and 27.98, 28.18 (5×CH_2), 63.42 (CH_2CO$_2$), 173.81 (CO$_2$); δ$_{Si}$ (79MHz, CDCl$_3$) 12.18 (Si(CH$_3$)$_2$), -108.54 (SiO); m/z (EI) 2268 (M$^+$), 2111, 1016, 157, 101, 85; (Found: C, 46.73; H, 8.35%; requires C, 46.61; H, 8.18%).

Preparation of Compound 95 Pentenyl(tetrathylene)monomethylglycol

1-bromopentene (2g, 1.34×10^{-2}mol), tri(ethylene)glycolmonomethylether (2.20g, 1.34×10^{-2}mol) and Na$_2$CO$_3$ (1.44g, 1.34×10^{-2}mol) were mixed together in refluxing acetone (30cm^3) for 4 hours. The solvent was removed under vaccum to produce a pale yellow liquid. This was purified by column chromatography (SiO$_2$/CH$_2$Cl$_2$).

ν$_{max}$ (film/cm^{-1}) 2791 (C-H), 2481 (C-H), 1630 (C=C), 1534 (C=C), 1481 (C-C), 1382 (C-H), 1283 (C-O), 1243 (C-H); δ$_H$ (400MHz, CDCl$_3$) 1.8 (2H, m, J 7.6, CH_2), 2.21 (2H, m, J

7.6, CH_2), 3.10 (3H, S, OCH_3), 3.31 (2H, m, J 7.9, OCH_2), 4.01 (12H, m, OCH_2CH_2), 4.95

(2H, m, J 2.1 *gem*, CH_2CH), 6.85 (1H, m, J 6.7, *cis*, J 19.8, *trans*, CH$_2$CH), δ$_C$ (100MHz,

CDCl$_3$) 27.91, 29.05 (2×CH$_2$), 58.78 (OCH$_3$), 66.71 (OCH$_2$), 68.32, 69.96, 70.11, 70.35,

70.58, 70.64 (6×OCH$_2$); (Found: C, 60.80; H, 10.24%; requires C, 60.85; H, 10.21%).

Preparation of the precursor to Compound 97

Igepal (25g, 5.86×10^{-2}mol), pyridine (4.68g, 5.86×10^{-2}mol) and dry toluene (50cm^3) were

refluxed for 2 hours. Chlorodimethylvinylsilane (14.4g, 1.17×10^{-1}mol) was added to

quench the reaction. The mixture was stirred for a further 2 hours. The reaction was

extracted with water, dried (MgSO$_4$) and solvent was removed under vacuum and purified

by column chromatography (SiO$_2$/hexane:ethylacetate) to produce a clear liquid.

Yield: 28.49g (95.2%); ν$_{max}$ (film/cm^{-1}) 2813 (C-H), 1658 (C=C), 1634, 1581, 1492 (C-C),

1454, 1381, 1363 (C-H), 1331, 1270 (Si-C), 1241, 1211, 1168 (C-O), 1103 (SiO); δ$_H$

(400MHz, CDCl$_3$) 0.21 (6H, s, Si(CH_3)$_2$), 0.70 (9H, s, C(CH_3)$_3$), 1.39 (6H, s, C(CH_3)$_2$),

1.69 (2H, s, CH_2C$_6$H$_4$), 3.64 (2H, t, J 5.7, SiOCH_2CH$_2$), 3.88 (18H, m, CH$_2$(OCH_2CH_2)$_4$),

5.76 (2H, m, J 2.2 *gem*, CH_2CH), 6.21 (1H, m, J 6.7 *cis*, J 20.1 *trans*, CH$_2$CH), 6.80 (2H,

d, J 10.1, C$_6$H$_4$), 7.25 (2H, d, J 10.1, C$_6$H$_4$); δ$_C$ (100MHz, CDCl$_3$) –2.10 (SiCH$_3$), 29.75

(3×CH$_3$), 29.91 (2×CH$_3$), 32.29 (C(CH$_3$)$_3$), 32.35 (C(CH$_3$)$_2$), 32.91 (CH_2Ar) 56.98

(SiOCH$_2$), 62.26, 62.84, 63.34, 63.71, 64.91, 65.02, 66.84, 67.30, 69.82 (9×OCH$_2$), 113.75

(CH_2CH), 126.99 (Ar), 133.27 (Ar), 137.37 (CH$_2$CH), 142.33 (Ar), 156.39 (Ar); δ$_{Si}$

(79MHz, CDCl$_3$) –33.65; *m/z* (EI) 510 (M$^+$) (Found: M$^+$ 510.3373, (EI), SiC$_{28}$H$_{50}$O$_6$,

requires 510.3376), 397, 353, 321, 277, 265, 189, 113, 101, 85, 57, 43, 29; (Found: C,

65.96; H, 9.83%; requires C, 65.84; H, 9.87%).

Preparation of the precursor to Compound 98. $CH_2CHSi(CH_3)O(CH_2CH_2O)_3C_4H_9$

Tri(ethylene)glycolmonobutylether (7.26g, 2.5×10^{-2}mol), pyridine (1.98g, 2.5×10^{-2}mol) and dry toluene (50 cm^3) were refluxed for 1 hour. Chlorodimethylvinylsilane (6.1g, 5.00×10^{-2}mol) was added to quench the reaction. The mixture was stirred for a further 2 hours. The reaction was extracted with water, dried (MgSO$_4$) and solvent was removed under vacuum and purified by column chromatography (SiO$_2$/hexane:ethylacetate) to produce a clear liquid.

Yield: 15.02g (93.4%); ν_{max} (film/cm^{-1}) 2823 (C-H), 1661 (C=C), 1627, 1584, 1495 (C-C), 1438, 1330, 1300 (C-H), 1265 (Si-C), 1230, 1221, 1166 (C-O), 1106 (SiO); δ_H (400MHz, CDCl$_3$) 0.20 (6H, s, Si(CH_3)$_2$), 0.97 (3H, t, J 7.8, CH$_3$), 1.42 (2H, m, J 7.8, m, OCH$_2$CH$_2$CH_2CH$_3$), 1.64 (2H, m, J 7.8, OCH$_2$CH_2CH$_2$CH$_3$), 3.46 (2H, t, J 6.6, SiOCH_2), 3.61 (12H, m, CH$_2$(OCH_2CH_2)$_4$), 5.98 (2H, m, J 2.3, gem, CH_2CH), 6.41 (1H, m, J 6.7 cis, J 12.9, trans, CH$_2$CH); δ_C (100MHz, CDCl$_3$) 0.60 (SiCH$_3$), 13.73 (CH$_3$CH$_2$CH$_2$CH$_2$O), 18.90 (CH$_3$CH$_2$CH$_2$CH$_2$O), 21.10 (CH$_3$CH$_2$CH$_2$CH$_2$O), 31.37 (CH$_3$CH$_2$CH$_2$CH$_2$O), 61.23, 69.69, 69.73, 70.00, 70.24, 72.12, (6×OCH$_2$), 118.91 (CH$_2$CH), 137.08 (CH$_2$CH); δ_{Si} (79MHz, CDCl$_3$) −35.23; m/z (EI) 290 (M$^+$), 233, 189, 145, 101, 57, 44; (Found: C, 57.84; H, 10.25%; requires C, 57.89; H, 10.41%).

Preparation of the precursor to Compound 99. $CH_2CHSi(CH_3)_2O(CH_2CH_2O)_3CH_3$

Tri(ethylene)glycolmonomethylether (39.41g, 0.24mol), pyridine (18.98g, 0.24mol) and dry toluene (100 cm^3) were refluxed for 2 hours. Chlorodimethylvinylsilane (57.9g, 0.48 mol) was added to quench the reaction. The mixture was stirred for a further 2 hours. The reaction was extracted with water, dried (MgSO$_4$) and solvent was removed under vacuum

and purified by column chromatography (SiO$_2$/hexane:ethylacetate) to produce a clear liquid.

Yield: 13.77g (94.6%); ν_{max} (film/cm^{-1}) 2879 (C-H), 1679 (C=C), 1643, 1595, 1454 (C-C), 1409, 1357, 1300 (C-H), 1291, 1264 (Si-C), 1253, 1201, 1169 (C-O), 1089 (SiO); δ_H (400MHz, CDCl$_3$) 0.34 (6H, s, Si(CH_3)$_2$), 3.46 (3H, s, OCH_3), 3.96 (12H, m, OCH$_2$CH$_2$(OCH_2CH_2)$_2$), 5.86 (2H, m, J 3.1, gem, CH_2CH), 6.19 (1H, m, J 6.7 cis, J 14.9, $trans$, CH$_2$CH); δ_C (100MHz, CDCl$_3$) 0.58 (SiCH$_3$), 59.03 (SiOCH$_2$), 69.81 (OCH$_3$), 70.57, 72.81, 72.14, 72.67, 72.80 (5×OCH$_2$), 125.54 (CH$_2$CH), 138.18 (CH$_2$CH); δ_{Si} (79MHz, CDCl$_3$) –36.48; m/z (EI) 248 (M$^+$) (Found: M$^+$ 248.3796, (EI), SiC$_{11}$H$_{24}$O$_4$, requires 248.3766), 217, 173, 163, 129, 119, 85, 75, 44, 31; (Found: C, 53.47; H, 9.58%; requires C, 53.19; H, 9.74%).

Preparation of Allyl Igepal silane. CH$_2$CHCH$_2$Si(CH$_3$)$_2$O(CH$_2$CH$_2$O)$_5$C$_6$H$_4$C$_8$H$_{17}$

Igepal (25g, 5.86×10^{-2}mol), pyridine (4.68g, 5.86×10^{-2}mol) and dry toluene (50 cm^3) were refluxed for 2 hours. Chlorodimethylallylsilane (31g, 0.23mol) was added to quench the reaction. The mixture was stirred for a further 2 hours. The reaction was extracted with water, dried (MgSO$_4$) and solvent was removed under vacuum and purified by column chromatography (SiO$_2$/hexane:ethylacetate) to produce a clear liquid.

Yield: 26.50g (92.9%); ν_{max} (film/cm^{-1}) 2849 (C-H), 2791, 1682 (C=C), 1634, 1491 (C-C), 1423, 1364, 1351 (C-H), 1270 (Si-C), 1241, 1176 (C-O), 1108 (SiO); δ_H (400MHz, CDCl$_3$) 0.16 (6H, s, Si(CH_3)$_2$), 0.79 (9H, s, C(CH_3)$_3$), 1.42 (6H, s, C(CH_3)$_2$), 1.51 (2H, d, J 6.5, CH_2Si), 2.74 (2H, s, C$_6$H$_4$CH_2), 3.65 (2H, t, J 6.5, SiOCH_2CH$_2$), 3.74 (18H, m, CH$_2$(OCH_2CH_2)$_4$), 4.97 (2H, m, J 2.7 gem, CH_2CH), 5.84 (1H, m, J 6.7 cis, J 14.8 $trans$,

CH$_2$CH), 6.90 (2H, d, J 11.7, C$_6$H$_4$), 7.31 (2H, d, J 11.7, C$_6$H$_4$); δ$_C$ (100MHz, CDCl$_3$) 0.40 (SiCH$_3$), 17.95 (SiCH$_2$), 28.57 (3×CH$_3$), 31.82 C(CH$_3$)$_3$), 31.98 (C(CH$_3$)$_2$), 32.09 (C(CH$_3$)$_2$), 32.41 (CH$_2$Ar), 567.11 (SiOCH$_2$), 61.80, 61.99, 62.48, 67.39, 69.94, 70.49, 70.73, 70.94, 72.65, (9×OCH$_2$), 113.99 (CH$_2$CH), 125.41 (Ar), 128.32 (Ar), 134.35 (CH$_2$$C$H), 142.29 (Ar), 156.56 (Ar); δ$_{Si}$ (79MHz, CDCl$_3$) −3.41; m/z (EI) 524 (M$^+$), 411, 367, 335, 291, 279, 247, 189, 115, 113, 57, 43, 29; (Found: C, 66.82; H, 10.04%; requires C, 66.37; H, 9.99%).

Preparation of allyltri(ethylene)butylsilane. CH$_2$CHCH$_2$Si(CH$_3$)$_2$O(CH$_2$CH$_2$O)$_3$C$_4$H$_9$

Tri(ethylene)glycolmonobutyl (4.95g, 2.4×10^{-2}mol), pyridine (1.89g, 2.4×10^{-2}mol) and dry toluene (25cm^3) were refluxed for 1 hour. Chlorodimethylallylsilane (6.46g, 0.89 mol) was added to quench the reaction. The mixture was stirred for a further 2 hours. The reaction was extracted with water, dried (MgSO$_4$) and solvent was removed under vacuum and purified by column chromatography (SiO$_2$/hexane:ethylacetate) to produce a clear liquid.

Yield: 26.50g (92.9%); ν$_{max}$ (film/cm^{-1}) 2874 (C-H), 1691 (C=C), 1639, 1482 (C-C), 1431, 1358 (C-H), 1281 (Si-C), 1240, 1181 (C-O), 1070 (Si-O); δ$_H$ (400MHz, CDCl$_3$) 0.03 (6H, s, Si(CH_3)$_2$), 0.54 (2H, d, J 7.4, SiCH_2), 0.81 (3H, q, J 7.8, RCH_3), 1.13 (2H, q, J 7.8, CH_2CH$_3$), 1.39 (2H, q, J 7.8, CH_2CH$_2$CH$_3$), 3.15 (2H, t, J 7.1, SiOCH_2CH$_2$), 3.81 (12H, m, (OCH_2CH$_2$), 5.14 (2H, m, J 2.9, *gem*, CH_2CH), 5.91 (1H, m, J 6.9 *cis*, J 20.43 *trans*, CH$_2$CH); δ$_C$ (100MHz, CDCl$_3$) 0.21 (2×SiCH$_3$), 14.91 (CH$_3$), 19.31 (SiCH$_2$), 24.31 and 26.71 (2×CH$_2$), 61.34, 61.84, 62.09, 62.18, 62.59, 63.01, 63.34 (7×OCH$_2$), 115.31 (CH$_2$CH), 134.91 (CH$_2$$C$H); δ$_{Si}$ (79MHz, CDCl$_3$) −3.18; m/z (EI) 304 (M$^+$), 289, 247, 203, 189, 159, 115, 101, 57, 44, 15; (Found: C, 59.31; H, 10.74%; requires C, 59.17; H, 10.59%).

Preparation of Allyltri(ethylene)methylsilane. $CH_2CHCH_2Si(CH_3)_2O(CH_2CH_2O)_3CH_3$

Tri(ethylene)glycolmonomethyl (3.94g, 2.4×10^{-2}mol), pyridine (1.89g, 2.4×10^{-2}mol) and dry toluene (25cm^3) were refluxed for 1 hour. Chlorodimethylallylsilane (6.46g, 0.89 mol) was added to quench the reaction. The mixture was stirred for a further 2 hours. The reaction was extracted with water, dried (MgSO$_4$) and solvent was removed under vacuum and purified by column chromatography (SiO$_2$/hexane:ethylacetate) to produce a clear liquid.

Yield: 5.74g, (91.2%); v_{max} (film/cm^{-1}) 2871 (C-H), 2783, 1681 (C=C), 1674, 1631 (C=C), 1591, 1501, 1438 (C-C), 1348, 1329 (C-H), 1281, 1265 (Si-C), 1201, 1168 (C-O), 1108 (SiO); δ_H (400MHz, CDCl$_3$) 0.27 (6H, s, Si(CH$_3$)$_2$), 1.68 (2H, d, J 8.8, SiCH$_2$), 3.27 (3H, s, OCH$_3$), 3.64 (12H, m, (OCH$_2$CH$_2$)$_3$), 5.02 (2H, m, J 2.4, *gem*, CH$_2$CH), 5.89 (1H, m, J 6.9 *cis*, J 19.8, *trans*, CH$_2$CH); δ_C (100MHz, CDCl$_3$) 1.38 (SiCH$_3$), 26.53 (SiCH$_2$), 59.29 (SiOCH$_2$), 61.78 (OCH$_3$), 70.58, 70.75, 70.81, 70.89, 72.19 (5×OCH$_2$), 113.80 (CH$_2$CH), 134.63 (CH$_2$CH); δ_{Si} (79MHz, CDCl$_3$) −3.01; *m/z* (EI) 262 (M$^+$) , 231, 187, 163, 143, 119, 99, 75, 44, 31; (Found: C, 54.83; H, 9.79%; requires C, 54.93; H, 9.99%).

Preparation of the precursor to Compound 104.

$CH_2CH(CH_2)_2CO_2(CH_2CH_2O)_5C_6H_4CH_2C(CH_3)_2C(CH_3)_3$

Igepal (15.78g, 3.7×10^{-2}mol) was added to a stirred mixture of pentenoic acid (3.6g, 3.7×10^{-2}mol) and trifluoroacetic anhydride (9.20g, 4.3×10^{-2}mol) in dry dichloromethane (50 cm^3). The flask was fitted with a CaCl$_2$ drying tube and the mixture stirred over night at room temperature. Solvent was removed under vacuum, before purification by column chromatography (SiO$_2$/CH$_2$Cl$_2$:CH$_3$OH).

Yield: 17.39g, (92.4%); v_{max} (film/cm^{-1}) 2954 (C-H),1786 (C=O), 1634 (C=C), 1611, 1582, 1513, 1447 (C-C), 1416, 1387, 1366 (C-H), 1349, 1295, 1246, 1175 (C-O); δ_H (400MHz, CDCl$_3$) 0.76 (9H, s, C(CH$_3$)$_3$), 1.42 (6H, s, C(CH$_3$)$_2$), 2.41(2H, m, J 7.1, CH$_2$CH$_2$CO$_2$), 2.63 (2H, m, J 7.1, CH$_2$CH$_2$CO$_2$), 2.75 (2H, s, C$_6$H$_4$CH$_2$), 3.37 (18H, m, CH$_2$(OCH$_2$CH$_2$)$_4$), 4.46 (2H, t, J 7.1, CO$_2$CH$_2$), 5.27 (2H, m, J 2.8, *gem*, CH$_2$CH), 5.36 (1H, m, J 6.7, *cis*, J 19.8, *trans*, CH$_2$CH), 6.35 (2H, d, J 11.9, Ar), 7.38 (2H, d, J 11.9, Ar); δ_C (100MHz, CDCl$_3$) 26.31 (CH$_2$), 28.57 (CH$_2$), 28.70 (3×CH$_3$), 32.23 (2×(CH$_3$), 32.43 (C(CH$_3$)$_3$), 32.54 (C(CH$_3$)$_2$), 34.78 (C$_6$H$_4$CH$_2$), 56.90, 59.95, 61.41, 63.35, 66.81, 67.12, 68.06, 69.07, 69.73, 69.99 (10×OCH$_2$), 113.61 (Ar), 115.61 (CH$_2$CH), 126.98 9 (Ar), 136.31 (CH$_2$CH), 142.48 (Ar), 156.13 (Ar), 173.22 (CO$_2$); *m/z* (EI) 508 (M$^+$), 395, 351,319, 275, 263, 237, 189, 187, 113, 99, 83, 57, 43, 29; (Found: C, 68.51; H, 9.45%; requires C, 68.48; H, 9.51%).

Preparation of the precursor to Compound 105. CH$_2$CHCH$_2$CO$_2$(CH$_2$CH$_2$O)$_3$C$_4$H$_9$

Tri(ethyleneglycol)monobutylether (10g, 4.8×10^{-2}mol) was added to a stirred mixture of pentenoic acid (4.81, 4.8×10^{-2}mol) and trifluoroacetic anhydride (11.72g, 5.6×10^{-2}mol) in dry dichloromethane (50 cm^3). The flask was fitted with a CaCl$_2$ drying tube and the mixture stirred over night at room temperature. Solvent was removed under vacuum, before purification by column chromatography (SiO$_2$/CH$_2$Cl$_2$:CH$_3$OH).

Yield: 11.74g, (84.8%); v_{max} (film/cm^{-1}) 1785 (C=O), 1684 (C=C), 1615, 1480 (C-C), 1416, 1384, 1365 (C-H), 1221, 1175 (C-H), 1168 (C-O),; δ_H (400MHz, CDCl$_3$) 0.52 (3H, q, J 7.3, CH$_2$CH$_3$), 1.19 (2H, m, J 7.3, CH$_2$CH$_3$), 1.37 (2H, m, J 7.3, CH$_2$CH$_2$CH$_3$), 2.22 (2H, m, J 6.2, CH$_2$CH$_2$CO$_2$), 2.37 (2H, m, J 6.2, CH$_2$CH$_2$CO$_2$), 3.20 (2H, t, J 7.2, OCH$_2$CH$_2$CH$_2$CH$_3$), 3.46 (10H, m, CH$_2$(OCH$_2$CH$_2$)$_2$), 3.62 (2H, t J 7.1, CO$_2$CH$_2$R), 5.11

(2H, m, J 2.2, *gem*, CH_2CH), 5.70 (1H, m, J 6.8, *cis*, J 19.8, *trans*, CH$_2$CH); δ_C (100MHz, CDCl$_3$) 13.25 (*C*H$_3$), 18.76 (CH$_3$*C*H$_2$), 27.60 (CH$_3$CH$_2$*C*H$_2$), 31.28 (*C*H$_2$CH$_2$CO$_2$), 66.64, 67.64, 68.48, 69.60, 69.87, 70.16 and 70.54 (7×O*C*H$_2$), 72.13 (CO$_2$*C*H$_2$), 115.44 (*C*H$_2$CH), 135.35 (CH$_2$*C*H), 168.10 (*C*O$_2$); *m/z* (EI) 274 (M$^+$) (Found: M$^+$ 274.1936, (EI), C$_{14}$H$_{26}$O$_5$, requires 274.1937), 217, 175, 172, 130, 128, 86, 44; (Found: C, 62.64; H, 9.67%; requires C, 62.48; H, 9.79%).

Preparation of the precursor to Compound 106. CH$_2$CH(CH$_2$)$_2$CO$_2$(CH$_2$CH$_2$O)$_3$CH$_3$

Tri(ethyleneglycol)monomethylether (11.36g, 6.9×10^{-2}mol) was added to a stirred mixture of pentenoic acid (6.95g, 6.9×10^{-2}mol) and trifluoroacetic anhydride (14.89g, 8.1×10^{-2}mol) in dry dichloromethane (50 cm^3). The flask was fitted with a CaCl$_2$ drying tube and the mixture stirred over night at room temperature. Solvent was removed under vacuum, before purification by column chromatography (SiO$_2$/CH$_2$Cl$_2$:CH$_3$OH).

Yield: 11.74g, (84.8%); ν_{max} (film/cm^{-1}) 1790 (C=O), 1644 (C=C), 1624, 1455 (C-C), 1424, 1392, 1345 (C-H), 1223, 1170 (C-H), 1169 (C-O); δ_H (400MHz, CDCl$_3$) 2.26 (2H, m, J 7.3, CH_2CH$_2$CO$_2$), 2.41 (2H, m, J 7.3, CH$_2$CH_2CO$_2$), 3.35 (3H, s, OCH_3), 3.50 (10H, m, CH$_2$(OCH$_2$CH$_2$)$_2$), 3.65 (2H, t J 7.3, CO$_2$CH_2), 4.95 (2H, m, J 2.2, *gem*, CH_2CH), 5.67 (1H, m, J 6.9, *cis*, J 18.9, *trans*, CH$_2$CH); δ_C (100MHz, CDCl$_3$) 31.43 (CH$_2$), 33.08 (CH$_2$), 58.94 (OCH$_3$), 63.17, 66.74, 67.85, 68.82, 69.77 (5×OCH$_2$), 70.79 (CO$_2$CH_2), 115.08 (CH$_2$*C*H), 136.35 (*C*H$_2$CH), 172.54 (CO$_2$); *m/z* (EI) 246 (M$^+$), 215, 171, 163, 146, 127, 119, 101, 83, 44, 31; (Found: C, 58.38; H, 9.27%; requires C, 58.52; H, 9.00%).

Preparation of via grignard reagents, Compound 109. Br(CH₂)₄O(CH₂CH₂O)₃CH₃

Tri(ethyleneglycol)monomethylether (3.94g, 2.4×10^{-2}mol) and NaH (0.57g, 2.4×10^{-2}mol) were mixed together in dry THF (30cm³). The mixture was then added to dibromobutane (10.36g, 4.8×10^{-2}mol) under nitrogen and refluxed overnight. The solution was filtered, and reduced under vacuum resulting in a clear liquid. The liquid was purified by column chromatography (SiO₂/ethyl acetate/hexane).

Yield: 3.25g, (45.2%); v_{max} (film/cm⁻¹) 1494, 1455 (C-C), 1432, 1384, 1354 (C-H), 1220 (C-O), 1189 (C-H), 1179 (C-O), 730 (C-Br); δ_H (400MHz, CDCl₃) 1.53 (2H, m, BrCH₂C*H₂*CH₂CH₂O), 1.60 (2H, m, BrCH₂CH₂C*H₂*CH₂O), 3.10 (3H, s, OCH₃) 3.41 (14H, m, (OC*H₂*C*H₂*)₃OC*H₂*), 3.53 (3H, t, *J* 7.6, C*H₂*Br); δ_C (100MHz, CDCl₃) 30.91 (2×*C*H₂), 31.53 (Br*C*H₂), 58.78 (OCH₃), 68.32, 69.96, 70.11, 70.24, 70.35, 70.38, 70.64 (7×O*C*H₂), *m/z* (EI) 299 (MH⁺) 268, 224, 180, 136, 122, 44, 31; (Found: C, 44.35; H, 7.45%; requires C, 44.16; H, 7.75%).

Preparation of Compound 111 Dimethylsilylpentylpolyethyleneglycol.
ClSi(CH₃)₂(CH₂)₅O(CH₂CH₂O)₄CH₃

Pentenyl(tetraethylene)monomethylether (5.8g, 2.1×10^{-2}mol), chlorodimethylsilane (2g, 2.1×10^{-2}mol) with H₂PtCl₆ 10μl of a 0.02mol dm⁻³ solution of H₂PtCl₆ in isopropyl alcohol were placed in a small vial. The vial was capped and placed in an oil bath and maintained at 60°C for one day. The product was a clear liquid.

Yield: 7.51g, (96.4%); v_{max} (film/cm⁻¹) 1494, 1455 (C-C), 1432, 1384, 1354 (C-H), 1286 (Si-C), 1220, 1189 (C-H), 1170 (C-O), 960 (Si-Cl); δ_H (400MHz, CDCl₃) 0.02 (6H, s,

2×SiCH$_3$), 0.51 (2H, t, J 6.03, SiCH_2), 1.18 (2H, m, J 6.03, SiCH$_2$CH_2), 1.34 (2H, t, J 6.03, SiCH$_2$CH$_2$CH_2), 1.6 (2H, m, J 6.03, SiCH$_2$CH$_2$CH$_2$CH_2), 3.35 (3H, s, OCH_3), 3.52 (2H, m, J 6.03, CH$_2$CH$_2$CH_2O), 3.64 (16H, m, (OCH$_2$CH$_2$)$_3$); δ_C (100MHz, CDCl$_3$) 0.72 (SiCH$_3$), 17.79 (SiCH$_2$), 22.77 (SiCH$_2$CH$_2$), 28.50 (SiCH$_2$CH$_2$CH$_2$), 33.80 (SiCH$_2$CH$_2$CH$_2$CH$_2$), 58.84 (OCH$_3$), 61.53, 63.22, 63.66, 66.83, 67.18, 68.06, 69.07, 70.15, 70.44 (9×OCH$_2$); δ_{Si} (79MHz, CDCl$_3$) 6.69; m/z (EI) 371 (MH$^+$), 340, 296, 277, 252, 208, 164, 94, 44, 31; (Found: C, 51.76; H, 9.37%; requires C, 51.80; H, 9.51%).

Preparation of Tri(ethylene)tosylatemonobutylether. CH$_3$C$_6$H$_4$SO$_3$(CH$_2$CH$_2$O)$_3$C$_4$H$_9$

Tri(ethyleneglycol)monobutylether (9.33g, 4.5×10^{-2}mol), tosyl chloride (8.62g, 4.5×10^{-2}mol) and pyridine (3.55g, 4.5×10^{-2}mol) were stirred at 0°C for one hour. The solution was allowed to reach room temperature, CH$_2$Cl$_2$ (100cm^3) was added and the solution was then washed with dilute HCl (100cm^3) and saturated NaHCO$_3$ solution (100cm^3). The organic layer was extracted and dried (MgSO$_4$) before removal of solvent under vacuum. The white solid was purified by column chromatography (SiO$_2$/CH$_2$Cl$_2$).

Yield: 16.05g, (99%); ν_{max} (Nujol mull/cm^{-1}) 2984 (C-H), 1600 (C=C), 1482 (C-H), 1369, 1342 (SO$_2$), 1243, (C-O), 1181, 1131, 1081 (C-H), 1051 (S=O); δ_H (400MHz, CDCl$_3$) 0.51 (3H, t, J 7.4, RCH_3), 0.94 (2H, m, J 7.4, CH_2CH$_3$), 1.16 (2H, t, J 7.4, CH_2CH$_2$CH$_3$), 2.02 (3H, s, ArCH_3), 3.02 (2H, t, OCH_2CH$_2$CH$_2$CH$_3$), 3.18 (10H, m, OCH_2CH_2), 3.73 (2H, t, J 7.3, OCH_2OSO$_2$), 6.93 (2H, d, J 10.3, ArH), 7.39 (2H, d, J 10.3, ArH); δ_C (100MHz, CDCl$_3$) 13.87 (CH$_3$), 19.23 (CH$_2$CH$_3$), 21.59 (CH$_2$CH$_2$CH$_3$), 31.67 (ArCH$_3$), 61.74 (OCH$_2$CH$_2$CH$_2$CH$_3$), 60.64, 69.20, 70.00, 70.35, 70.51, 70.55 (6×OCH$_2$), 129.94, 129.76, 133.00 and 144.72 (4×Ar); m/z (EI) 360 (M$^+$) (Found: M$^+$ 360.1609, (EI), C$_{17}$H$_{28}$O$_6$S,

requires 360.1607), 303, 259, 215, 189, 171, 145, 101, 79,77, 57, 44, 29; (Found: C, 56.41; H, 7.74%; requires C, 56.65; H, 7.83%).

Preparation of Tri(ethylene)azide monobutylether. $N_3(CH_2CH_2O)_3C_4H_9$

The tri(ethylene)tosylatemonobutylether (1.87g, 5.0×10^{-2}mol) was dissolved in dry CH_3CN (30cm^3) NaN_3 (0.65g, 1.0×10^{-2}mol) was added and the solution refluxed under nitrogen overnight. Solvent was removed under vacuum and the remaining yellow solution dissolved in CH_2Cl_2 (50cm^3). Following extraction with water the organic layer was dried ($MgSO_4$) and reduced under vacuum. The yellow liquid was purified by column chromatography (SiO_2/Ethylacetate, R_f: 0.83).

Yield: 1.96g, (85%); ν_{max} (film/cm^{-1}) 2959 (C-H), 1742, 1639 (N=N), 1599, 1461 (C-H), 1376, 1300 (C=O), 1241 (C-O), 1127, 1048; δ_H (400MHz, CDCl$_3$) 0.82 (3H, t, J 7.1, RCH_3), 1.23 (2H, t, J, 7.4, CH_2CH$_3$), 1.46 (2H, t, J 7.4, CH_2CH$_2$CH$_3$), 2.14 (2H, t, CH_2N$_3$), 3.28 (2H, t, OCH_2CH$_2$CH$_2$CH$_3$), 3.49 (10H, m, OCH_2CH$_2$); δ_C (100MHz, CDCl$_3$) 14.91 (CH$_3$), 19.31 (CH$_2$CH$_3$), 21.42 (CH$_2$CH$_2$CH$_3$), 57.98 (CH$_2$N$_3$), 62.01 (OCH$_2$CH$_2$CH$_2$CH$_3$), 63.42, 63.81, 64.92, 65.76, 66.01 (5×OCH$_2$); m/z (EI) 231 (M$^+$), 188, 174, 158, 144, 114, 73, 70, 57, 54, 40, 43, 29, 15; (Found: C, 51.56; H, 9.34%; requires C, 51.93; H, 9.15%).

Preparation of Compound 117 Tri(ethylene)aminemonobutylether.
$NH_2(CH_2CH_2O)_3C_4H_9$

Tri(ethylene)azidemonobutylether (0.74g, 2.99×10^{-3}mol), triphenylphosphine (0.86, 3.29×10^{-3}mol), water (0.08g, 4.9×10^{-3}mol) were mixed together in THF (10cm^3). The

solution was stirred at room temperature overnight. The solution was reduced under vacuum, yielding a yellow liquid.

Yield: 0.48g, (84.4%) ν_{max} (film/cm^{-1}) 2927 (C-H), 1597 (NH), 1461 (C-H), 1378, 1300 (C-O), 1249 (C-O), 1121, 981; δ_H (400MHz, CDCl$_3$) 0.87 (3H, t, J 6.2, RCH_3), 1.33 (2H, q, J 6.2, CH_2CH$_3$), 1.51 (4H, m, CH_2CH$_2$CH$_3$ and NH_2), 2.80 (2H, m, CH_2NH$_2$), 3.41 (2H, m, OCH_2CH$_2$CH$_2$CH$_3$), 3.58 (10H, m, OCH_2CH_2); δ_C (100MHz, CDCl$_3$) 14.03(CH$_3$), 19.41 (CH$_2$CH$_3$), 21.70 (CH$_2$CH$_2$CH$_3$), 34.89 (CH$_2$NH$_2$), 61.80 (OCH$_2$CH$_2$CH$_2$CH$_3$), 60.71, 6.03, 70.14, 70.51, 70.66 (5×OCH$_2$); m/z (EI) 205 (M$^+$) (Found: M$^+$ 205.2812, (ES), C$_{10}$H$_{23}$NO$_3$, requires 205.1043), 148, 135, 118, 104, 74, 57, 44, 43; (Found: C, 70.38; H, 11.52%; requires C, 70.24; H, 11.22%).

Preparation of Compound 116: Preparation of Igepaltosylate.

CH$_3$C$_6$H$_4$SO$_3$(CH$_2$CH$_2$O)$_5$C$_6$H$_4$C$_8$H$_{17}$

Igepal (20.25g, 4.7×10^{-2}mol), tosyl chloride (18.09g, 9.5×10^{-2}mol) and pyridine (3.7g, 4.7×10^{-2}mol) were mixed together and stirred at 0°C overnight. The reaction was allowed to reach room temperature. CH$_2$Cl$_2$ (250cm^3) was added and the solution was then washed with dilute HCl (250cm^3) and saturated NaHCO$_3$ solution (250cm^3). The organic layer was extracted and dried (MgSO$_4$) before removal of solvent under vacuum. The white solid was purified by column chromatography (SiO$_2$/CH$_2$Cl$_2$).

Yield: 27.4g, (98.5%); ν_{max} (Nujol mull/cm^{-1}) 2956 (C-H), 1603 (C=C), 1581 (C-H), 1534, 1484 (C-H), 1395, 1364 (SO$_2$), 1386, 1365, 1296 (C-O), 1246, 1187, 1053 (S=O), 946, 850, 786 (C-H); δ_H (400MHz, CDCl$_3$) 0.65 (9H, s, (CCH_3)), 1.33 (6H, s, C(CH_3)), 1.70 (2H, s, CH_2C(CH$_3$)$_2$C(CH$_3$)$_3$), 2.40 (3H, s, CH_3Ar), 3.37 (2H, t, J 7.5, ArOCH_2), 3.57

(16H, m, OCH_2CH_2), 4.09 (2H, m, OCH_2SO$_2$), 6.83 (2H, d, ArH), 6.93 (2H, d J 10.3, Ar), 7.39 (2H, d, J 10.3, ArH), 7.78 (2H, d, J 13.9, ArH); δ_C (100MHz, CDCl$_3$) 21.52 (CCH_3), 31.66 (CCH_3), 32.20 (C$(CH_3)_2$), 37.81 (C(CH_3)), 56.86 (CH_2Ar), 57.61 (CH_3Ar), 67.15, 68.54, 68.59, 69.15, 69.69, 69.75, 70.36, 70.41, 70.46, 70.52 (10×OCH_2), 113.64, 126.90, 127.85, 129.72, 132.89, 142.24, 144.68, and 156.24 (8×Ar); m/z (EI) 580 (M$^+$), 467, 423, 409, 391, 365, 347, 335, 277, 259, 189, 171, 113, 77, 57, 43, 29; (Found: C, 64.59; H, 8.42%; C$_{31}$H$_{48}$O$_8$S requires C, 64.11; H, 8.33%).

Preparation of IgepalAzide. N$_3$(CH$_2$CH$_2$O)$_5$C$_6$H$_4$C$_8$H$_{17}$

Igepaltosylate (12.83g, 2.2×10^{-2}mol) was dissolved in dry CH$_3$CN (100cm^3); NaN$_3$ (2.87g, 4.4×10^{-2}mol) was added and the solution was refluxed under nitrogen overnight. CH$_2$Cl$_2$ (100cm^3) was added to the cooled solution, which was washed with water (100cm^3). The organic layer was extracted, dried (MgSO$_4$) and reduced. The resulting yellow liquid was purified by column chromatography (SiO$_2$/Ethyl acetate, R$_f$: 0.83)

Yield: 8.39g, (84.5%); ν_{max} (film/cm^{-1}) 2953 (C-H), 1611 (N=N), 1581 (C-H), 1521, 1457, 1414, 1395, 1386, 1365, 1296 (C-O), 1246, 1187, 1013, 946, 850, 786 (C-H); δ_H (400MHz, CDCl$_3$) 0.25 (9H, s, (CCH_3)$_3$), 0.78 (6H, s, C(CH_3)$_2$), 1.19 (2H, s, CH_2C(CH$_3$)$_2$C(CH$_3$)$_3$, 2.86 (2H, m, CH_2N=N=N), 3.19 (18H, m, OCH_2CH$_2$), 6.32 (2H, d, J 11.8, ArH), 6.73 (2H, d, J 11.8, ArH); δ_C (100MHz, CDCl$_3$) 31.64 (CCH_3), (32.28 3×CH_3), 32.45 (C$(CH_3)_2$), 32.87 (C$(CH_3)_2$), 37.89 (CH_2CCH$_3$), 56.97 (CH_2N=N=N), 67.26, 69.80, 69.90, 70.00, 70.56, 70.61, 70.68, 70.78, 71.01 (9×OCH_2), 113.72 (Ar), 126.98 (Ar), 142.32 and 156.35 (2×Ar); m/z (EI) 451 (M$^+$), 407, 363, 336, 292, 262, 248, 219, 161, 135, 131, 187, 115, 86, 77, 45, 29; (Found: C, 63.59; H, 9.65%; requires C, 63.83; H, 9.15%).

Preparation of Compound 117. $NH_2(CH_2CH_2O)_5C_6H_4C_8H_{17}$

Igepalazide (5.0g, 1.1×10^{-2}mol), triphenylphosphine (3.17g, 1.2×10^{-2}mol), H_2O (0.32g, 1.8×10^{-2}mol) were mixed together in THF (30cm^3). The solution was stirred overnight at room temperature before being reduced under vacuum to yield a yellow liquid. To the liquid was added pentane (20cm^3) and hexane (20cm^3). The mixture was stirred at room temperature for 1 hour, filter and reduced. The remaining liquid was purified by column chromatography (SiO$_2$/Hexane:Ethyl acetate, 3:2, R$_f$ 0.3).

Yield (3.90g, 83.5%); v_{max} (film/cm^{-1}) 2927 (C-H), 1646 (NH$_2$), 1611 (C=C), 1513, 1461 (C-H), 1366, 1297 (C-O), 1187, 1132, 950, 829, 722 (C-H); δ_H (400MHz, CDCl$_3$) 0.25 (9H, s, (CCH_3)), 0.79 (6H, s, C(CH_3)), 0.96 (2H, m, NH_2), 1.19 (2H, s, CH$_2$Ar), 2.36 (2H, m, CH_2NH$_2$), 3.04 (2H, t, J ArOCH_2CH$_2$), 3.20 (16H, m, OCH_2CH_2), 6.34 (2H, d, J 11.8, ArH), 6.77 (2H, d, J 11.8, ArH); δ_C (100MHz, CDCl$_3$) 31.64 (CCH$_3$), (32.28 3×CH$_3$), 32.45 (C(CH$_3$)$_2$), 32.87 (C(CH$_3$)$_2$), 37.89 (CH$_2$CCH$_3$), 39.54 (CH$_2$NH$_2$), 67.26, 69.80, 69.90, 70.00, 70.56, 70.61, 70.68, 70.78, 71.01 (9×OCH$_2$), 113.72 (Ar), 126.98 (Ar), 142.32 and 156.35 (2×Ar); m/z (FAB) 448 (M$^+$Na) 426 (MH$^+$), 368, 310, 266, 224, 161, 148, 128, 100, 85, 57, 43, 29; (Found: C, 64.75; H, 9.95%; requires C, 64.30; H, 9.67%).

Chromium Complexations

Cr(CO)$_6$ (2g, 9.09×10^{-3}mol) and trimethylphenylsilane (2.73g, 1.82×10^{-2}mol) were stirred with dry toluene (25cm^3) under a nitrogen atmosphere. Upon solvent removal a green liquid was achieved.

Cr(CO)$_6$ (2g, 9.09×10^{-3}mol) and trimethylphenylsilane (2.73g, 1.82×10^{-2}mol) were refluxed in dry toluene (25cm^3) under a nitrogen atmosphere. Upon solvent removal a green liquid was achieved.

Cr(CO)$_6$ (2g, 9.09×10^{-3}mol) and trimethylphenylsilane (2.73g, 1.82×10^{-2}mol) were stirred with dry THF (25cm^3) under a nitrogen atmosphere. Upon solvent removal a green liquid was achieved. A green solid precipitated from the liquid.

PLATINUM REACTIONS

Preparation of [SiO$_{3/2}$]$_8${OSi(Me)$_2$C$_6$H$_5$}$_8$

Tetramethylammonium silicate (1.26g, 1.11×10^{-3}mols) was slowly added to a mixture of heptane (50cm^3), dimethylformamide (100cm^3) and chlorodimethylphenylsilane (50cm^3) previously stirred for twenty minutes at room temperature. The slightly exothermic reaction was allowed to cool to room temperature and was subsequently cooled to 2°C. Distilled water (100cm^3) was added dropwise. The organic layer was then separated and washed with water until the washings attained pH 7. The organic layer was then removed by vacuum distillation.

Yield (1.57g, 86.95%); ν_{max} (Nujol mull/cm^{-1}) 3011 (C-=C), 2941 (C-H), 2871, 1601 (C=C), 1491, 1431 (C-H), 1404, 1008 (Si-O); δ_H (400MHz, CDCl$_3$) 0.07 (3H, s, SiCH$_3$), 0.10 (3H, S, SiCH$_3$), 7.18 (5H, m, Ar); δ_C (100MHz, CDCl$_3$) 0.62 (Si(CH$_3$)$_2$), 120.54 (Ar), 126.57 (Ar), 131.81 (Ar), 139.45 (Ar); m/z (EI) 1626 (M$^+$) (Found: M$^+$ 1624.2178 (EI) Si$_{16}$C$_{64}$H$_{88}$O$_{20}$, requires 1624.2177), 1549, 1472, 77 (Found: C, 47.10; H, 5.22%; requires C, 47.26; H, 5.45%).

Preparation of Compound 123 [SiO$_{3/2}$]$_8$\{OSi(Me)$_2$C$_2$H$_4$\}$_8$

Tetramethylammonium silicate (3.79g, 3.33×10^{-3}mols) was slowly added to a mixture of heptane (100cm^3), dimethylformamide (200cm^3) and chlorodimethylvinylsilane (100cm^3) previously stirred for twenty minutes at room temperature. The slightly exothermic reaction was allowed to cool to room temperature and was subsequently cooled to 2°C. Distilled water (100cm^3) was added dropwise. The organic layer was then separated and washed with water until the washings attained pH 7. The organic layer was then reduced under vacuum at 55°C. The reduced organic solvent was then cooled to 4°C and the precipitated solid was recrystallised from acetone.

Yield (3.10g, 76%); v_{max} (Nujol mull/cm^{-1}) 2942 (C-H), 2861, 1607 (C=C), 1471, 1432 (C-H), 1008 (Si-O); δ_H (400MHz, CDCl$_3$) 0.07 (3H, s, SiCH$_3$), 0.10 (3H, s, SiCH$_3$), 4.85 (2H, m, J 2.5, *gem*, CH_2CH), 5.61 (1H, m, J 6.2 *cis*, J 19.1 *trans*, CH$_2$CH); δ_C (100MHz, CDCl$_3$) 0.62 (Si(CH$_3$)$_2$), 114.81 (*C*H$_2$CH), 137.31 (CH$_2$*C*H); *m/z* (EI) 1233 (M$^+$) (Found: M$^+$ 1233.8039 (EI) Si$_{16}$C$_{32}$H$_{80}$O$_{20}$, requires 1233.8129), 1208, 1181, 27 (Found: C, 31.14; H, 6.51%; requires C, 31.17; H, 6.53%).

Attempted Complexation of H$_2$PtCl$_6$xH$_2$O with [SiO$_{3/2}$]$_8$\{OSi(Me)$_2$C$_2$H$_4$\}$_8$

[SiO$_{3/2}$]$_8$\{OSi(Me)$_2$C$_2$H$_4$\}$_8$ (0.373g, 3.05×10^{-4}mol) and H$_2$PtCl$_6$xH$_2$O (0.25g, 6.10×10^{-4}mol) were placed in a small flask with THF (15cm^3) and water (0.2cm^3). The mixture was refluxed for 4 hours to produce an orange solution.

The cooled solution was then neutralised with NaHCO$_3$ (0.249g, 2.98×10^{-3}mol) then filtered and the solvent removed under vacuum.

Attempted Complexation of PtCl$_2$ with [SiO$_{3/2}$]$_8${Osi(Me)$_2$C$_2$H$_4$}$_8$

PtCl$_2$ (0.085g, 3.22×10^{-4}mol) was dissolved in MEK (30cm^3) at room temperature. A solution of [SiO$_{3/2}$]$_8${OSi(Me)$_2$C$_2$H$_4$}$_8$ (0.407g, 6.43×10^{-4}mol) in MEK (10cm^3) was added with vigorous stirring, under a nitrogen atmosphere. The mixture was refluxed overnight, before removal of the solvent under vacuum to leave a black solid.

Attempted ligand exchange between Compound 122 [(CH$_3$)$_2$SiCHCH$_2$]$_2$O-PtP{^{t}Bu}$_3$ with [SiO$_{3/2}$]$_8${OSi(Me)$_2$C$_2$H$_4$}$_8$

[SiO$_{3/2}$]$_8${OSi(Me)$_2$C$_2$H$_4$}$_8$ (0.1g, 8.17×10^{-5}mol) was dissolved in CH$_2$Cl$_2$ (20cm^3). A solution of the platinum complex (0.048g, 8.17×10^{-5}mol) in CH$_2$Cl$_2$ (20cm^3) and added at room temperature with stirring. The mixture was stirred for 12 hours, before removal of the solvent under vacuum producing a black solid.

[SiO$_{3/2}$]$_8${OSi(Me)$_2$C$_2$H$_4$}$_8$ (0.1g, 8.17×10^{-5}mol) was placed in a small vial with the platinum complex (0.048g, 8.17×10^{-5}mol). The vial was heated to approximately 200°C with an airgun for 10 mins. The emission of a white vapour was noticed, leaving a black solid in the bottom of the vial.

[SiO$_{3/2}$]$_8${OSi(Me)$_2$C$_2$H$_4$}$_8$ (0.1g, 8.17×10^{-5}mol) was dissolved in CHCl$_3$ (20cm^3). A solution of the platinum complex (0.19g, 3.27×10^{-4}mol) in CHCl$_3$ (20cm^3) and added at room temperature with stirring. The mixture was refluxed for 12 hours, before removal of the solvent under vacuum producing a black solid.

CHAPTER SIX

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