

**ROUTES TO SILSESQUIOXANES FUNCTIONALIZATION – CAPPING OF DDSQS  
FOR THE SYNTHESIS OF ASYMMETRIC POSS COMPOUNDS**

**By**

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## **ABSTRACT**

### **ROUTES TO SILSESQUIOXANES FUNCTIONALIZATION – CAPPING OF DDSQS FOR THE SYNTHESIS OF ASYMMETRIC POSS COMPOUNDS**

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Polyhedral oligomeric silsesquioxanes (POSS) have been explored for over 7 decades. These organic/inorganic nanostructures are extremely versatile compounds that are compatible with polymer systems, hence making them ideal components for the synthesis of new materials. Their properties may vary based on the organic peripheral unit, but they generally exhibit high thermal degradation temperatures, low dielectric constant and high degree of hardness as coating agents. Cubic silsesquioxanes and their double decker (DDSQ) counterparts have been the most useful because these compounds possess the architecture that accommodates functionalization. However, most of the progress recorded to date has been limited to the use of DDSQs to synthesize functionally symmetric POSS compound. These compounds do display the desired physicochemical properties, but their applications pose the challenge of tethering them with two dissimilar polymeric chains.

In this thesis, efforts have been made to develop a route for the selective synthesis of asymmetric POSS compounds. The research utilized the versatility of protecting groups to effect selective functionalization of the DDSQ en route to the desired target. The asymmetric POSS cage has the potential to allow its dispersal into two dissimilar polymer matrices, generating a POSS/polymer composite that is unprecedented.

This dissertation is dedicated to my parents, wife and two daughters.

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## KEY TO ABBREVIATIONS

**APCI = Atmospheric Pressure Chemical Ionization**

**BzTMAH = Benzyltrimethylammonium hydroxide**

**DCM = Dichloromethane**

**DDSQ = Double Decker Oligomeric Silsesquioxane**

**DSC = Differential Scanning Calorimetry**

**DPS = Diphenyl-functionalized Silsesquioxane**

**HMBC = Heteronuclear Multiple Bond Correlation**

**ICBM = Intercontinental Ballistic Missile**

**LC/MS = Liquid Chromatography-Mass Spectrometry**

**NASA = National Aeronautics and Space Administration**

**NMR = Nuclear Magnetic Resonance Spectroscopy**

**NOESY = Nuclear Overhauser Effect Spectroscopy**

**MS = Mass Spectrometry**

**MW = Molecular Weight**

**OIBS = Octa-isobutyl Silsesquioxane**

**OIBS-EDN = Octa-isobutyl Silsesquioxane Endo-disilanol**

**OPS = Octaphenyl Silsesquioxane**

**ORTEP = Oak Ridge Thermal Ellipsoid Plot**

**PFG = Pulse-Field Gradient**

**POSS = Polyhedral Oligomeric Silsesquioxane**

**PRN = POSS Refined Nanocomposite**

**SBS = Styrene-Butadiene-Styrene**

**T4 = Tetraorganylsilsesquioxane**

**T6 = Hexaorganylsilsesquioxane**

**T8 = Octaorganylsilsesquioxane**

**T10 = Decaorganylsilsesquioxane**

**T12 = Dodecaorganylsilsesquioxane**

**TBAF = Tetrabutylammonium Fluoride**

**THF = Tetrahydrofuran**

**Tg = Glass Transition Temperature**

**TGA = Thermogravimetric Analysis**

**TMS = Tetramethylsilane**

**TPS = Thermal Protection System**

## **CHAPTER 1: Introduction**

### **1.1 Background and Scope**

This dissertation recounts my efforts toward developing protocols for the selective synthesis of asymmetric Polyhedral Oligomeric Silsesquioxanes (POSS). Double Decker Oligomeric Silsesquioxane tetraols [DDSQ(OH)<sub>4</sub>] are used as starting materials with different functionalizable chlorosilanes as capping agents. This chapter therefore gives a brief background on the constituents and structure of POSS compounds, their patterns of aggregation into polymers and the overall goals and relevance of the research. Special emphasis is also devoted to polyhedral oligomeric silsesquioxane chemistry, ranging from its genesis to synthesis and then applications as macromers for organic-inorganic hybrid polymers.

### **1.2 Nanostructures and Nanocomposites**

From a scientific viewpoint, materials are defined by both their macroscopic and microscopic structures. The creation of advanced materials is dependent on our understanding of their compositional makeup; precisely from the atomic level to an aggregation of such units into a macromer, and on and on. Interestingly today, materials on their own without blending do not satisfy the coveted requirements of low cost and high performance. With such a driven goal aimed at optimal functionalization, the modification of traditional materials via some sorts of scientific manipulations with nanostructures is therefore inevitable. An unambiguous path to achieving this is to understand materials from their nanoscopic structures and how they self-assemble into nanocomposite prior to blending with traditional materials. Building blocks with nanosize

dimensions have, for instance, made the assemblage of new polymeric materials with enhanced physical properties easy. A good starting point is therefore a brief comprehension of what nanoparticles and nanocomposites are.

### **1.2.1 Nanostructures**

According to R. W. Cahn in his book "*The Coming of Materials Science*", a nanostructure material is any object with volume dimensions within the nanoscopic scale (1–100 nm).<sup>1</sup> Technically, this scale refers to the molecular scale with the average material properties tending to fluctuate due to the behavior of its constituent particles. This often causes variations in the materials' properties, hence making their surface-area effect (thickness, wideness, etc.) more prominent.<sup>2</sup> Such materials can either be one-dimensional materials with surface thickness between 0.1-100 nm or nanotubes; two-dimensional tubes with diameters between 0.1-100 nm but longer length; or three-dimensional spherical nanoparticles with a 0.1-100 nm in every spatial direction. POSS molecules are ideal examples of environmentally friendly, non-volatile, and odorless nanostructures that exhibit enhanced performance over their non-hybrid counterparts like metals and ceramics.

### **1.2.2 Nanocomposites**

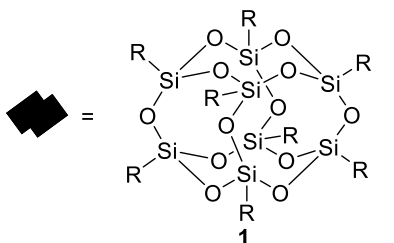
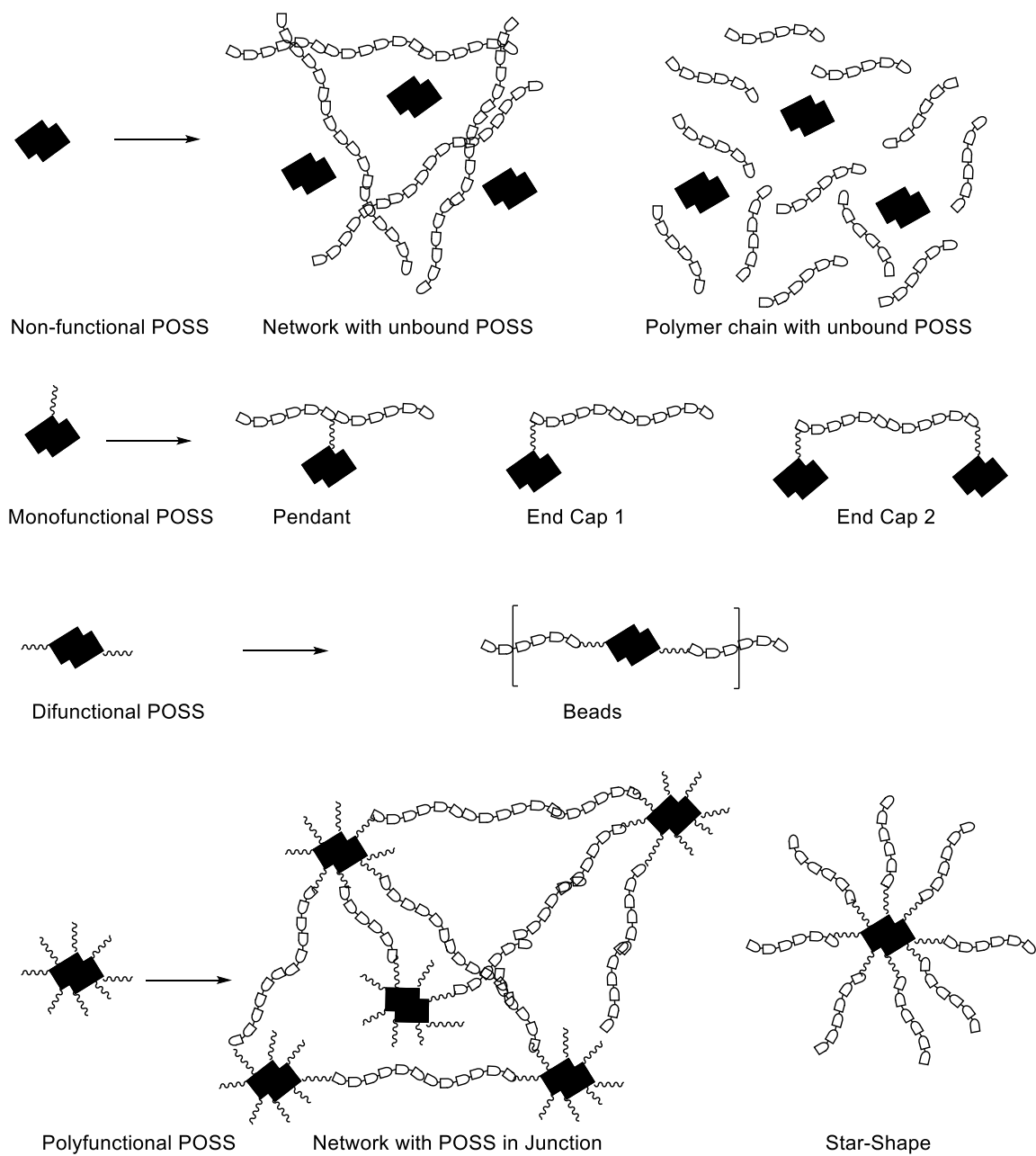
A nanocomposite on the other hand is a solid multiphase matrix bearing at least one nanoscale structure. Nanocomposites are often obtained as aggregates of nanostructures and used to fabricate new materials with flexible and enhanced physical properties.<sup>3</sup> The properties of such composites are determined by both the bulk properties of the constituent components and the intricate interactions between different phases in them. Importantly, these nanofillers are lighter materials and require only small loadings

for property enhancements.<sup>4</sup> Consequently, such materials often exhibit remarkable differences in their mechanical (strength, modulus, rigidity, oxidation resistance), electrical, thermal stability, viscosity, and optical properties compared to their nanostructural constituents.

### **1.3 Polyhedral Oligomeric Silsesquioxanes (POSS)/Polymer Composites**

Polymers are unique functional materials because of their macromolecular nature. They also occupy a unique role in industry often because of their light weight and ductility. Polymeric nanocomposites are themselves polymers that have been strengthened with dispersed nanosized materials in the polymeric matrix. Thus, with the aim to design polymers with improved strength and flexibility, the matrices are reinforced with materials like fiber or Polyhedral Oligomeric Silsesquioxanes (POSS) molecules to form composites with different physico-chemical properties from the original materials. Polyhedral Oligomeric Silsesquioxanes are a wide range of functional materials that exist as cage or cage-like oligomeric silsesquioxanes. They can be inert, mono- or multi-functional. This multifunctionality makes it easy for POSS molecules to interact with the polymer host in a three-dimensional fashion leading to the formation of a variety of hybrid composite shapes (**Figure 1**). Based on the nature of the vertex group, POSS molecules can either have a nonreactive (methyl, isobutyl, cyclopentyl, cyclohexyl, phenyl) or reactive (methacrylate, acrylate, styrene, norbornene, amine, epoxy, alcohol, and phenol) substituent that offers potentials for their dispersion through polymerization or grafting into a polymer chain or network.<sup>5</sup>

**Figure 1: Major POSS/Polymer Architectures<sup>5</sup>**



~ = functional group on POSS

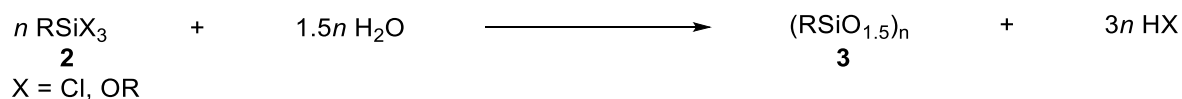
= polymer chain

The presence of the organic peripherals makes POSS molecules compatible with many polymers. POSS reinforced nanocomposites (PRN) are therefore polymers bearing POSS in which POSS molecules are the dispersed (discontinuous phase) in the polymer matrix (continuous phase), giving composites with average property contributions from both the POSS molecule and its host organic polymer matrix.<sup>6-8</sup> The resulting hybrid composite is generally a lightweight material with improved strength and performance.

#### 1.4 Silsesquioxanes

Silsesquioxanes are a diverse class of nano-scaled three-dimensional materials with the general formula  $(\text{RSiO}_{1.5})_n$ , where R is a hydrogen atom or an organic group, and  $n \geq 4$ . Structures are hybrid organic/inorganic nano-building blocks having amenable features for further chemical transformations (nano-building blocks) into nanocomposites. Etymologically, silsesquioxane is a three fragment coinage with the 'sil' denoting silicon, the 'sesqui' the latin word 'semisque' or three-halves, typifying a Si:O ratio of 1:1.5 in a molecule, and 'oxane' designating the oxygen atom.<sup>9</sup> Generally, these compounds are obtained, among other methods, from the polycondensation of trifunctional organosilicon monomers,  $\text{RSiX}_3$ , where R is a stable organic substituent and X, a highly reactive group like an alkoxide or a halogen (**Scheme 1**).<sup>10</sup>

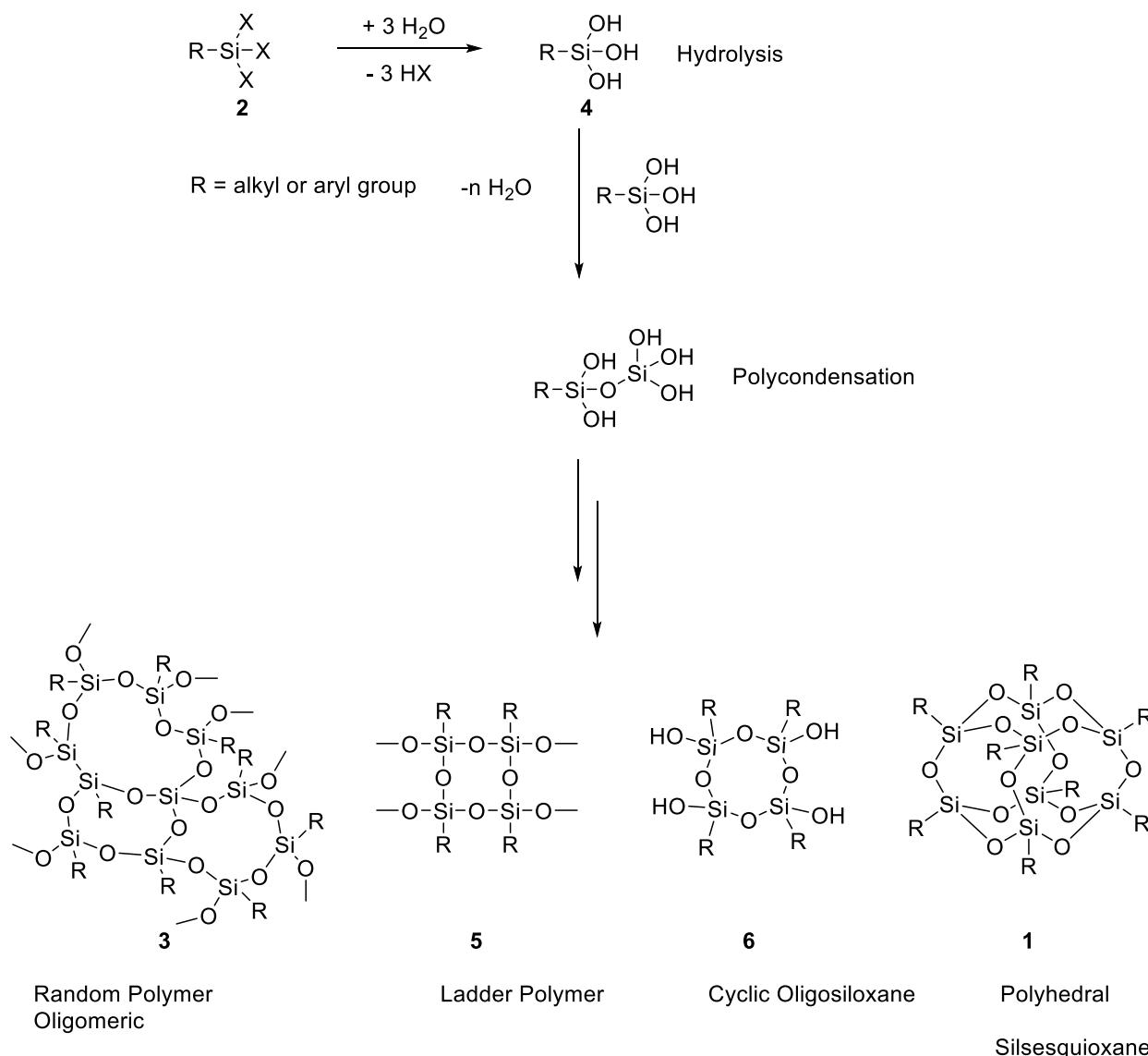
#### Scheme 1: Hydrolytic Polycondensation of $\text{RSiX}_3$





The synthesis is generally a consecutive, two-steps process generally involving two steps: Step one (1) is the rapid hydrolysis of the trifunctional chloro- or alkoxy-silane into the trisilanol followed by step two (2) which entails condensation processes that lead to different silsesquioxane frameworks (**Scheme 2**).

**Scheme 2: Polycondensation and Effects of Reaction Conditions on the Hydrolysis of  $\text{RSiX}_3$** <sup>9</sup>



The steps are quite complicated and even more so when there can be mutual competitive effects from the conditions for their formation. Thus, formation of various architectures is

condition dependent with factors such as, initial concentration of monomer and nature of R and X substituents, type of solvent, quantity of water added, temperature and catalyst being crucial. The effects of these factors on the reaction course has not been fully understood to date. This challenge has been ascribed by Voronkov *et al.* to the complexed polycondensation processes (**Scheme 2**) and the strong mutual effect of the factors above.<sup>9</sup> However, over decades of research in the field, the following deductions have been reached:

- Polycondensations conducted at higher temperatures favor formation of fully condensed cages.
- Water is important for hydrolysis and cyclization. The concentration of the silanol is kept low by the slow addition of water.<sup>11</sup> Whilst higher monomer concentration favors formation of silsesquioxane polymers, dilute solutions are biased toward intramolecular cyclization leading to formation of POSS compounds.
- Right reaction solvent choice stabilizes the silanol groups by hydrogen-bonding of the Si-OH to the alcohol or ether function as well as to the remaining alkoxy groups.<sup>11</sup> Thus polar solvents such as alcohols, can solvate the siloxane intermediates favoring polymer formation. Non-polar organic solvents, on the other hand, suppress intermolecular reactions in favor of intramolecular condensation for the formation of POSS compounds.
- The nature of X in the precursor monomer influences the reaction kinetics. Thus, with X = Cl, OH the hydrolysis is much faster compared to cases where X = alkoxy and even more so, the reaction can be autocatalytic with the production of HCl as the condensation by-product.

- The pH of the solution in the reaction vessel is also crucial. A highly acidic medium will favor formation of oligosilsesquioxanes, whereas polymeric species dominate under basic environments.<sup>12</sup>
- The nature of the R substituent is also important. When R = hydrogen, or methyl the polycondensation is very fast in favor of the formation of silsesquioxane polymers. Thus, sterics and inductive effects are determining factors here. The R group to some extent influences both the solubility and yield of the silsesquioxane species. Silsesquioxanes that are less soluble precipitate easily and push the equilibrium process towards formation of intermediates that leads to this less soluble species.<sup>9,11</sup>

Thus, depending on the conditions for their syntheses, a variety of rigid frameworks ranging from amorphous structures, ladder-like, cyclic oligosiloxanes, and Polyhedral Oligomeric Silsesquioxanes (POSS) can be obtained (**Scheme 2**).<sup>10</sup> The silica inorganic core provides the molecular rigidity, good thermal and mechanical properties of the molecules while the organic periphery accommodates functionalization that enhances material processability. Their properties may vary based on the peripheral organic functional group, but they generally exhibit high thermal decomposition temperature, low dielectric constant, and high degree of hardness as a coating agent. With over seventy (70) years of exploration of this chemistry, silsesquioxanes have found wide applications in polymers,<sup>13–15</sup> catalysis,<sup>16</sup> biomedical materials,<sup>17,18</sup> and semiconducting materials for optoelectronic devices.<sup>19</sup> To this end, classic organic/inorganic materials of the -Si-O-Si- framework have garnered much research interest because of the exceptional tailorable properties they exhibit.

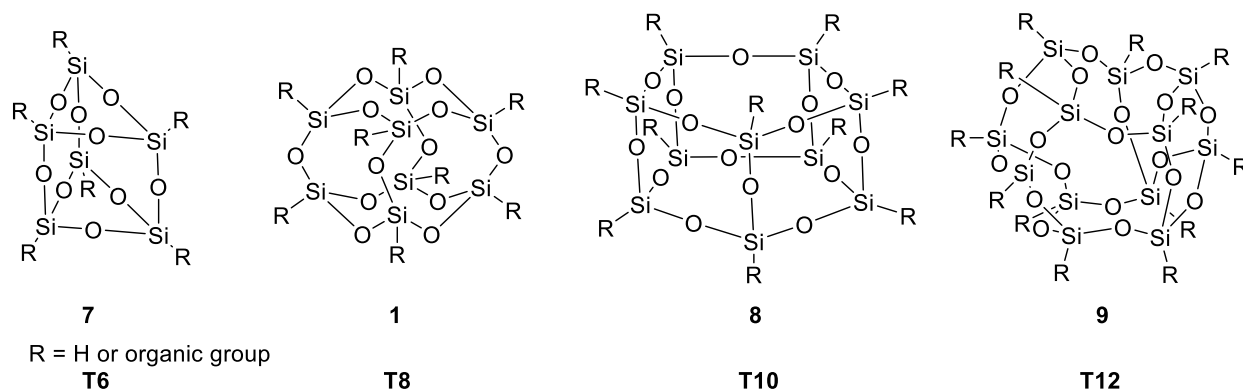
## 1.5 Polyhedral Oligomeric Silsesquioxanes (POSS)

Polyhedral oligomeric silsesquioxanes (POSS) are a framework of silicon-oxygen polyhedral core with an inert or reactive organic peripheral unit. They have the general formula  $[\text{RSiO}_{3/2}]_n$ , where  $n$  is an integer 6, 8, 10, 12, and 14. Generally, they are abbreviated as  $T_n$ , where  $n$  = number of Si on the cage. Such condensed oligomeric organosiliceous compounds are formed under various reaction conditions including solvent, concentration, catalyst, temperature, and the organic substituent in the starting silane.<sup>11,20</sup> As part of the silsesquioxane family, POSS molecules have each Si bound to 1.5 O-atoms (sesqui-) and a hydrocarbon unit (-ane) giving rise to cages with different degrees of symmetry. A large variety of hexa-, octa-, deca- and dodeca-functional POSS compounds with  $R = \text{H}$  or organyl are known.<sup>21-23</sup>

Based on the conditions for their formation and hence the formula/structure of the compound, POSS molecules are broadly classified into two categories (**Figures 2**):

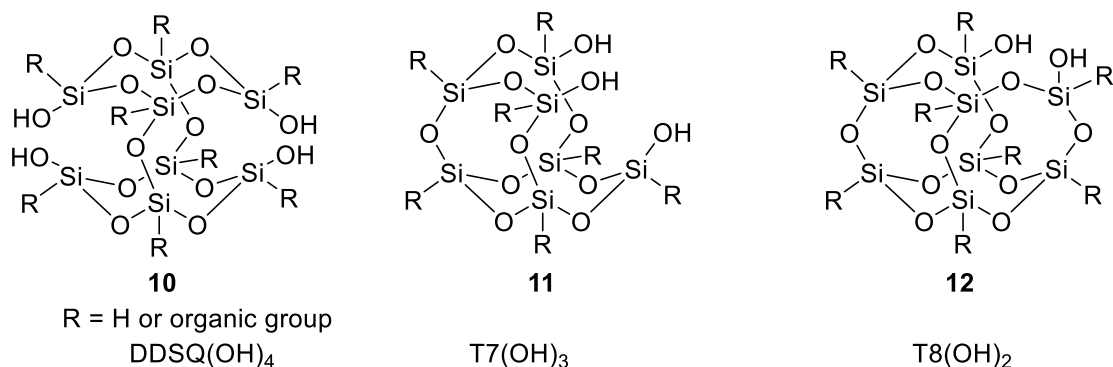
- (i) Completely Condensed Silsesquioxanes
- (ii) Incompletely Condensed Silsesquioxanes

**Figure 2: Framework of Silsesquioxanes (i) Completely Condensed (ii) Incompletely Condensed**



(i) Completely Condensed Silsesquioxanes

**Figure 2 (cont'd)**

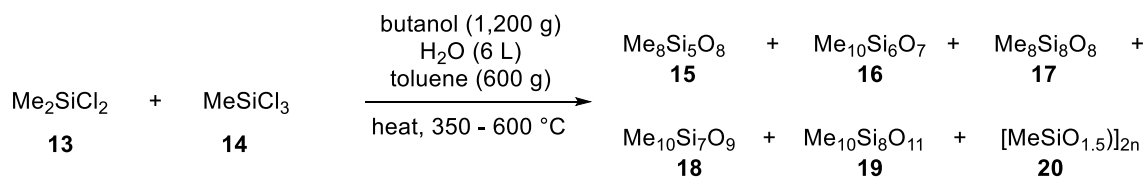


(ii) Incompletely condensed silsesquioxanes.

In addition to displaying high thermal, mechanical, and chemical stabilities<sup>24,25</sup> derived from the siloxane (Si–O–Si) frameworks, these three dimensional compounds have attracted enormous attention in the research fields of hybrid materials because of their diverse functional organic side chains (R groups) and the inert inorganic core that are remarkably compatible with organic materials.<sup>26</sup> This makes them valuable building blocks in polymer chemistry for the synthesis of new materials including nanocomposites<sup>27–29</sup> and catalysts for polymerization<sup>30</sup>.

Credit for the discovery of the completely condensed silsesquioxanes is given to Scott (of Dow Corning) in 1946 for the synthesis of methyl-substituted oligomeric silsesquioxanes.<sup>31</sup>

**Scheme 3: Synthesis of Six Methylpolycyclopolysiloxanes by Coadhydrolysis and Thermal Rearrangement**

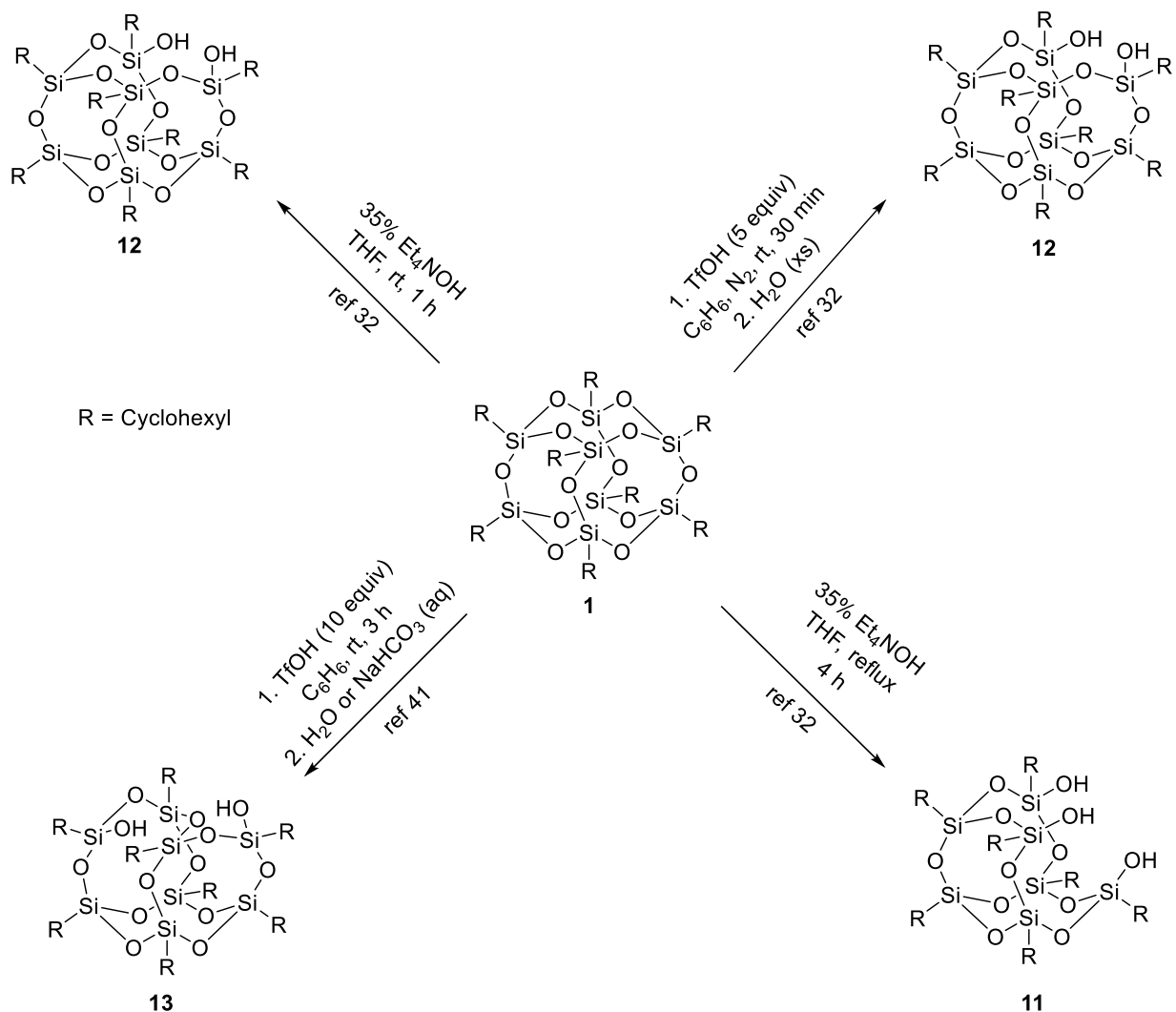


Though not fully characterized then, Scott in his pursuit to understand the chemistry of chlorosilanes, showed that six methylpolycyclopolysiloxanes could be obtained from the thermal rearrangement of the cohydrolysis product of dimethyldichlorosilane and methyltrichlorosilane. Thus, completely condensed methyl-substituted oligomeric silsesquioxanes with varied molecular formulae were obtained. Exact structures were not assigned to these compounds because of the number of several isomeric possible structures. However, the structures were later elucidated by Barry to have cubic and hexagonal prismatic shapes.<sup>32</sup>

While fabrication of other R-substituted silicon frameworks of the  $R_8T_8$  structure (R = *n*-propyl, ethyl, and *n*-butyl) were initiated by Barry and Gilkey,<sup>33</sup> Olsson in 1958 first reported the synthesis of octaphenyloctasilsesquioxane ( $Ph_8T_8$ ) from the acid catalyzed hydrolysis of phenyltrichlorosilane ( $PhSiCl_3$ ) in methanol.<sup>34</sup> The hexa- ( $T_6$ ), deca- ( $T_{10}$ ) and dodeca- ( $T_{12}$ ) silsesquioxane are now known.<sup>35,36</sup>

On the contrary, development of methodologies for the synthesis of incompletely condensed silsesquioxanes is credited to the Feher group.<sup>37-42</sup> Feher recorded a remarkable feat in silsesquioxane chemistry with his success in synthesizing the incompletely condensed silsesquioxanes. Under both acid and base catalyzed conditions, selective cleavages of the fully condensed precursors have rendered various incompletely condensed silsesquioxane frameworks. (**Scheme 4**).

### Scheme 4: Acid and Base Catalyzed Routes to Incompletely Condensed Silsesquioxanes



Such incompletely condensed silsesquioxanes are outstanding precursors for a range of applications including the assemblage of novel silsesquioxane-containing polymer and other Si-O and Si-O-M models. For instance, POSS silanols possess the necessary architecture to trap catalysts, hence making them suitable for application as catalysts in industrial processes such as the epoxidation of olefins.<sup>43</sup>

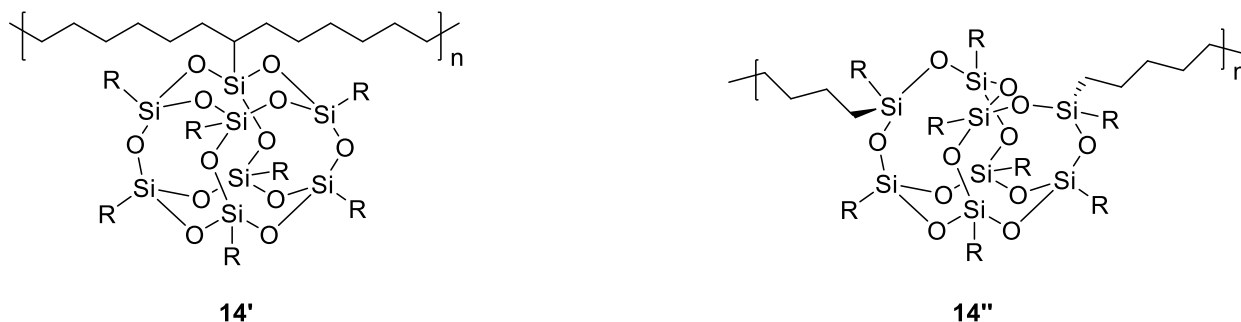
## 1.6 Benefits of POSS Compounds

POSS cages exhibit a myriad of desired properties that can be optimized for specific applications. Compared to traditional fillers, POSS molecules are environmentally benign and odorless and thus are non-volatile emitting compounds below 300 °C.<sup>44</sup> A majority of research and applications in the field focuses on the integration of POSS molecules into polymeric structures via grafting, copolymerization and blending for the purpose of reinforcing the composite. Over the years, their incorporation into polymer matrices have been demonstrated to decrease material flammability and viscosity, and to enhance the mechanical properties, oxidative resistance and thermal stability of the polymer composites.<sup>45–47</sup> The hybrid organic-inorganic framework promotes composite miscibility when integrated into a polymer matrix, making them superior tailorable molecules compared to other traditional fillers.

Importantly also, polyhedral oligomeric silsesquioxanes (POSS) have been extensively utilized in space-survivable coatings, ablative and fire resistant materials.<sup>15,48,49</sup> Their physical sizes make incorporating them into polymers reduce the chain mobility, and improve both the thermal and mechanical properties. Thus, completely condensed cages that are thermally stable are either chemically bound/grafted to the polymer backbone (**14'**, **Figure 3**) or incorporated via chemical modification of a preformed polymer where the POSS acts as pendant to the polymer backbone (**14''**, **Figure 3**).



**Figure 3: Polymer Architecture with POSS Blends via (14') Grafting and (14'') Copolymerization**

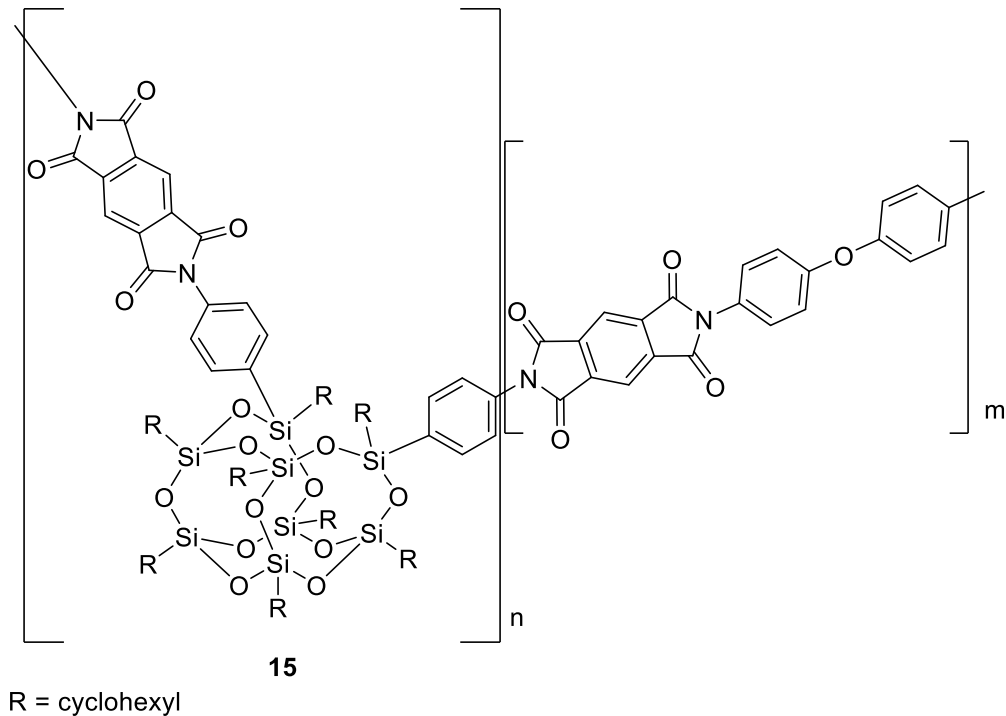


The various blending methods make modifications facile and offer access to different material designs, hence enabling light-weight materials for energy efficiency, aerospace, electronics and strong infrastructural applications to be assembled. Polymeric blocks linked to form block copolymers where chemically incompatible building blocks self-assemble into a number of ordered frameworks have been reported.<sup>50,51</sup> Upon integration into polymeric materials, properties such as glass transition temperature ( $T_g$ ), dielectric constant, and chemical resistance of the resulting structures are enhanced. For example, Lee and Haddad's work on POSS–SBS polymers illustrated that the POSS not only enhances the  $T_g$  of the butadiene fraction as supposed, but also promotes the storage modulus at the melt temperature ( $T_m$ ) of the styrene.<sup>141</sup>

In space exploration particularly, protective covers are needed as shields against harsh environments. To this end, and owing to the good thermal and physical properties of some polymers, these materials have been extensively utilized in spacecraft thermal blankets, solar arrays, and space inflatable structures.<sup>52,53</sup> Worth mentioning is the fact that ordinary polymeric materials suffer from serious degradation in Low Earth Orbit (LEO). Various research groups have attributed this degradation to the high concentration

of atomic oxygen (AO) in this region and its reactivity with organic substances.<sup>54–59</sup> For quite some time, organic polymers like kapton polyimide, have recorded extensive applications including its use as thermal blanket materials in spacecrafts, solar arrays and other space inflatable structures.<sup>60,61</sup> In the LEO, this material, kapton polyimide (PI), is subject to extreme radiations and hence can be bombarded by high energy, charged particles that could lead to its degradation. AO, in this region, having translational energies above many reaction barriers, causes the degradation of the polymer. Thus, if spacecraft are to survive the ubiquitous aggressive conditions in space, the design of space-survivable materials is imperative. Lately, it has been observed that polymeric materials intercalated with POSS molecules make the matrix resistant to AO due to the higher Si-O bond energy (approx 6eV) which is above the collision energy of AO in LEO.<sup>62</sup> With the presence of nanodispersed POSS molecules in the POSS-PI film (**Figure 4**), a protective silica layer is formed on the polyimide surface upon reaction of the film with AO. Sandra et al. have shown that exposure of a POSS-Polyimide film to AO causes erosion of the surface organic material and reaction of the AO with the POSS molecule to form a silica-based shielding layer. This is responsible for the observed AO resistance and the insignificant effects on modulus, glass transition temperature  $T_g$ , and coefficient of thermal expansion ( $\alpha$ ) in the resulting film.<sup>63</sup>

**Figure 4: Structure of a typical POSS Polyimide**



In order to enhance resistance to AO therefore, polyimides are now coated with functionalized POSS molecules to make the Si-O bond of the resulting matrix unaffected by the exposure to AO. Thus when a POSS-Kapton encounters AO, the organic material degrades while the silicon and oxygen atoms in the matrix react with AO to passivate the polyimide surface; hence making the hybrid nature of POSS compounds a key feature for their use as ideal delivery systems as nano-dispersed silica that are unaffected by weather.<sup>64,65</sup> Also, in the aerospace industry, polyimide compositions have been used for optical applications. Thus as membrane reflectors, the polyimide composites for such applications are prone to repeated and drastic heating and cooling cycles in orbit as a result of their exposure to interchanging periods of sunlight and shade.<sup>66</sup> Since satellites do survive in orbit for as long as the materials used to make them remain functional, this thermal and chemical durability is of great value

As ablative materials, POSS compounds are used in thermal protection systems (TPS) as heat shields, especially in the aerospace industry.<sup>67,68</sup> Ablative TPS are effective heat shields used in Intercontinental Ballistic Missile (ICBMs), the clustering of inertly cooled combustion chambers,<sup>69</sup> and in payload and aerodynamic surfaces of all NASA planetary entry probes and vehicles against the severe thermal effects from hypersonic flight<sup>70</sup> and other propulsion devices.<sup>71</sup>

POSS/Polymer protective composites also find applications in the electronics and telecommunications industries as protective and stress buffer coatings. Thus the composite materials are often overlaid on electronic materials as in semiconductors, dielectric layers for multilayer integrated circuits and multi-chip modules, high temperature solder masks, passivating coatings on electronic devices, and the like.<sup>72,73</sup> Due to their high dielectric strengths, high volume resistivity, and low dissipations, silsesquioxanes are used to laminate electrical materials through fiber-reinforced composites. Functionalized silsesquioxanes have also been used in light emitting diodes.<sup>73,74</sup>

## **1.7 Problem Identification, Research Justification, Research Aim and Objectives**

### **1.7.1 Problem Identification**

Today, it is sufficiently evident that polymers and plastics are major components of a good number of commercial products and applications. However, besides the enormous benefits conferred by these materials, evaluation of recent progresses on the synthesis and applications of these materials have disclosed some drawbacks in relation to their resistance to oxidation and degradation at higher temperatures. Standard polymers, for

instance, are used as coatings of underlying materials, and to some extent, have been effective at minimizing oxidative degradation. However, over time, they often experience various effects ranging from cracking due to thermal and mechanical stresses, abrasion, and debris impact.<sup>75,76</sup> Upon cracking, the protective surface is compromised, and the underlying polymeric material is prone to degradation from its exposure to the oxidizing environment. Prior to the use of POSS compounds for this purpose, polymer oxidative properties have been ameliorated to better tolerate harsh environments using certain fillers. Recent efforts to surmount these challenges have been the development of hybrid materials/plastics that can provide synergistic properties between those of traditional organic polymers and inorganic systems like ceramics. Such hybrid products would ideally exhibit properties of the organic polymer systems (i.e. processability, toughness, cost) and those of the core inorganic portions (i.e. thermal and oxidative stability).

### **1.7.2 Research Justification and Aims and Objectives**

Generally, polymeric materials are lightweight, ductile and easy to synthesize. Approaches that improve polymer properties while retaining their lightweight and ductile nature are known. However, compared to metals and ceramics, these materials exhibit some shortcomings including their low modulus and strength. In order to improve these mechanical properties, reinforcement enhancing structures/fillers such as fibres and POSS compounds are often added to the polymer matrix. These fillers have the ability to enhance the mechanical strength, heat and impact resistance, and also to abate the electrical conductivity and permeability due to exposure to oxygen and water vapor.<sup>77</sup>

Given their material toughness, light weight, and ease of processing, polyhedral oligomeric silsesquioxanes (POSS) are integral components in the materials and polymer industries for the synthesis of thermally and oxidatively stable materials. More so even, these materials have emerged as nonpareil with regards to processability, toughness and low cost. Thus work to advance our understanding on the prevailing and prospective properties (mechanical, thermal, flame retardation and viscoelastic properties) and applications of POSS nanocomposites, their morphology and polymer synthesis, is crucial to research chemists and materials engineers. To this end, the overarching goal of this research is to unravel routes for entry into functionalized asymmetric POSS cages using existing and new capping agents. The research

issues to be addressed here include:

- (i) The development of cost-effective and efficient processing routes for entry into POSS cages.
- (ii) The recognition of polymerizable chlorosilanes and clustering of a novel and flexible precursor for the facile entry into asymmetric POSS compounds that are graftable.
- (iii) The development of protocol(s) for the selective synthesis of asymmetric systems (A/B POSS cages).

### **1.8 Potentials for Asymmetric POSS Compounds (A/B Systems)**

As illustrated in section 1.3 above, polyhedral oligomeric silsesquioxanes are an attractive class of compounds for both polymer and engineering purposes. Their unique nanoscaled structure coupled with their good solubility in organic solvents makes them tailorable and compatible materials with companion materials like polymers. As a result, POSS compounds are beneficial for the synthesis of hybrid materials with a wide range of

applications. Despite the enormous progress made so far on the study of symmetrical POSS cages, there is only scanty work reported in the literature for the synthesis and applications of the analogous products resulting from either the side-capping of incompletely condensed cages with two different polymerizable groups (A/B Systems) or the direct synthesis of such systems starting from traditional chloro- or alkoxy-silanes. To this end, ongoing explorations in our laboratories on this chemistry is devoted to uncovering techniques for the synthesis of novel POSS compounds of the asymmetric types. Additionally, efforts are also directed to the synthesis of new capping agents for the functionalization of double decker oligomeric Silsesquioxanes into asymmetric blocks with potential new features. Achieving such a feat will make the design of block copolymers with asymmetric systems more accessible as it provides a platform for capping agents of different nature and properties to be incorporated into polymer matrices.

The challenge is to be able to fabricate high temperature nanocomposites without compromising the requisite properties of these POSS compounds. Thus, in the context of nanoparticle architecture, such bridging/capping might offer access to greater materials design from which a range of potential products that are oxidatively resistant, thermally stable, non-flammable and lightweight materials for energy efficiency, aerospace, and other applications could be reached.

Compounds based on asymmetric (A/B) architecture from tetrafunctional POSS substrates have only been illusory or nascent since the discovery of silsesquioxane chemistry. On the contrary however, steady progress has been realized in the synthesis and applications of the symmetric analogues. With the recent spate of developments

unfolding in our laboratory on assembling such frameworks, it is envisioned that selective masking or protection of one or more of the functionalities on the cage could enable entry into our desired target. To this end, the advantages of mono- or multi-protection of organic functionalities via silylation, benzylation, benzoylation, borylation, etc. and 'solid support' chemistry are important paths for development.



## **CHAPTER 2: Prior Strategies for the Synthesis of Completely and Incompletely Condensed POSS Cages**

### **2.1 Introduction**

There is quite extensive research that have been done on POSS chemistry, most of which has been dominated by the octafunctional oligomeric silsesquioxanes. This chapter is by no means exhaustive, but rather a survey of synthetic routes to polyhedral oligomeric silsesquioxanes. Transformations are herein elaborated for selected methodologies relevant to this project. Thus, focus is limited to synthetic techniques for the hexa-, octa-, deca, and dodeca-oligomeric silsesquioxanes. Importantly, because the past three decades have seen particular interest on the chemistry of POSS compounds of the  $T_8$  cage types, the syntheses of the octaphenyl-, octacyclohexyl-, octacyclopentyl-, and octaisobutyl-silsesquioxanes are especially noteworthy. Thus, even though some mention is made of other caged architectures ( $T_6$ ,  $T_{10}$  and  $T_{12}$ ), this chapter discusses some techniques for assembling double deckers of both the fully and incompletely condensed cubic analogues of the  $T_8$  compounds.

### **2.2 Synthetic Strategies for POSS Compounds**

Polyhedral oligomeric silsesquioxanes are an important class of compounds comprising several Si-O-Si constituent rings linked in a finite three-dimensional pattern to form prismatic or cubic architectures. They can have various organic peripherals including aryls such as phenyl and benzyls, and aliphatics, vinyl, methacryl, amine and epoxy groups. Several synthetic routes have been documented in the literature for the synthesis

of these compounds, the most explored being those that follow the polycondensation of trifunctional silanes,  $\text{RSiX}_3$ , under various reaction conditions. The R group is the organic functional group and the X, the condensable moiety. Broadly, below are the four (4) major approaches<sup>78</sup> by which POSS compounds have been synthesized:

- (i) Hydrolytic condensation of trifunctional silane monomers
- (ii) Selective cleavage of the silyl-ether groups on the inorganic backbone
- (iii) Co-condensation of organosilicon monomers and/or oligomers of different structure and composition.
- (iv) Condensation of oligoorganycyclosiloxanes.

The first method, the most widely used approach, involves condensation of a precursor monomer and tandem cyclization to give the desired POSS molecule. The next two entail the selective breaking and rearrangement of Si-O-Si bond(s). The last approach differs from the first in the sense that the co-hydrolysis involves two different functional monomers.

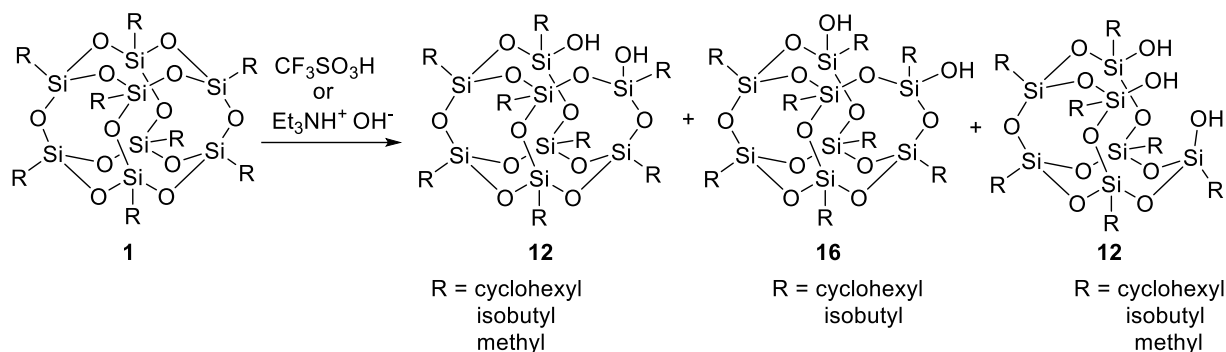
### 2.2.1 Hydrolytic Condensation of Trifunctional Silane Monomers

This approach is useful for the synthesis of homo-substituted POSS molecules where all the peripheral substituents are identical, as well as cage-like silsesquioxanes. The condensations are condition dependent<sup>79</sup> and can afford both the fully condensed (**Scheme 5a**)<sup>77</sup> silsesquioxane and the incompletely condensed (**Schemes 5b**) counterpart<sup>37</sup>. The polycondensation of a trifunctional monomer,  $\text{RSiX}_3$  gives, in addition to the octaorganyl  $\text{T}_8$  POSS cage as the major product, side products such as the deca- $\text{T}_{10}$  and dodeca- $\text{T}_{12}$  derivatives (**Scheme 5a**).<sup>79,80</sup>



can afford the respective silanols,  $R_8Si_8O_{11}(OH)_2$ ,  $R_8Si_8O_9(OH)_4$ ,  $R_7Si_7O_9(OH)_3$  (**Scheme 6**).<sup>37,85,86,98,111</sup>

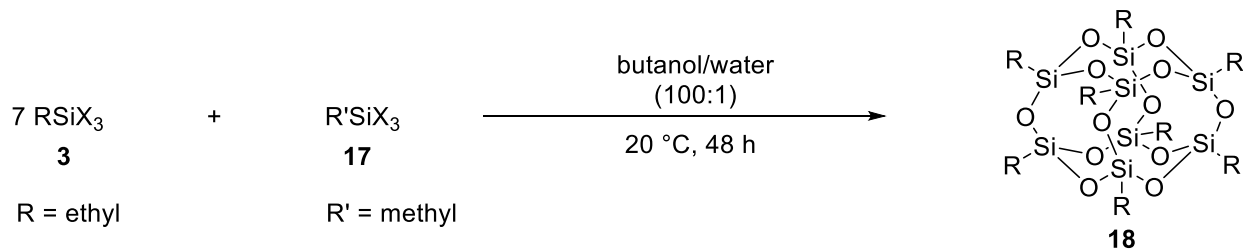
**Scheme 6: General Scheme for the Synthesis of Incompletely Condensed POSS Cages via Acid- and Base-mediated Selective Cleavage**



**2.2.3 Co-condensation of Organosilicon Monomers and/or Oligomers of Different Structures and Composition**

POSS cages with more than one type of organic peripheral unit can be obtained from the co-hydrolysis of a mixture of trifunctional monomers,  $RSiX_3$  and  $R'SiX_3$  to give a statistical mixture of all possible combinations of R and R' heterosubstituted oligosilsesquioxanes (**Scheme 7**).<sup>9,78</sup> In this case, the initial reactivity of the starting trifunctional silanes is crucial but adjusting their ratio accordingly can lead to a considerable yield of the desired monosubstituted octamer.

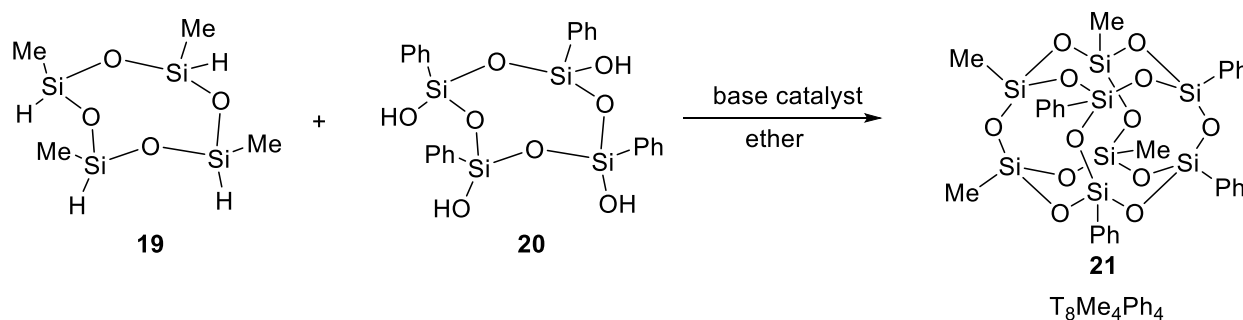
**Scheme 7: Synthesis of Monosubstituted POSS Cage from two Different Monomers**



## 2.2.4 Condensation of Oligoorganylcyclosiloxanes

The condensation of oligoorganylcyclosiloxanes for the synthesis of completely condensed POSS compounds was first reported for the dehydrogenation of 1,3,5,7-tetramethylcyclotetrasiloxane with 1,3,5,7-tetraphenylcyclotetra-1,3,5,7-siloxane tetraol in ether under base catalysis (**Scheme 8**).<sup>87</sup> In the specific case below, two cyclic siloxanes bearing different R substituents undergo condensation to afford a completely condensed POSS cage with alternating R groups.

### Scheme 8: Synthesis of POSS from the Condensation of Oligoorganylcyclosiloxanes



In the subsequent sections, literature reports involving the aforementioned strategies for the synthesis of both completely and incompletely condensed POSS compounds are discussed. Several approaches that have been adopted to functionalize these organosilsesquioxanes are also reviewed. The octa-functionalized cages are particularly referenced as is evidenced in the increasing research attention in the past several decades due to their easy tailorability and hence, important applications in polymer chemistry and material science.

### 2.3 Synthesis of Completely Condensed Silsesquioxane

Regardless of the tremendous progress realized to date, the chemistry of POSS compounds remains underexploited. Noteworthy however is the genesis of these compounds that dates far back to the pioneering work of Scott<sup>31,88</sup> in 1946 for the synthesis of fully condensed silsesquioxanes (**Scheme 3**). From this discovery, a remarkable growth in curiosity in the use of discrete molecular oligomeric silsesquioxanes often obtained from the hydrolytic condensation of trifunctional silanes ensued.

Studies with *c*-C<sub>6</sub>H<sub>11</sub>SiCl<sub>3</sub> and PhSiCl<sub>3</sub> have also been strongly documented; all of which are illustrating that the condensations of trifunctional organosilicon compounds can result into a diverse range of products with general formula (RSiO<sub>3/2</sub>)<sub>n</sub>. Such product architectures include random polymeric networks of a ladder-like polymer<sup>89</sup> resulting from intermolecular condensation, incompletely condensed structures and the fully condensed polyhedral products; that arise from intramolecular condensation (**Scheme 5**).<sup>90</sup>

In the recent past, material and polymer scientists/engineers have improved the thermo-oxidative stability of the polymers through the use of nanostructured materials and composites such as caged silsesquioxanes for both the insertion of graftable functional/reactive organic groups and the ultimate dispersion of such molecular materials into polymeric matrices. Importantly also, the percentage loading of POSS cages into a polymer matrix can directly influence the physical and mechanical properties, including strength, polymer modulus, interfacial properties and so on.<sup>91,92</sup>

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include random polymeric networks of a ladder-like polymer<sup>89</sup> resulting from intermolecular condensation, incompletely condensed structures and the fully condensed polyhedral products; a consequence of intramolecular condensation (**Scheme 5**).<sup>90</sup>

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### **2.3.1 Synthesis and Functionalization of Condensed T<sub>6</sub> Cages**

Silanetriols have particularly been shown to be suitable precursors to caged silsesquioxanes, giving rise to a number of different cages. Compared to T<sub>8</sub>R<sub>8</sub>, the synthesis of T<sub>6</sub> compounds by this method has been limited to a relatively small substrate scope. However, like their T<sub>8</sub> counterparts discussed in the sections that follow, T<sub>6</sub> cages can be transformed to incompletely condensed cages that can be used as models for silica surfaces and supports for transition metal catalysts.<sup>38</sup> **Scheme 9** shows synthetic routes to T<sub>6</sub>R<sub>6</sub> from either RSiCl<sub>3</sub> or RSi(OMe)<sub>3</sub> as precursor silanes.<sup>10</sup>

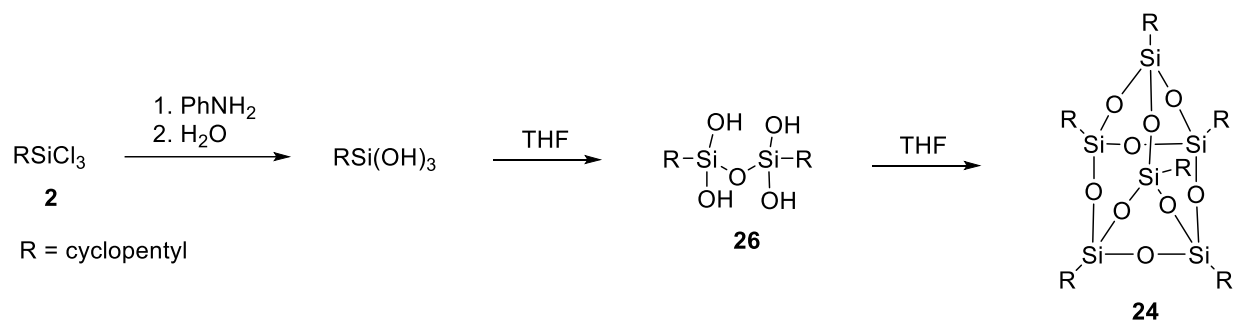






cyclopentyl) from the hydrolytic condensation of cyclopentyl substituted silanetriol (Scheme 12).<sup>94</sup>

**Scheme 12: Synthesis of R<sub>6</sub>T<sub>6</sub> from the Hydrolytic Condensation of Cyclopentyl Substituted Silanetriol (R = cyclopentyl)**



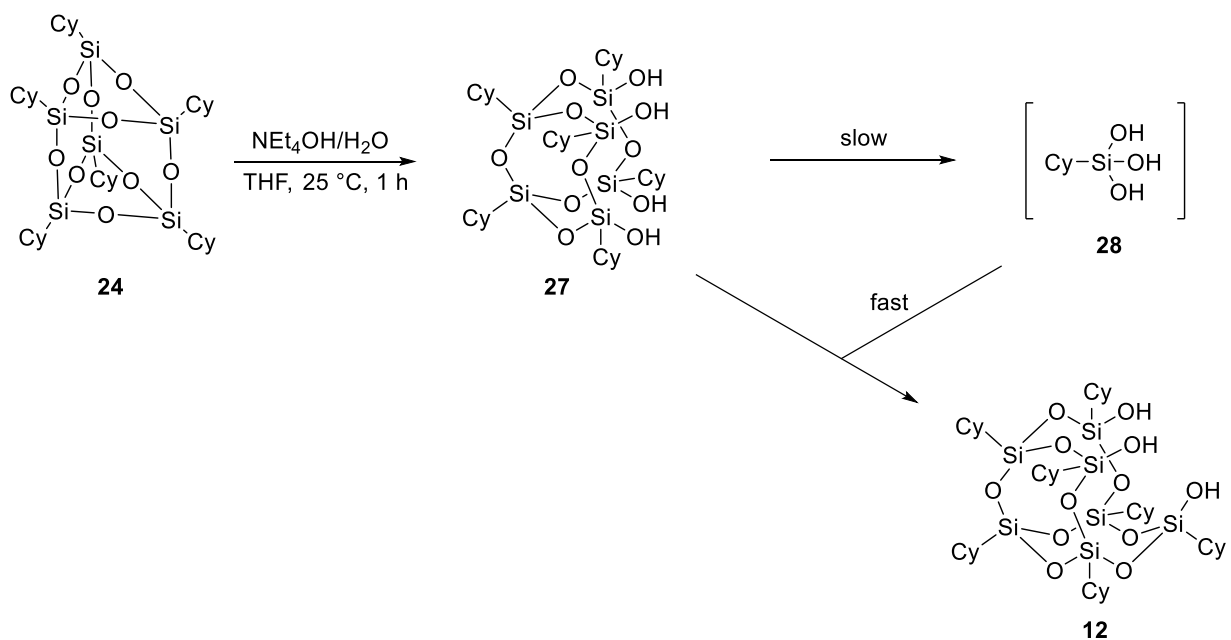
The possibility that similar compounds bearing secondary alkyl substituents can be obtained via same route was proposed.

**2.3.1.1 Base-catalyzed Cleavage and Homologation of T<sub>6</sub> Oligosilsesquioxanes**

A wide variety of fully condensed silsesquioxane frameworks have been developed since their discovery by Scott in 1946.<sup>31</sup> Remarkable progress has particularly been realized in the area of functionalizing the organic peripheral unit on the silicon backbone.<sup>41,95–97</sup> However, regardless of the progress recorded on this chemistry so far, research on the selective cleavage of the inorganic Si-O-Si core had been limited. Lately, this has changed and a good deal of investigation is now on the selective cleavage of one or more Si–O–Si linkages prior to derivatization.<sup>41,98</sup> The Feher group has made progress in this area and today condensed silsesquioxane cages can be transformed into novel compounds by cage breaking to give the incompletely condensed counterparts that can be functionalized or homologated.

Nguyen, *et. al.* described an approach for modeling POSS cages with the  $R_6Si_6O_9$  frameworks into precursor products usable in polymer synthesis and as ligands for transition-metal catalysts (**Scheme 13**).<sup>99</sup> Thus  $Cy_6Si_6O_9$  ( $Cy = c-C_6H_{11}$ ) was subjected to hydrolysis with aqueous  $NEt_4OH$  in THF to afford *endo*- $C_{2h}$ - $Cy_6Si_6O_7(OH)_4$ , which was further hydrolyzed (via  $CySi(OH)_3$  fragments) into the homologated *endo*- $C_3$ - $Cy_7Si_7O_9(OH)_3$ .

**Scheme 13: Hydrolysis  $Cy_6Si_6O_9$  ( $Cy = c-C_6H_{11}$ ) and Homologation to the Heptacyclohexyl Silsesquioxanetrisilanol**

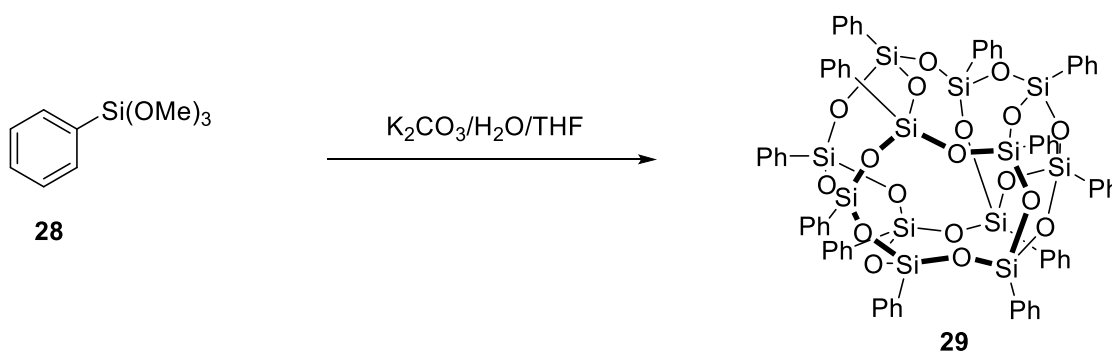


POSS trisilanol ligands with reactive pendant groups possess the necessary structure to immobilize catalyst. For instance, titanium-silsesquioxane catalyst system have been used in ethylene polymerization.<sup>100</sup>

### 2.3.2 Synthesis of Condensed T<sub>12</sub> POSS Compounds

Little reported work is documented on methodologies that involve the direct synthesis of T<sub>12</sub> cages. In 2012 however, Lee, *et al.*<sup>116</sup> devised an effective route for the synthesis of caged dodecaphenylsilsesquioxane (T<sub>12</sub>-phenyl) via a base catalyzed hydrolysis of a phenyltrimethoxysilane precursor under ambient conditions. Prior to this development, the possibility of selectively synthesizing just a single isomer of any one cage silsesquioxane had been an unmet synthetic challenge.<sup>117,118</sup> This challenge was attributed to a complex mixture of factors, including precursor monomer employed, type of catalyst and the reaction conditions. Importantly also, the hydrochloric acid produced under aqueous conditions makes controlling the hydrolysis– condensation equilibrium even more difficult. Thus, upon addition of phenyltrimethoxysilane (PTMS) onto a solution of potassium carbonate dissolved in distilled water and THF and stirred at room temperature for 14 days, a white precipitate of dodecaphenylsilsesquioxane was formed (**Scheme 14**).

**Scheme 14: Synthetic Scheme for T<sub>12</sub>-phenyl**



Mechanistic studies followed by <sup>29</sup>Si NMR disclosed that a transient T<sub>1</sub> species is the major intermediate in the condensations involved (**Scheme 15**). Unlike the T<sub>8</sub> cage silsesquioxanes which several groups<sup>145-149</sup> proposed to go through the more stable T<sub>2</sub>

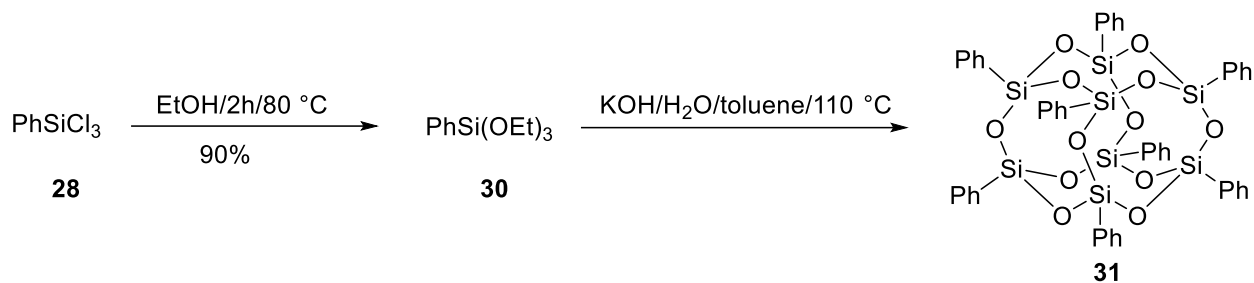


crucial, this difficulty has been ascribed to the complex hydrolysis and condensation kinetics and thermodynamics involved in their formation. With octaphenylsilsesquioxanes for instance, the task (overcoming poor yield) is even more daunting with the virtual insolubility of this compound in almost all organic solvents and the ability for it to undergo decomposition before melting. Consequently, while better yields are realized for some POSS synthesis under acid catalyzed conditions, others are obtained under base catalysis.

Generally, the cubic silsesquioxanes are much easier to prepare owing to their relatively better solubility in organic solvents and hence the ease to purify them. Additionally, a wide range of functional groups have been introduced onto the cage, either by direct synthesis from the monomer or by cage-opening and functionalization of the resulting cubic structure.<sup>89,101,102</sup>

Among the various approaches to synthesize silsesquioxanes, the octafunctional analogues are mostly obtained from the hydrolysis of trifunctional chlorosilanes in suitable organic solvents. Both acid and base catalyzed routes to the cubic silsesquioxanes have been reported with better yield often observed from the base catalyzed routes. While acid catalyzed hydrolysis favors linear polymers and branched polysiloxanes, base catalyzed hydrolysis<sup>89</sup> (**Scheme 16**) is often biased toward cube and pseudo-ladder silsesquioxanes.

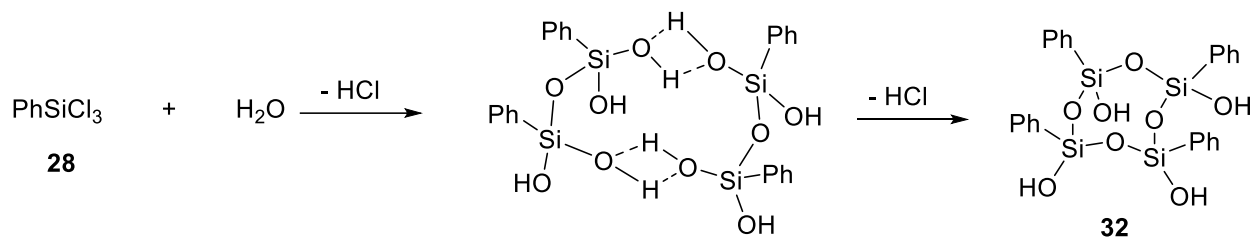
**Scheme 16: Base-promoted Synthesis of Cubic Octaphenylsilsesquioxane from Phenyltrichlorosilane**



To date, there are no clear-cut procedures for the effective synthesis of the deca- and dodeca-silsesquioxanes. Mostly, they are obtained as minor products in the synthesis of the octafunctional analogues.

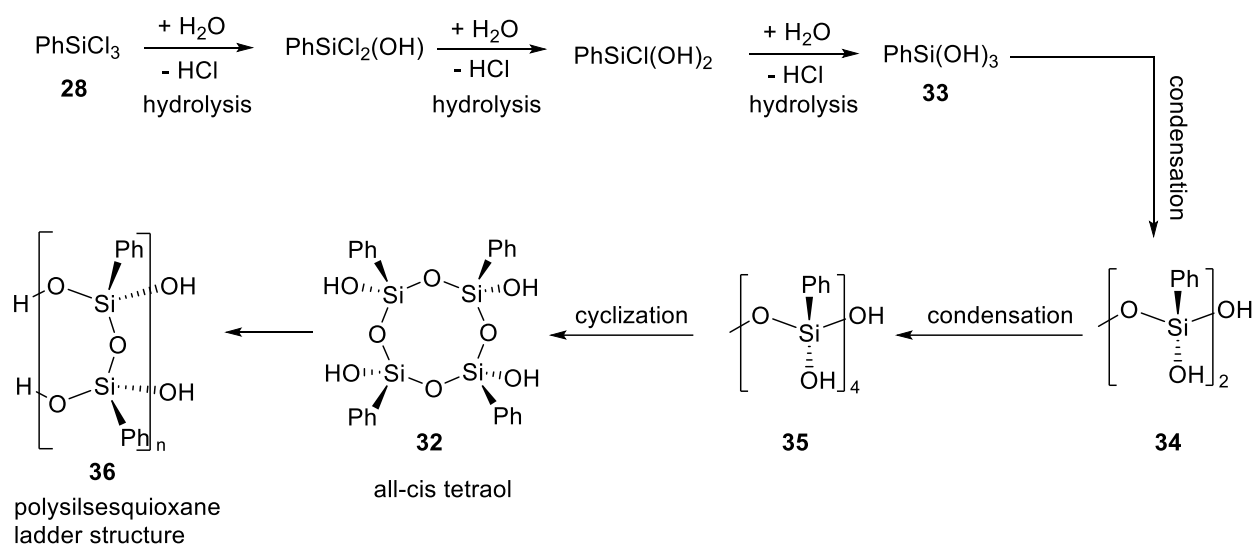
A mechanistic study for the acid catalyzed synthesis of poly(phenylsilsesquioxane) was documented by the Yamamoto group (**Schemes 17, 18**).<sup>103</sup>

**Scheme 17: Reaction Scheme for the Acid Catalyzed Synthesis of the Half-cage all-cis-Tetrasilanol**



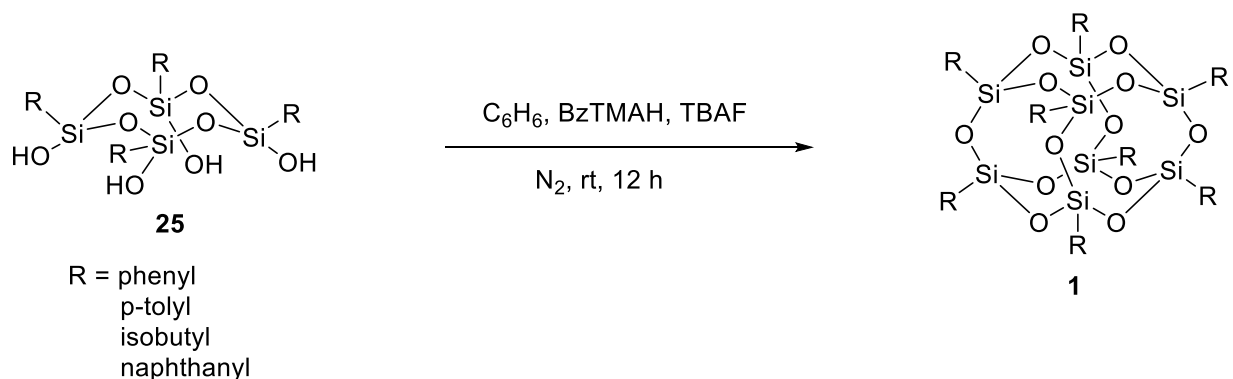
In that study, it was illustrated that phenyltrichlorosilane initially undergoes hydrolysis to afford the silanetriol, which first condenses to form a dimer. The dimer undergoes further condensation via a linear tetramer and subsequent cyclization to yield the all-cis-tetramer (**Scheme 18**).

### Scheme 18: Pathway for the Acid Catalyzed Hydrolysis of PhSiCl<sub>3</sub>



This product can now undergo slow transformation in the solid state to give the fully condensed octaphenylsilsesquioxane species (**Scheme 19**).

### Scheme 19: Typical Reaction Scheme for the Synthesis of Completely Condensed T8 POSS from cis-Cyclic T4 Tetraol



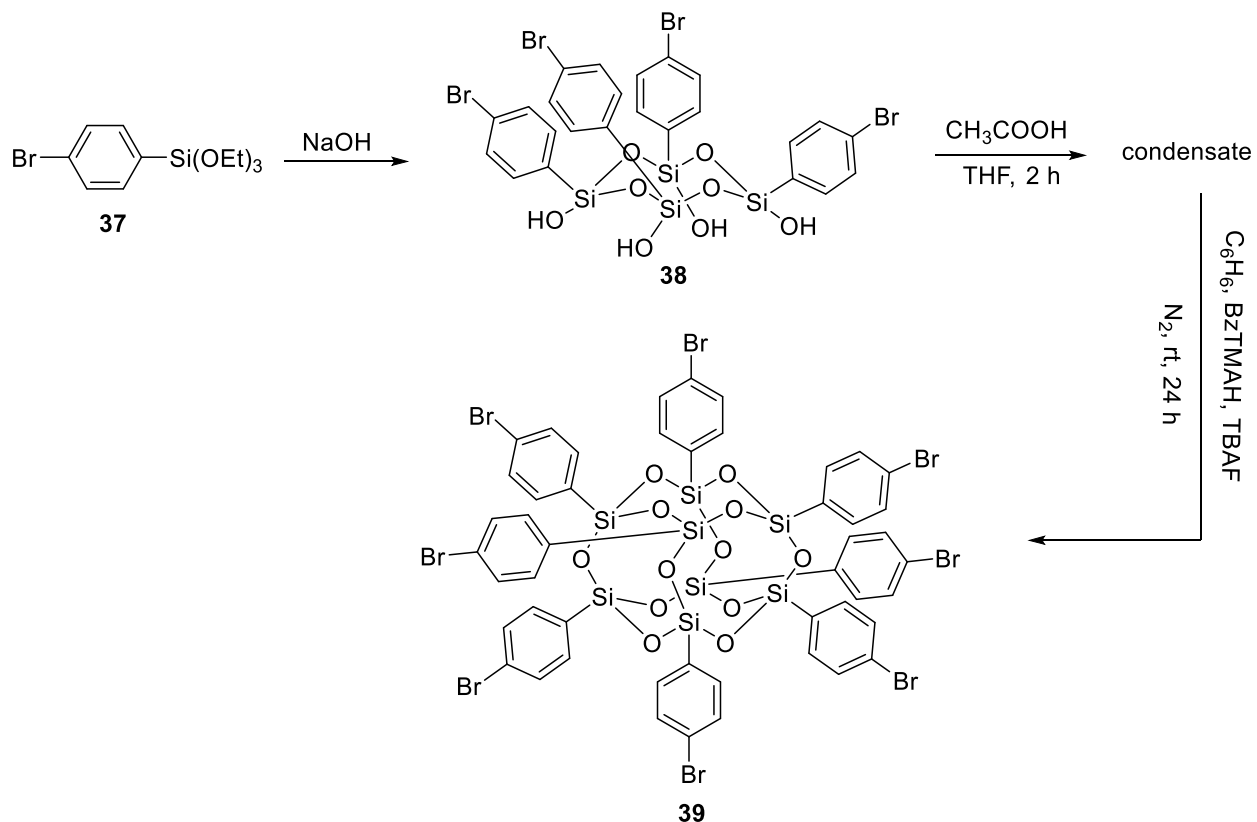
It is worth mentioning that the all-cis tetramer, cis(1,3,5,7-tetrahydroxy)-1,3,5,7-tetraphenylcyclooctasiloxane, had been isolated by several groups but the Feher team<sup>104</sup> was the first to report its crystal structure. This half cage (all-cis tetramer) has been obtained by both acid and base explored routes. For instance, Shchegolikhina et al.



developed a base-catalyzed approach for the synthesis of the tetramer from stoichiometric amounts of NaOH in n-butyl alcohol. This base catalyzed approach is also proposed to go through similar species as shown in Scheme 15 above, but much better yields observed.

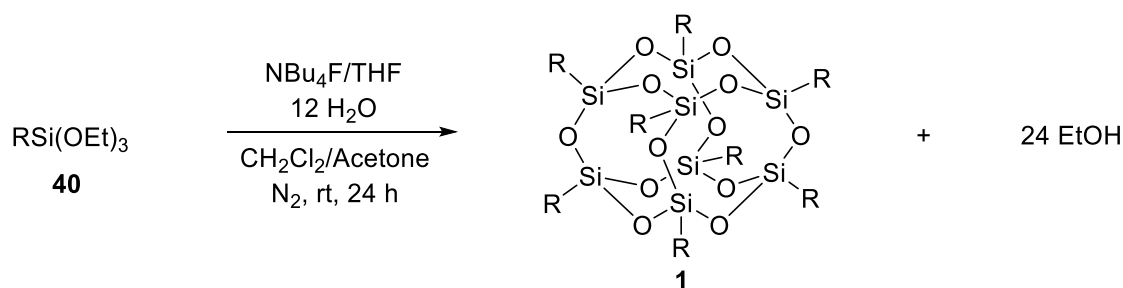
To illustrate such a pathway, the octakis(4-bromo phenyl)octasilsesquioxane was obtained by the Hursthouse group<sup>105</sup> in pure form from the cyclic tetra(4-bromo-phenyl) tetrasiloxanetetraol sodium salt (**Scheme 20**) prepared following the same literature procedure as reported for **Scheme 15** above.

**Scheme 20: Synthesis of octakis(4-bromophenyl)octasilsesquioxane from the Cyclic Tetrakis(4-bromophenyl) tetrasiloxanetetraol Sodium Salt**



Interestingly, modification of reaction conditions and use of different reagents and starting chloro- and alkoxy-silanes have seen the formation of a good number of octameric silsesquioxanes with potentially wider industrial applications. For instance, Hursthouse described another variation for the synthesis of T<sub>8</sub> POSS cages with improved yields from the treatment of trialkoxysilanes with a THF solution of tetrabutylammonium fluoride (Scheme 21).<sup>105</sup>

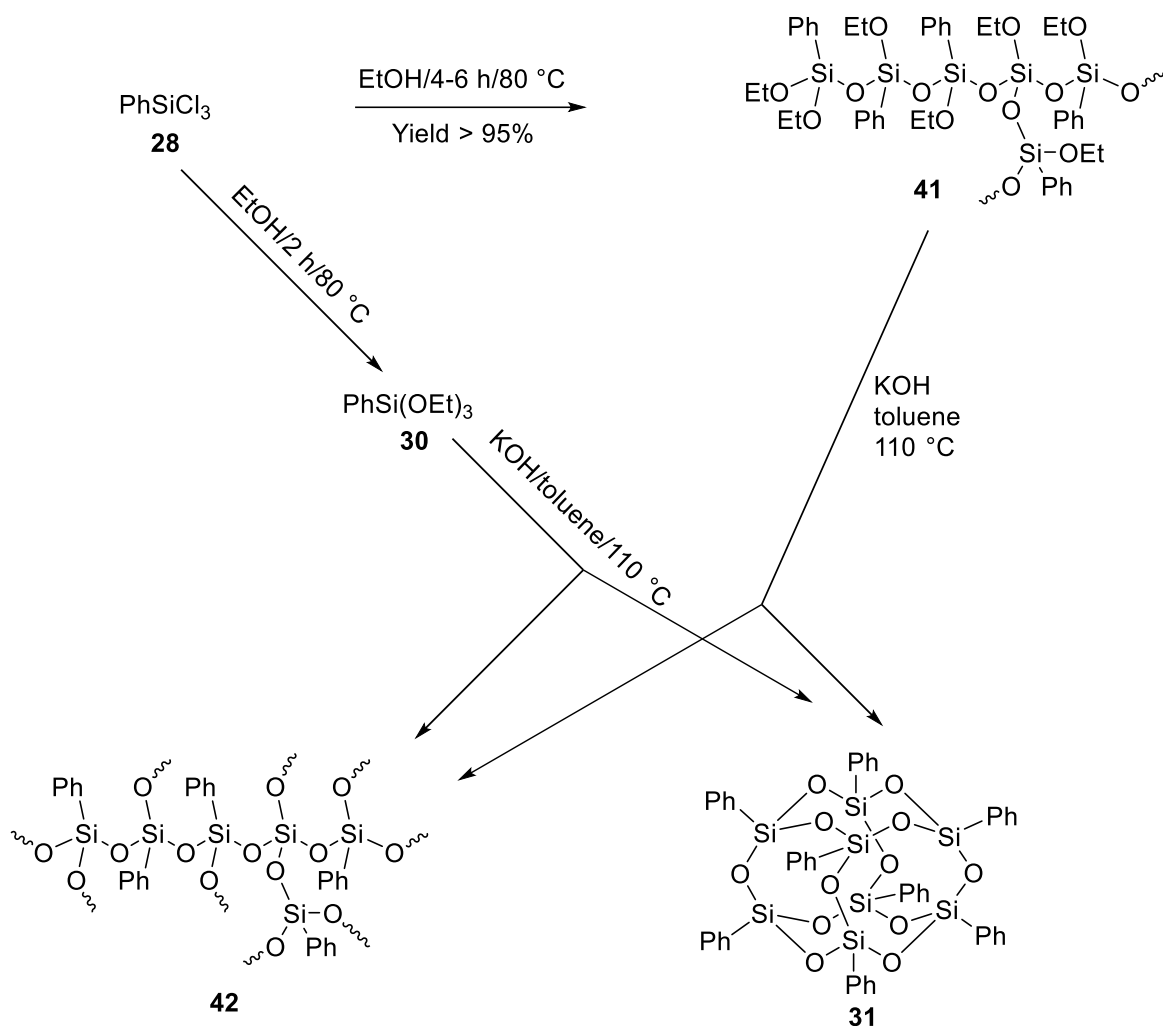
**Scheme 21: Synthesis of T<sub>8</sub> POSS cages from the Hydrolysis of Trialkoxysilanes Tetrabutylammonium Fluoride**



R = hexyl, octyl, isobutyl, phenyl, cyclopentyl, cyclohexyl

In a more general and efficient approach, functionalized T<sub>8</sub> POSS cages, particularly the octaphenyl- silsesquioxanes were obtained in yields of up to 80% by the Laine group (Scheme 22).<sup>106</sup> In addition to this product, the polymeric analogue, polyphenylsilsesquioxane was also obtained as a by-product.

## Scheme 22: General Pathways for the Formation of OPS and PPS

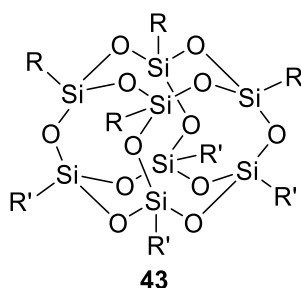


### 2.3.3.2 Synthesis of Bifunctional Janus Cubes

Janus structures are completely condensed silsesquioxanes bearing two different R peripherals with each tetrameric unit carrying a unique R corner substituent. The resulting structure from the condensation of two different half-cubes,  $\text{cis-}[\text{RSi}(\text{ONa})\text{O}]_4$  and  $\text{cis-}[\text{R}'\text{Si}(\text{ONa})\text{O}]_4$ , is a fully condensed bifunctional silsesquioxane cage with two unique functional peripheral groups (**Figure 5**). Thus, the successful synthesis of various R-

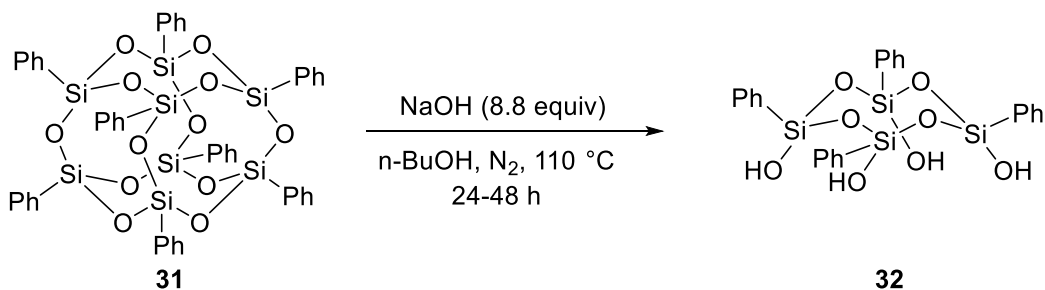
substituted cis tetramers provides the platform to access two-faced condensed cubic silsesquioxanes, otherwise known as ‘Janus’ cubes.<sup>110</sup>

**Figure 5: General Structure of a Two-Faced Janus Cube**



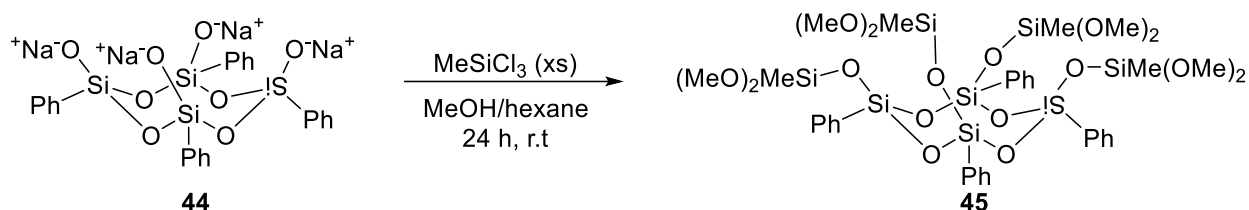
The bifunctional ‘Janus’ structures are designed to allow surface modification and/or thin films with nanometer-length control of individual layers.<sup>110</sup> Additionally, these structures can accommodate deposition or layer-by-layer nano-coatings of hydrophobic/hydrophilic character and hence either serve as interfaces or control self-assembly wherever complementary or dissimilar chemical functional moieties are employed.<sup>110</sup> The Laine group<sup>110</sup> is credited for their tremendous efforts in developing routes to a variety of Janus cubes from various half cube tetraorganyl sodium salts. Starting with the fully condensed octaphenylsilsesquioxane, Asuncion *et al.*<sup>110</sup> conducted a base-promoted hydrolysis to symmetrically cleave OPS and obtain the corresponding tetrasodium salt (**Scheme 23**).

**Scheme 23: Synthetic Route to Half-cage Tetraphenylsiloxane Tetrasodium Salt**



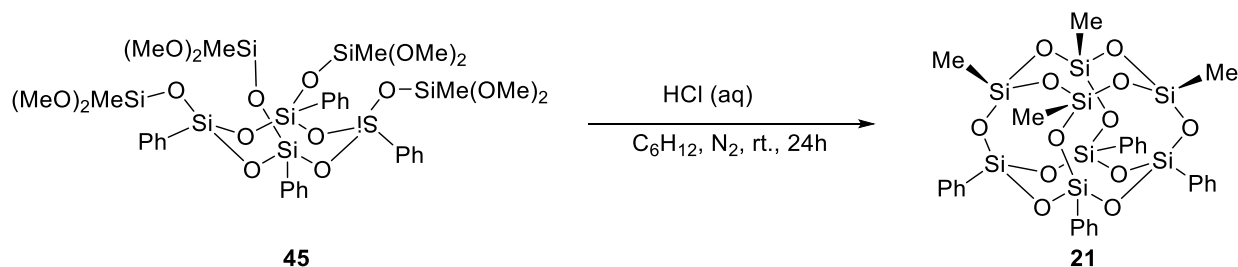
The half-cube was characterized using NMR spectroscopy after converting the tetraphenyl tetrasodium salt into the tetramethyltetra-phenyl ( $\text{Me}_4\text{Ph}_4$ ) dimethoxy half cube derivative  $[\text{PhSi}(\text{O})\text{O}(\text{Me})\text{Si}(\text{OCH}_3)_2]_4$  upon reaction with  $\text{MeSiCl}_3$  in methanol at room temperature (**Scheme 24**).

**Scheme 24: Synthesis of the Tetramethyltetra-phenyl ( $\text{Me}_4\text{Ph}_4$ ) dimethoxy Half-cube**



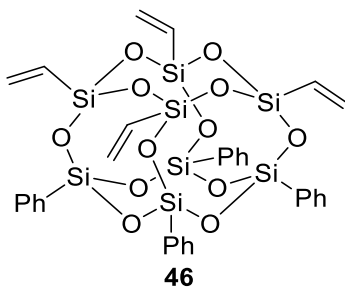
Further reaction of the  $\text{Me}_4\text{Ph}_4$  dimethoxy half cube via hydrolysis with  $\text{H}_2\text{O}$  and concentrated  $\text{HCl}^{110}$  generated the fully condensed  $\text{Me}_4\text{Ph}_4$  Janus cube in 85% yield (**Scheme 25**).

**Scheme 25: Synthesis of  $[\text{PhSiO}_{1.5}]_4[\text{MeSiO}_{1.5}]$  Janus Silsesquioxane Cube**



The tetraphenyl tetrasodium salt half cage was also functionalized into the dimethoxy derivatives of different trichlorosilanes in methanol followed by acid hydrolysis to afford their corresponding Janus silsesquioxanes. The structure for a typical tetraphenyltetra-vinyl dimethoxy derivative,  $[\text{PhSiO}_{1.5}]_4[\text{vinylSiO}_{1.5}]$  **46** obtained by the same process (**Figure 6**).

**Figure 6: The tetraphenyltetra vinyl,  $[\text{PhSiO}_{1.5}]_4[\text{vinylSiO}_{1.5}]$ , Janus from the functionalized  $\text{Ph}_4$  half cube sodium salt with vinyltrichlorosilane**

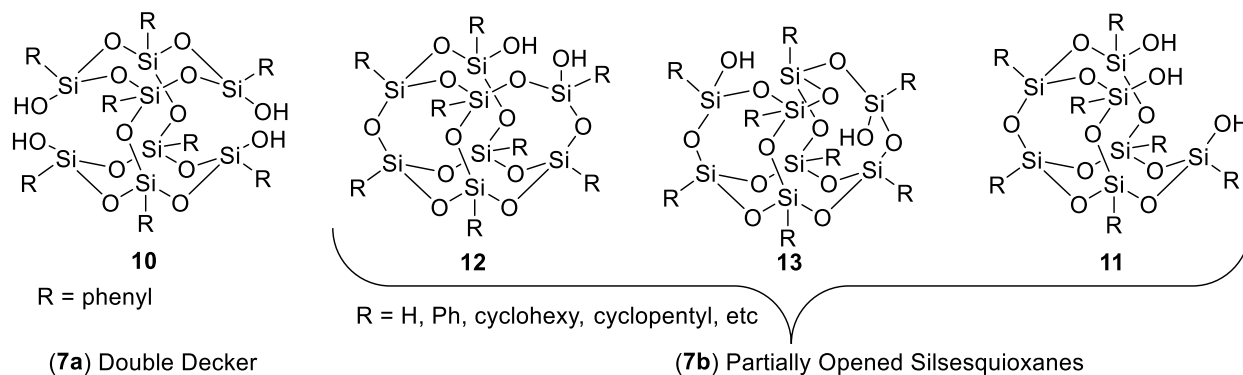


However, the precise oligomerization and hydrolysis mechanism for these structures is yet to be understood.

### 2.3.4 Incompletely Condensed POSS Cages

Contrary to moving from monomeric chlorosilanes to condensed oligomers, fully condensed silsesquioxanes have also been ring-opened to offer a range of structures (**Figure 7**) that can be either double decker (**Figure 7a**) or other partial/corner ring-opened (**Figure 7b**) silsesquioxanes. Both acid and base catalyzed routes to incompletely condensed silsesquioxane cages have been reported.

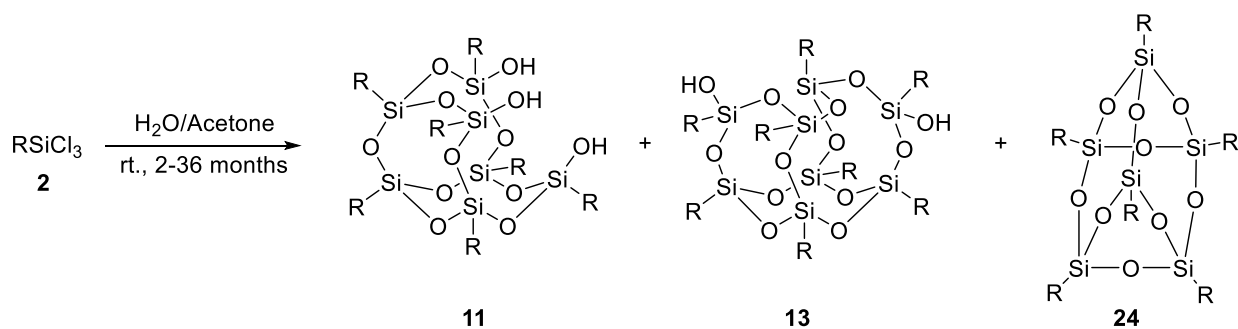
**Figure 7: Incompletely Condensed Silsesquioxanes, (7a) Double Decker, and (7b) Partially Opened Silsesquioxane**





condensed trisilanol [ $\text{Cy}_7\text{Si}_7\text{O}_9(\text{OH})_3$ ] **11**, disilanol [ $\text{Cy}_8\text{Si}_8\text{O}_{11}(\text{OH})_2$ ] **13** and a completely condensed hexacyclohexylsilsesquioxane [ $\text{Cy}_6\text{Si}_6\text{O}_6$ ] **24** from the kinetic hydrolytic condensation of monomeric cyclohexyltrichlorosilane ( $\text{CySiCl}_3$ ) in acetone/water medium (**Scheme 27**).<sup>112</sup>

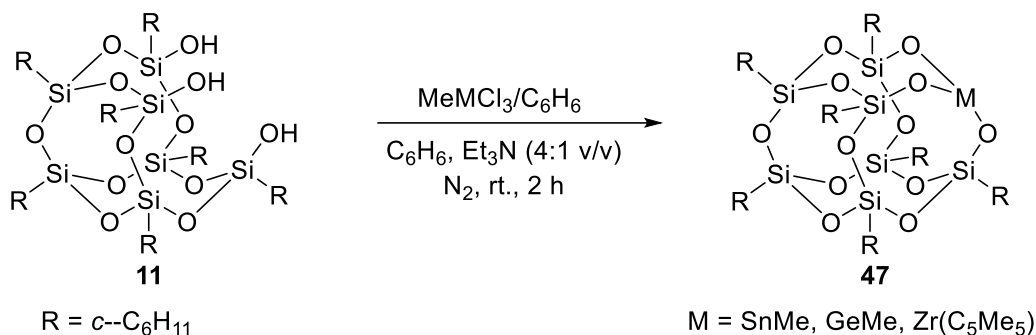
**Scheme 27: General Reaction Scheme for the hydrolytic condensation of cyclohexyltrichlorosilane ( $\text{CySiCl}_3$ ) in aqueous acetone**



Formation of the trisilanol results from the hydrolytic removal of one silicon atom from a stable octameric silsesquioxane, hence making it susceptible to reactions that can fill the vacant vertex. Functionalization of the trisilanol via corner-capping of the trisilanol silsesquioxane framework with trifunctional monomeric  $\text{MeGeCl}_3$ ,  $\text{MeSnCl}_3$ , and  $\text{CpZrCl}_3$  afforded condensed strain-free products bearing seven silicon atoms with one much larger transition metal atom (**Scheme 28**).<sup>84,90,102,143,144</sup>

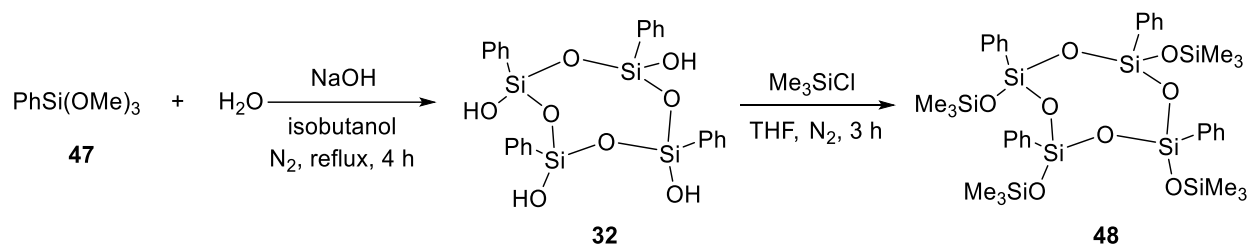


**Scheme 28: Corner-capping Octacyclohexyl silsesquioxane trisilanol with Trifunctional Monomers**



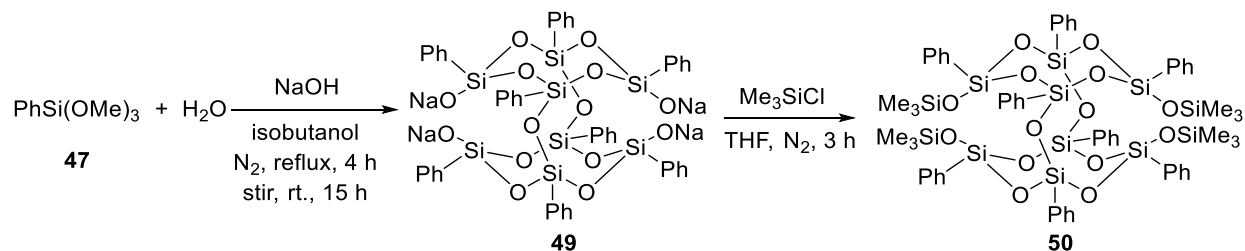
In a complete variation to the above strategy, a more detailed approach showing the formation and reactivity of species obtained from the base-catalyzed hydrolysis of phenyltrialkoxysilanes in various reaction solvents was investigated by Kawakami and Lee.<sup>113</sup> The duo noted interesting observations based on the feed ratio of the metallic hydroxide, MOH, to the trialkoxyphenylsilane unit. Thus, cyclic sym-cis  $(\text{PhSiO}_2)_4$  tetraphenylsilsesquioxanetetraol tetrasodium salt was the major product when equimolar amounts of NaOH to the Si compound were subjected to refluxing water-*i*-propanol or water-*i*-butanol system (**Scheme 29**).

**Scheme 29: Synthesis and Functionalization of tetraphenylsilsesquioxanato tetrasodium salt**



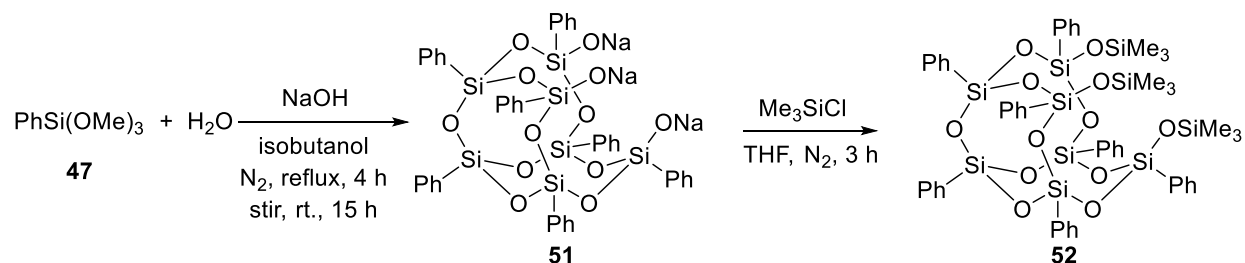
On the contrary, when an excess of the NaOH was added to the silicon compound, cubic octaphenylsilsesquioxane was obtained as the major product (**Scheme 30**).

### Scheme 30: Synthesis of Cubic Octaphenylsilsesquioxane from Phenyltrimethoxysilane



The heptaphenylsilsesquioxanetriol trisodium salt was also obtained after 20 h reaction time and, at a prolonged reaction time involving the consumption of the trisilanol above, the double-decker octaphenyl silsesquioxanetetraol tetrasodium salt was formed in high yield (**Scheme 31**).

### Scheme 31: Synthesis of heptaphenylsilsesquioxanato trisodium salt from Phenyltrimethoxysilane



### 2.3.5 Cage Cleaving

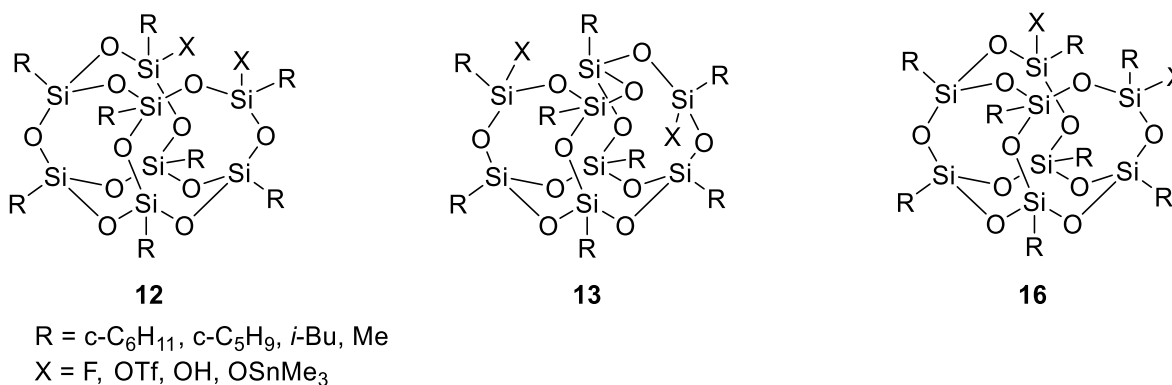
Cleavage of completely condensed silsesquioxanes can be effected to give various incompletely condensed counterparts. For instance, Feher *et al.*<sup>41</sup> reported both the selective acid and base promoted cleavage of one Si-O-Si of fully condensed  $[\text{RSiO}_{3/2}]_n$  frameworks and the manipulation of functional groups for use as precursors in the synthesis of hybrid inorganic/organic materials. Also, Laine and Roll<sup>13</sup> and Li and Kawakami<sup>125</sup> independently demonstrated the formation of incompletely condensed octaphenylsilanol POSS from the hydrolysis of the completely condensed cage. In our

particular case aimed at desymmetrizing double decker oligomeric Silsesquioxanes, the work reported in the literature by Laine and Roll<sup>13</sup> for the cleavage of completely condensed Ph<sub>8</sub>T<sub>8</sub> was of great interest.

### 2.3.5.1 Acid-Catalyzed Approaches

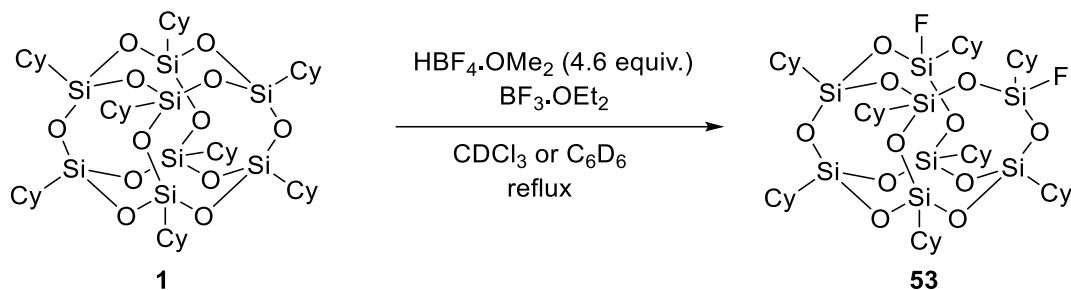
Under acid promoted approaches, Feher and coworkers<sup>42,90,95,98,112</sup> synthesized a variety of difunctionalized open caged silsesquioxanes from the selective cleavage of a single siloxane (Si-O-Si) linkage (**Figure 8**).

**Figure 8: Difunctional POSS cages obtained by the Selective Cleavage of One Si-O-Si Linkage**



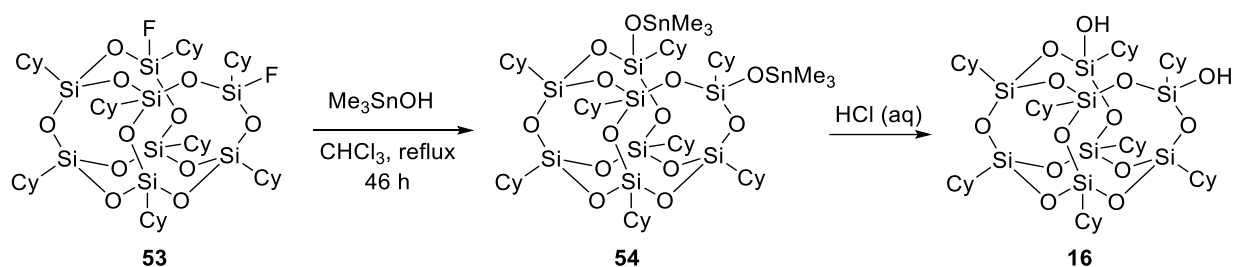
According to their procedure, briefly refluxing a mixture of R<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> (R = cyclohexyl or cyclopentyl), excess of HBF<sub>4</sub>·OMe<sub>2</sub> and BF<sub>3</sub>·OEt<sub>2</sub> in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> can afford a C<sub>2v</sub>-symmetric difluoroPOSS framework resulting from the fissure of one Si–O–Si linkage of the condensed cage precursor (**Scheme 32**).<sup>108</sup>

### Scheme 32: Synthesis of *exo*-Octacyclohexyl Octasilsesquioxane Difluoride



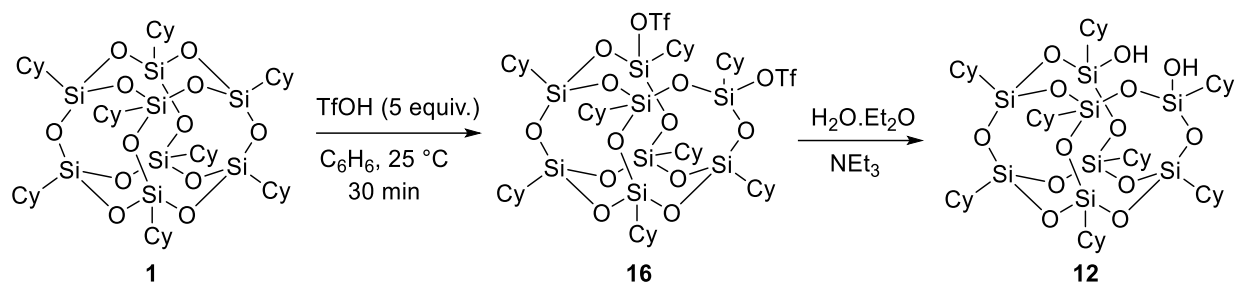
Hydrolysis of this difluoride with  $\text{Me}_3\text{SnOH}$  and aqueous  $\text{HCl}$  can proceed with retention of the stereochemistry at the silicon-bearing fluorine atom to afford the disilanol (**Scheme 33**).

### Scheme 33: Hydrolysis of *exo*-octacyclohexyl octasilsesquioxane difluoride to the disilanol



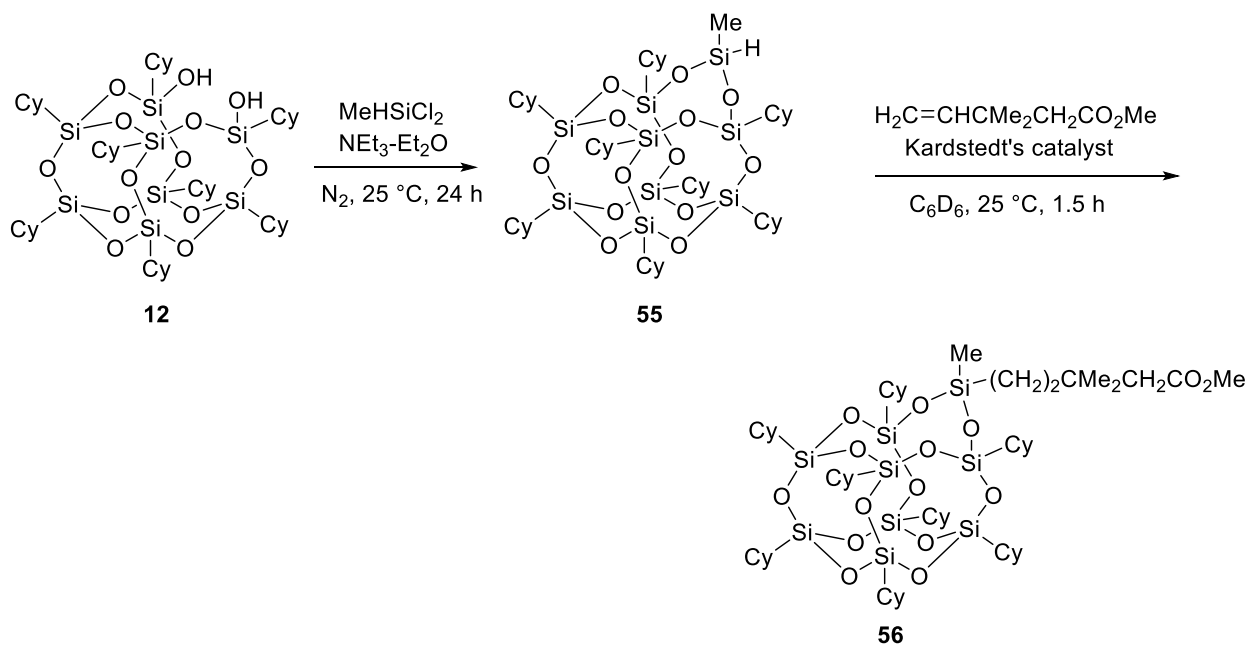
Interestingly, this group demonstrated that the  $\text{HBF}_4$  is more important for the selective cleavage of one Si-O-Si linkage rather than acting as a fluoride source. This conclusion was reached when their trial with 5 equivalents of  $\text{TfOH}$  which lacks a fluoride, in benzene afforded the disilanol product in 30 minutes. However, the ditriflate resulting from  $\text{TfOH}$  is difficult to handle and undergoes spontaneous hydrolysis upon exposure to water to give the *endo*-disilanol. This *endo* disilanol was also obtained from the addition of  $\text{H}_2\text{O} \cdot \text{Et}_2\text{O}$  and excess triethylamine to the ditriflate (**Scheme 34**).

**Scheme 34: Synthetic scheme for endo-octacyclohexyl octasilsesquioxane disilanol from  $\text{Cy}_8\text{Si}_8\text{O}_{12}$**



The structure of the endo disilanol was confirmed by capping with  $\text{MeHSiCl}_2$  in the presence of  $\text{NEt}_3$  followed by subsequent hydrosilylation with Kardstedt's catalyst to give the functionalized structure A below (**Scheme 35**).

**Scheme 35: Functionalization of endo disilanol with  $\text{MeHSiCl}_2$  and subsequent Hydrosilylation**

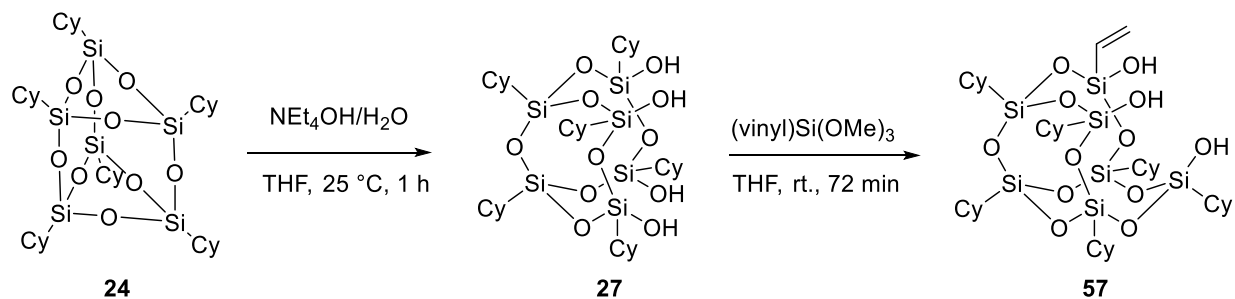


**2.3.5.2 Base-Catalyzed Approaches**

Similar cages to those shown in Schemes 5-6 have also been obtained via base-catalyzed techniques. In addition, an interesting hydrolysis of condensed  $\text{Cy}_6\text{Si}_6\text{O}_9$  ( $\text{Cy} =$

c-C<sub>6</sub>H<sub>11</sub>) framework followed by homologation to the heptacyclohexyl silsesquioxanetrilsilanol was reported by Ziller *et al.*<sup>38</sup> For instance, with a (vinyl)Si(OMe)<sub>3</sub> monomer, Cy<sub>6</sub>Si<sub>6</sub>O<sub>9</sub> (Cy = c-C<sub>6</sub>H<sub>11</sub>) undergoes hydrolysis and homologation in aqueous NEt<sub>4</sub>OH to afford trilsilanol A' (**Scheme 36**).

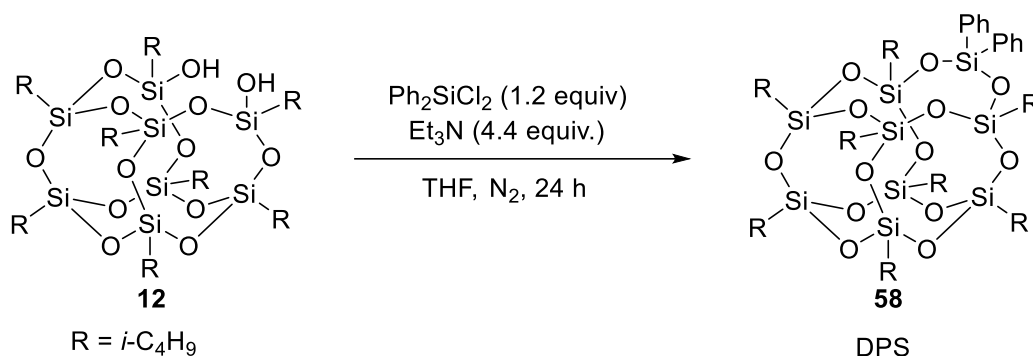
**Scheme 36: Hydrolysis and Homologation of Cy<sub>6</sub>Si<sub>6</sub>O<sub>9</sub> to endo-Cs-Cy<sub>6</sub>(vinyl)Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub>**



Upon exposure of Cy<sub>6</sub>Si<sub>6</sub>O<sub>9</sub> **24** with aqueous NEt<sub>4</sub>OH in THF for 1 h, two Si-O-Si linkages were selectively cleaved to give a tetrasilanol **27** with complete retention of stereochemistry at Si.<sup>39,100,114</sup> This structure however undergoes decomposition into the Cy<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub> upon prolonged reaction time of several hours with a loss of the two silicon signals of tetrasilanol and appearance of the new Si signals characteristic of the trilsilanol.<sup>38</sup>

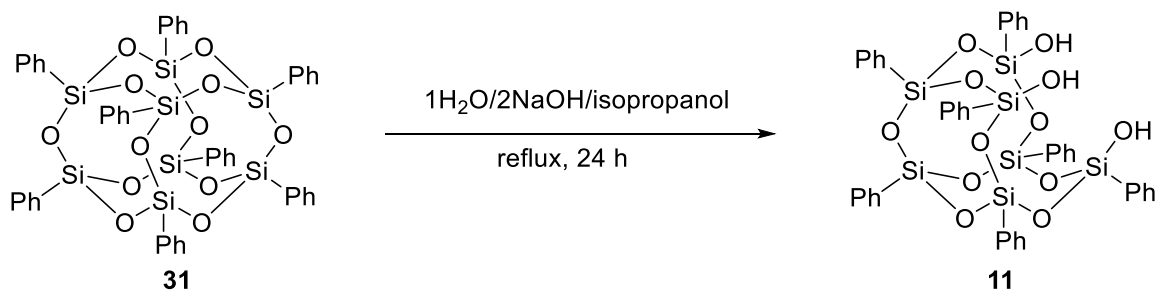
Later, Li *et al.*<sup>47</sup> developed a protocol for the synthesis of diphenyl-functionalized silsesquioxane (DPS) based on octa-isobutyl silsesquioxane endo-disilanol (OIBS-EDN) obtained from the fully condensed octa-isobutyl silsesquioxane (OIBS) following the selective Si-O-Si bond cleavage route reported by the Feher group and subsequent derivatization with the addition of diphenyldichlorosilane (**Scheme 37**).<sup>115</sup>

**Scheme 37: Synthesis of  $(i\text{-C}_4\text{H}_9)_8\text{Si}_8\text{O}_{13}(\text{C}_6\text{H}_5)_2$  from  $\text{endo-}(i\text{-C}_4\text{H}_9)_8\text{Si}_8\text{O}_{10}(\text{OH})_2$**

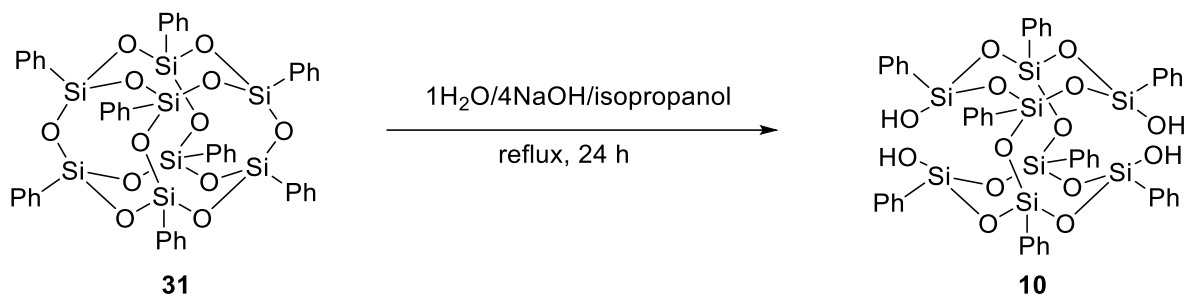


In a somewhat different approach, a review assembled by Laine and Roll in 2011 disclosed various ways of generating a number of open-caged silsesquioxanes from their fully condensed precursors, particularly for the condensed octafunctional POSS cages.<sup>13</sup> Thus varying the feed ratio of the metallic base to that of the  $\text{PhSiO}_{1.5}$  unit, a variety of open cage structures were achieved (**Schemes 38-39**).

**Scheme 38: Synthesis of Heptaphenyl Silsesquioxanetrissilanol from the Base-Catalyzed Hydrolysis of Condensed  $\text{Ph}_8\text{T}_8$**



### Scheme 39: Synthesis of Octaphenyl Silsesquioxanetetrasilanol from the Base-Catalyzed Hydrolysis of Condensed Ph<sub>8</sub>T<sub>8</sub>



#### 2.3.6 Symmetric Polyhedral Oligomeric Silsesquioxanes

As stated earlier, double decker oligomeric silsesquioxanes (DDSQ) are a special case of open cage silsesquioxanes with two cyclosiloxane rings in parallel planes linked by two oxygen bridges (**Figure 9**). To date, only double deckers with phenyl moieties as organic substituents are known.

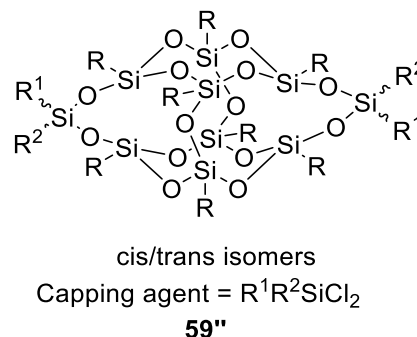
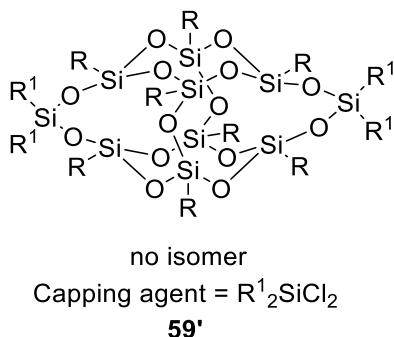
**Figure 9: Structures of Double Decker Oligomeric Silsesquioxanes (DDSQ)**



Functionalization of the open ends by capping with a suitable di- or tri-functional group results in the generation of a functionalized symmetric POSS compound. Based on the capping agents used, the resulting functionalized POSS can either be a single compound or one that displays geometric isomers (cis- and trans-isomers) (**Figure 10**). Interestingly, the cis and trans isomers display different physical properties, like melting point and solubility.

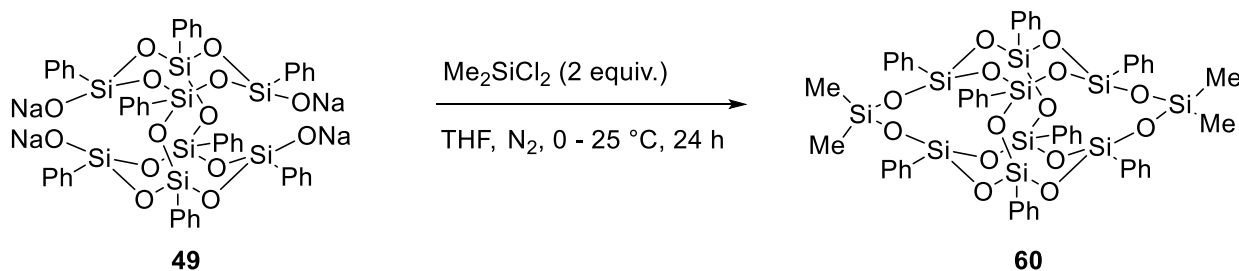


**Figure 10: Structures of Symmetric POSS Compounds (59') no isomer (59'') cis/trans isomers**



Thus, the bridging of incompletely condensed double decker oligomeric silsesquioxanes with chlorosilanes is quite intriguing; and can lead to different product types based on the type of silylating agent. For instance, Kawakami and Lee obtained the tetramethyldisilylDDSQ cage as the only product in quantitative yield upon treatment of the DDSQ(ONa)<sub>4</sub> with dimethyldichlorosilane – a symmetrical capping agent (Scheme 40).<sup>113</sup>

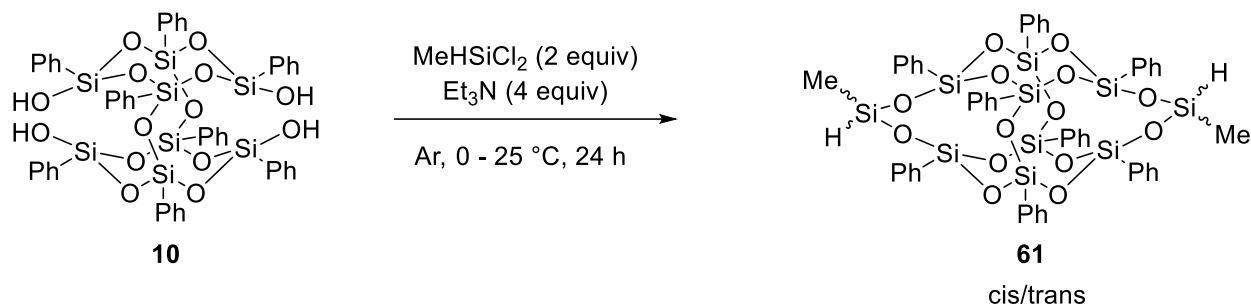
**Scheme 40: Synthesis of DDSQ(Me)<sub>4</sub> from Double-Decker Silsesquioxane Tetrasodium Salt DDSQ(ONa)<sub>4</sub>**



However, if the bridging dichlorosilane has two different substituents, the bridging reaction occurs to afford geometric isomers as described above. Such geometric isomers (cis and trans) are known for several capping agents. For instance, the Zheng group reported the synthesis of 9,19-di(hydro)-9,19-dimethyloctaphenyl double-decker silsesquioxane

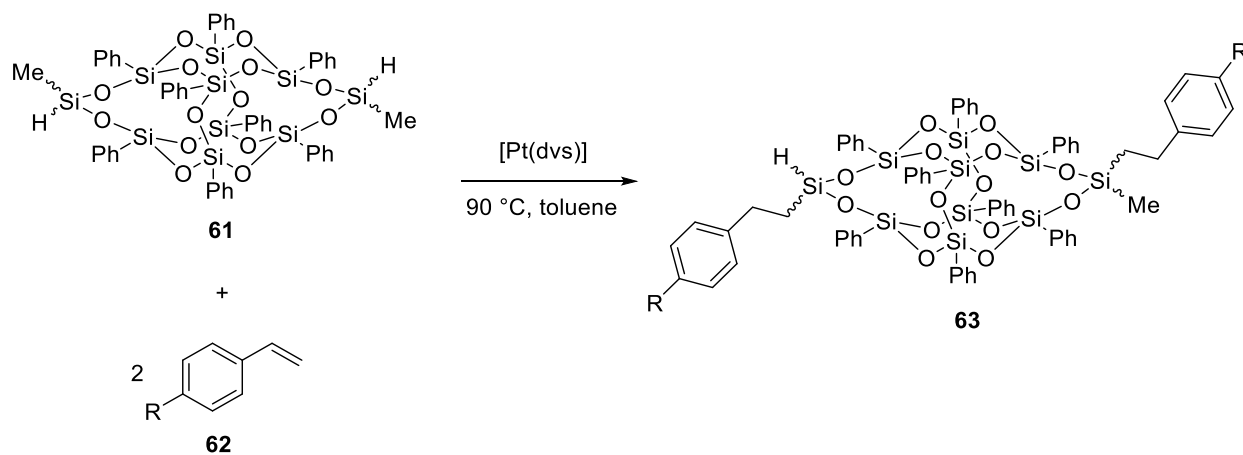
monomer by treating the double decker tetrasilanol with MeHSiCl<sub>2</sub> and Et<sub>3</sub>N (Scheme 41).<sup>129</sup> The mixture was not separated into its pure cis/trans forms.

**Scheme 41: Synthesis of 9,19-di(hydro)octaphenyl double-decker silsesquioxane from DDSQ(OH)<sub>4</sub>**



In 2017, the Marciniak group reported the cis/trans structures backed with the x-ray structures of 9,19-dihydro-9,19-dimethyloctaphenyl double-decker silsesquioxane (DDSQ-2SiH).<sup>109</sup> This product was further subjected to hydrosilylation using various styrylarenes as comonomer (**Scheme 42**).

**Scheme 42: Hydrosilylation of 9,19-di(hydro)octaphenyl Double-Decker Silsesquioxane with para-substituted Styrenes**

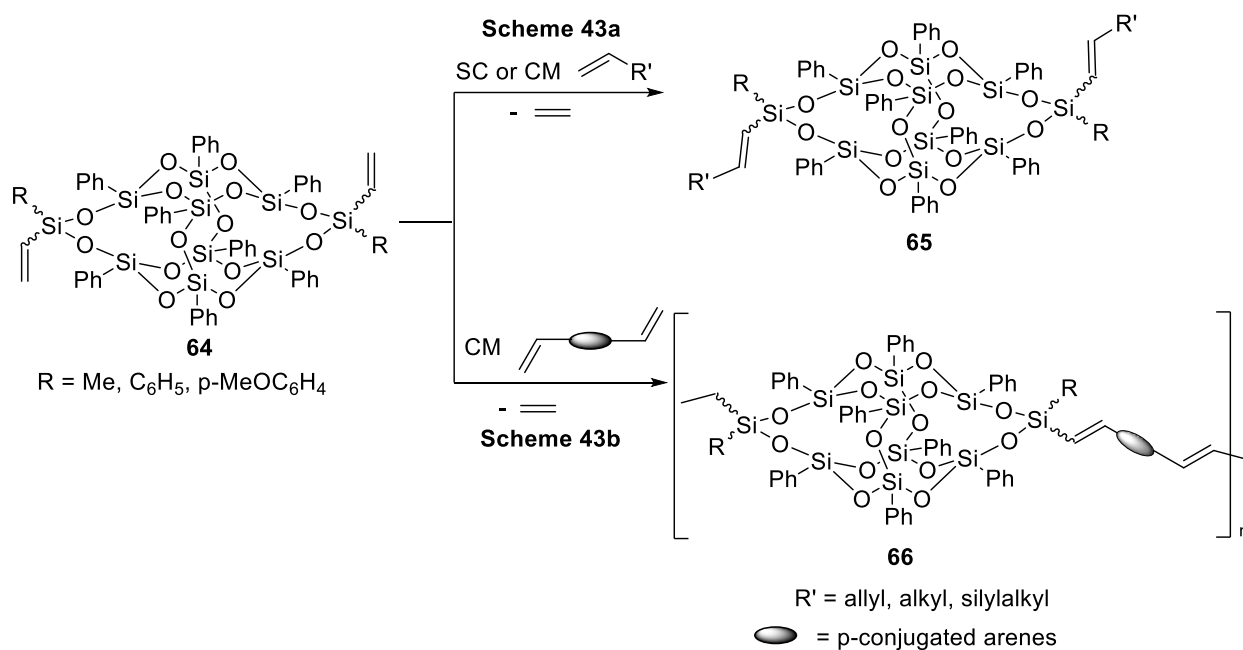


R = 1-methylnaphthyl, 9-methylantracenylyl, pentafluorophenyl

In addition to the dihydro difunctional double decker derivative, the divinyl counterparts were also obtained and similarly subjected to both hydrosilylation, cross-metathesis

(**Scheme 43a**) and silylative cross-coupling (**Scheme 43b**) to afford molecular and macromolecular modified products.

**Scheme 43: Cross Metathesis or Silylative Cross Coupling of 9,19-di(vinyl)octaphenyl Double-Decker Silsesquioxane with various Olefins and conjugated Arenes**



Thus, the nature of the substituents on the chlorosilane is crucial and may accommodate various transformations including hydrosilylation,<sup>109,126</sup> Heck coupling, metathesis, etc<sup>109,134,135</sup> reactions.

## CHAPTER 3 Asymmetric Polyhedral Oligomeric Silsesquioxanes

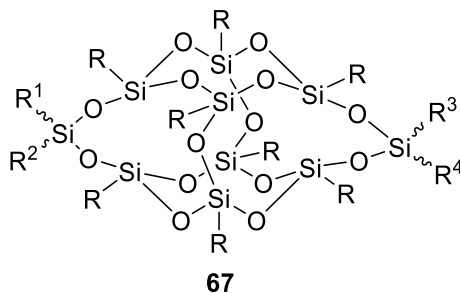
### 3.1 Multifunctional Reagents

Multifunctional reagents are important synthons in organic synthesis. Asymmetric POSS compounds are known, but not those with a DDSQ architecture. Double-decker oligomeric silsesquioxanes are highly symmetrical compounds bearing reactive functionalities. Desymmetrization by way of functionalizing these compounds with different capping agents has been daunting, particularly so with the multiple identical functional groups that are distributed in the structure. This has negatively impacted progress on developing functionalized silsesquioxanes that can be tethered to two dissimilar polymer chains with potentials to improve the physical and mechanical properties of the resulting composite. In recent times, however, some progress has been recorded in this direction.

### 3.2 Asymmetric Double-Decker Oligomeric Silsesquioxanes (DDSQs) from Prefunctionalized Divinyl-Capped DDSQs

Asymmetric double-decker compounds are functionalized DDSQs that are side-capped with two different chlorosilanes or capping agents (**Figure 11**).

**Figure 11: Typical Structure of an Asymmetric POSS Compound, 'A/B Cage'**





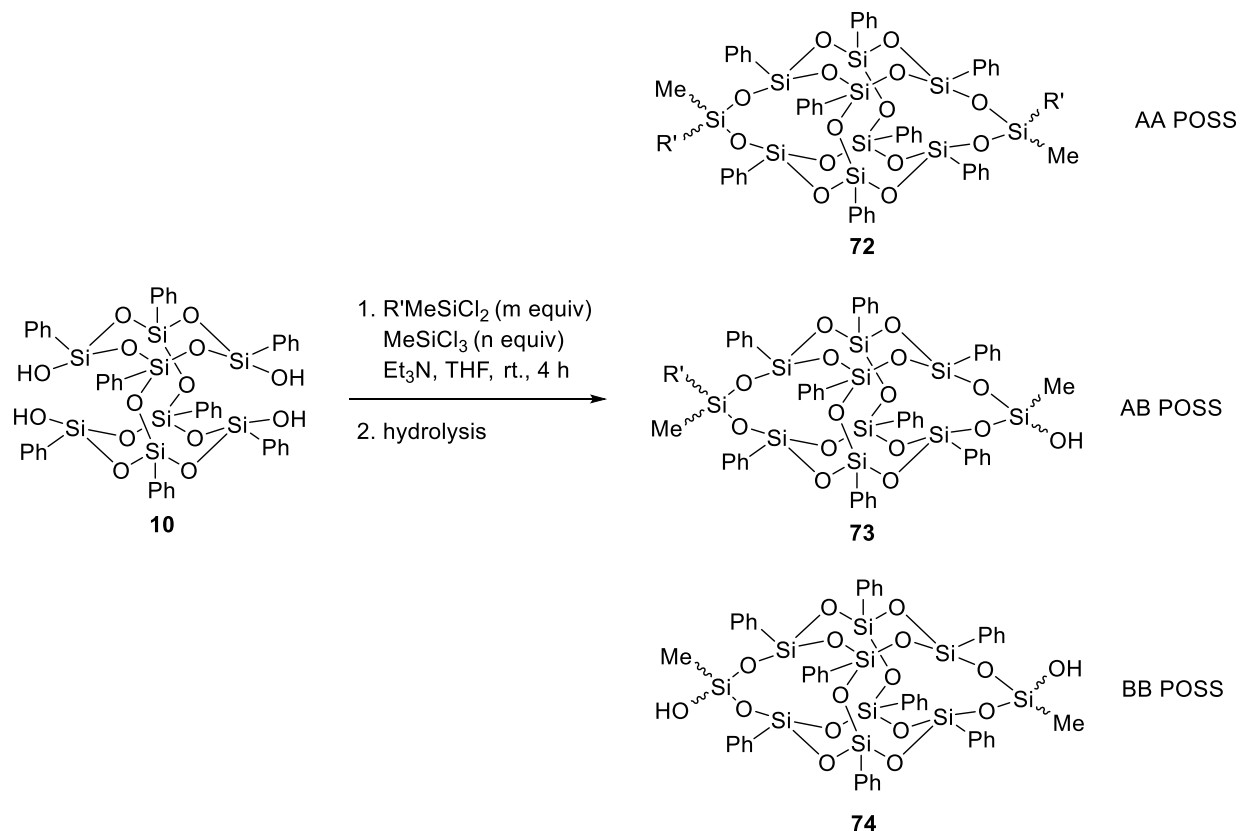
Even though this route reported an exclusive asymmetric product with high E-selectivity, yet the techniques is limited to the use of vinyl-capped precursors and styryl motifs to give the desymetrized product via metathesis.

### **3.3 Synthesis and Separation of Asymmetrically Capped Double-Decker Silsesquioxanes Mixtures**

In a rather different approach with research efforts in our lab, a colleague working on separating the cis- and trans-systems of capped  $T_8$  double deckers described a non-selective approach for the synthesis and isolation of asymmetric POSS compounds. Unlike the Marciniac team that reported an exclusive asymmetric product with no side products, the Lee group were able to obtain six different isomers that were cleanly separated and analyzed. This discovery has not only revealed and unraveled another route to asymmetric DDSQs but also contributed to several other documented routes for the separation of the cis and trans isomers which had only been achieved by fractional crystallization.<sup>107–109</sup> In his specific case, Vogelsang *et al.*<sup>107</sup> disclosed that functionalized DDSQs bearing different bridging chlorosilanes can be separated by nonpolar-LC based on polarity differences resulting from the different number of silanol groups in the final products. For this reason, the capping agents were carefully chosen to provide a product mixture with zero, one, and two hydroxyl groups that could afford the needed polarity differences to enable their clean separation. Trichlorosilane was therefore used as one capping agent in all cases against other different chlorosilanes. In addition to the cis/trans products present in the product mixture, an interesting class of novel capped cage, the asymmetric POSS cage was also obtained. Thus, the addition of an equimolar premixture

of  $\text{Me}(\text{R}^1)\text{SiCl}_2$  and  $\text{MeSiCl}_3$  to a THF solution of  $\text{DDSQ}(\text{OH})_4$  followed by  $\text{Et}_3\text{N}$ , and stirring at room temperature for 4 h afforded a product mixture of cis/trans POSS cages and an asymmetric analogue (**Scheme 45**).

**Scheme 45: Synthetic Pathway for AA, AB and BB Capped POSS Cages**



The simultaneous introduction of the two different chlorosilanes to the stirring solution of  $\text{DDSQ}(\text{OH})_4$  **10** created competition at the capping sites (based on kinetics) that led to mixtures of three different products; two sets of symmetric stereoisomers and one stereoisomeric mixture asymmetrically capped DDSQ cages making a total of six products.

However, this procedure is also limited to the use of a mixture of polar and non-polar capping agents for their effective separation and/or purification.

### **3.4 Attempts to the Selective Synthesis of Asymmetrically Capped DDSQ Cages**

The above discoveries in sections 3.2-3.3 and their limitations for asymmetric double deckers is intriguing, hence illustrating the need to unravel better synthetic routes and potential applications of this novel class of silsesquioxanes. The development of an approach to selectively synthesize these types of compounds is therefore imperative. The challenge might be surmountable with some manipulation of the chemistry of protecting groups. To this end, several protecting strategies including silylation, benzylation, benzoylation, borylation and other immobilizing agents (silicon supports) could be the envisaged path. If this is achievable for full protection of the DDSQ(OH)<sub>4</sub>, selective functionalization subsequent to cage closing would provide access to desymmetrization via silylation.

#### **3.4.1 Masking and Demasking Techniques – A Tool for Asymmetric Synthesis**

Selectivity in multifunctional compounds is normally carried out using protection techniques. This allows some reactive functionalities in a molecule to be either regio- or chemo-selectively blocked temporarily while another reactive site can undergo transformation. The resulting compound is normally a stable protected substrate that allows deprotection (removal of the masking agent) with reagents that do not destroy the original scaffold or react with the regenerated functional group(s).

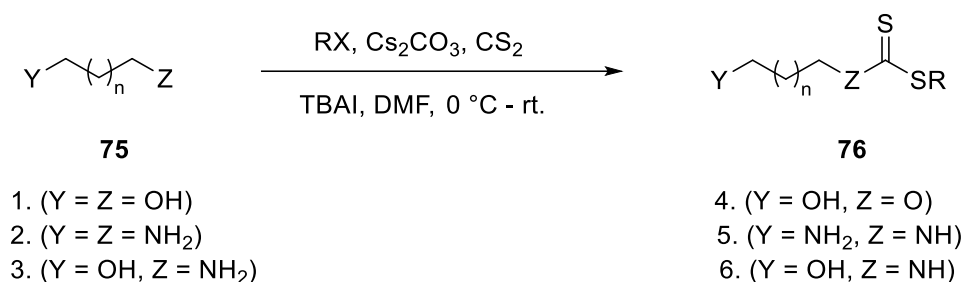
#### **3.4.2 Protection of Hydroxyl and Amino Groups with Thiocarbonates**

Nagle *et. al.* demonstrated the selective monoprotection of diol, diamines and alcohol using cerium type bases.<sup>133</sup> In his approach, mono dithiocarbamates were synthesized in



good yields from the coupling of various alcohols, amines and amino alcohols using alkyl bromides,  $\text{CS}_2$ ,  $\text{Cs}_2\text{CO}_3$  and TBAI in DMF<sup>133</sup> (**Scheme 46**).

**Scheme 46: Monothiocarbonation of diols and diamines**

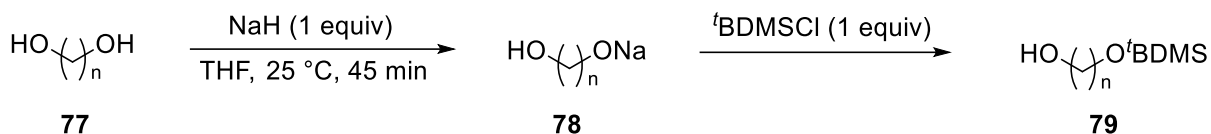


This protocol is amendable to multifunctional substrates as they illustrated in the selective bis-thiocarbonation of 1,2,6-hexanetriol by coupling with  $\text{CS}_2$  and p-methoxybenzyl chloride.

**3.4.3 Protection of Hydroxyl Groups with Silyl Reagents**

Substrates bearing hydroxyl groups have also been protected using silyl reagents for the formation of silo-ether derivatives. Their formation and removal have been achieved under a wide variety of mild reaction conditions. They are readily cleaved by hydrolysis with MeOH, mild acids, mild bases and fluoride ion source.<sup>13,14,64,119,125,133</sup> These techniques have been used in several synthetic strategies for the synthesis of various organic compounds and natural products. McDougal and coworkers,<sup>119</sup> for instance demonstrated the selective monosilylation of symmetric 1,n-diols at room temperature and attributed the source of selectivity to the properties of the monosodium salt of the diol (**Scheme 47**).

### Scheme 47: General Reaction Scheme for the Monosilylation of Symmetric 1,n-diols

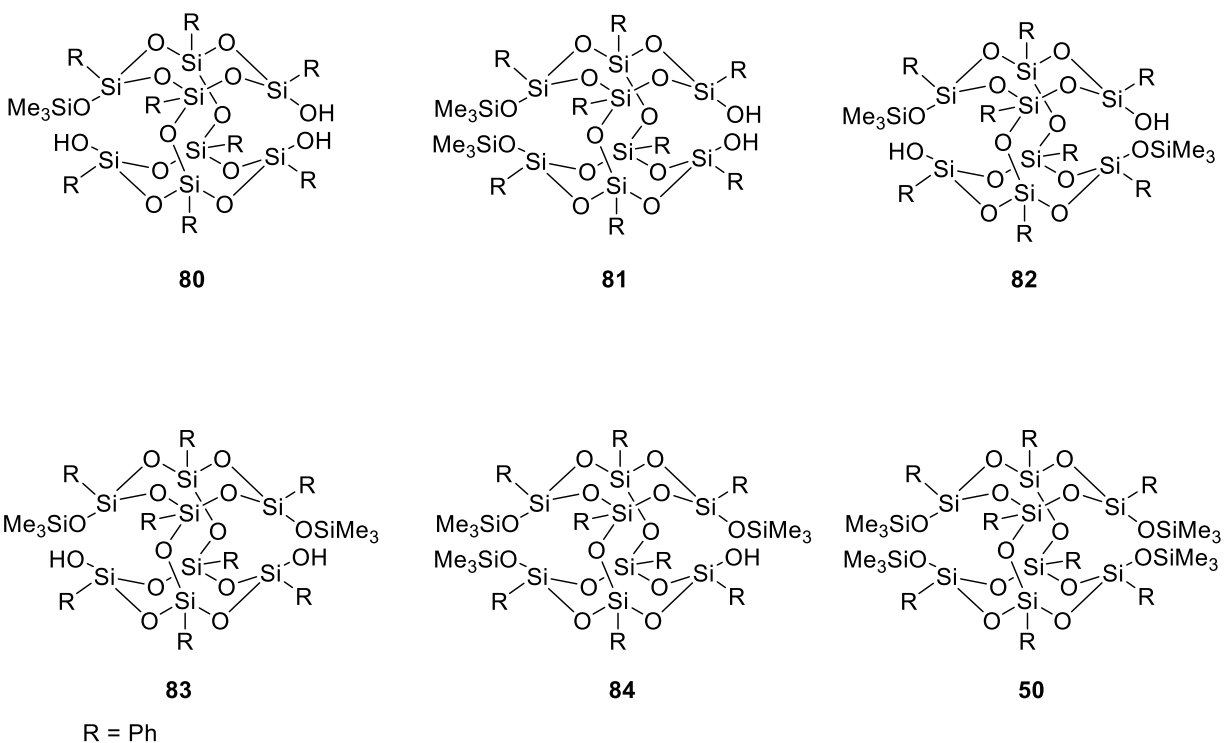


The rationale with this technique is to enable us to introduce a dichloroorganosilane on the free Si-ONa/Si-OH group after the TMS intermediate formation, then deprotection of the TMS group(s) and finally introduction of a second capping agent. Extension of these developments to silsesquioxane cages with the intention to assemble asymmetric A/B systems is yet to be reported.

#### 3.4.3.1 Use of Silylating Agents as Protecting Groups on DDSQ(OH)<sub>4</sub>

Possible structures that could result from the protection of the hydroxyl groups with silylating agents are shown in **Figure 12**.

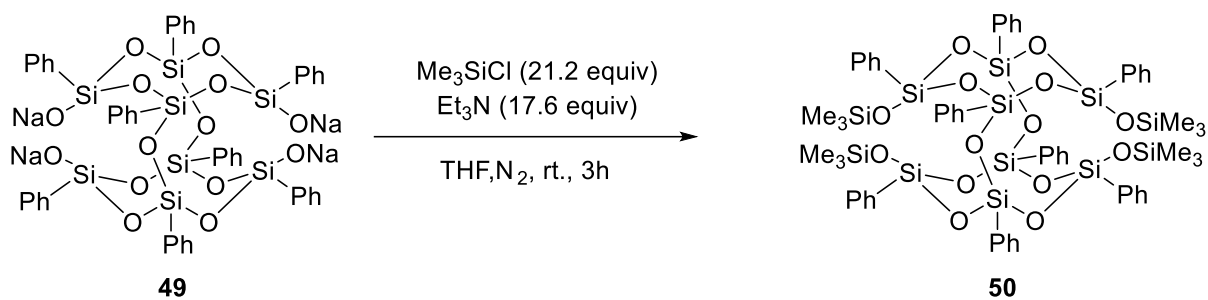
**Figure 12: Protected DDSQs with TMSCl**



Structures **80**, **82** and **83** are more likely to provide the requisite protection for the introduction of two different capping agents that could afford the desired asymmetric POSS compound.

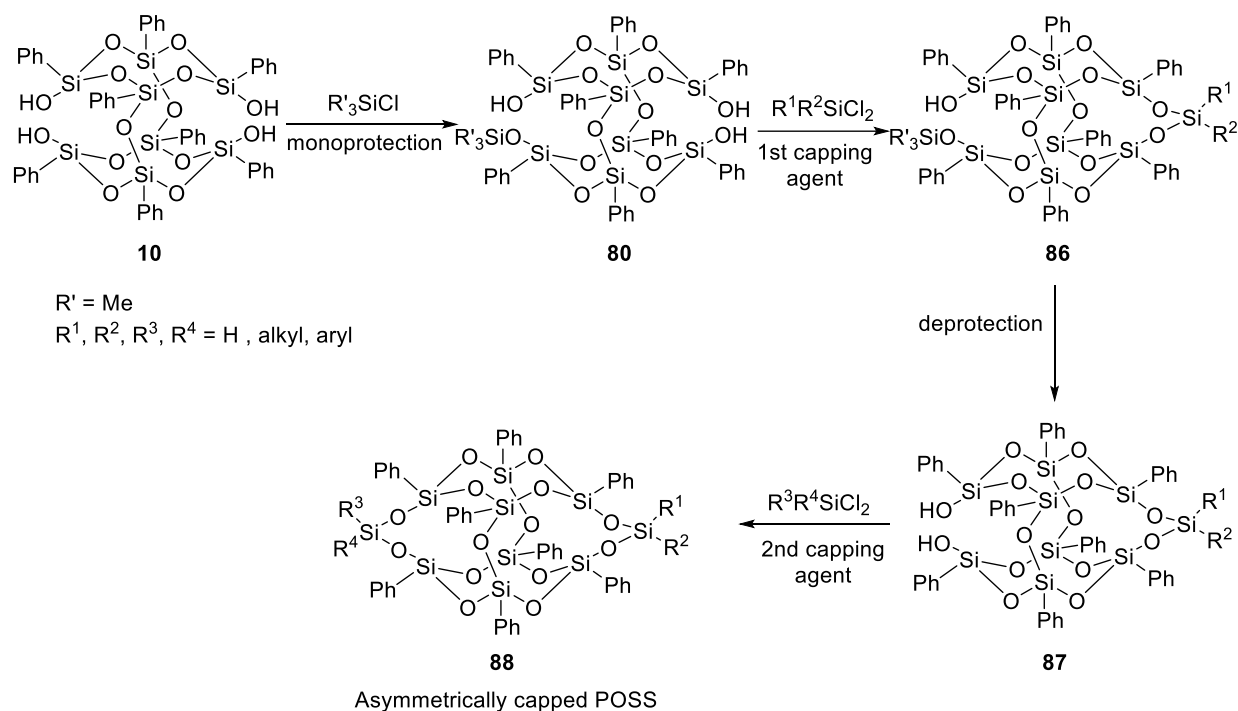
As an application of this technique to silsesquioxane chemistry, Kawakami and Lee<sup>113</sup> have demonstrated that the hydroxyl functionalities of double decker oligomeric Silsesquioxanes can be efficiently masked with TMSCl to form a stable TMS-protected DDSQ (**Scheme 48**).

### Scheme 48: Silylation of DDSQ(ONa)<sub>4</sub> with Trimethylchlorosilane



In our case, to selectively mask tetrafunctional substrate DDSQ silanol,<sup>64,119</sup> it is envisioned that the masking agent should partner with the active reagent by selectively blocking one or more of the reactive functionalities while capping/closing manipulations are carried on the other end with a selected capping agent. The protected hydroxyl group could then be de-blocked followed by introduction of a different capping agent to complete the construct of the A/B cages (**Scheme 49**).

### Scheme 49: Monoprotection of hydroxyl groups with trialkylsilyl chloride



### 3.5 Use of Solid Support/Immobilizing Agent in the Synthesis of Asymmetrically Capped DDSQs

Silsesquioxanes could be blocked using solid surface support/immobilized reagents. Similar to the case with TMSCl, one side of the cage could be blocked using an immobilized reagent like 'Red-Sil'<sup>123</sup> or Merrifield resin.<sup>136</sup> The rationale here is to covalently bind/immobilize one part of the reactant to a solid support, where owing to site isolation, only one side would react. Thus, the solid surface supports should provide anchorage to symmetrical cages using a linker while the open end of the molecule is closed with one equivalent of the organo dichlorosilane capping agent.

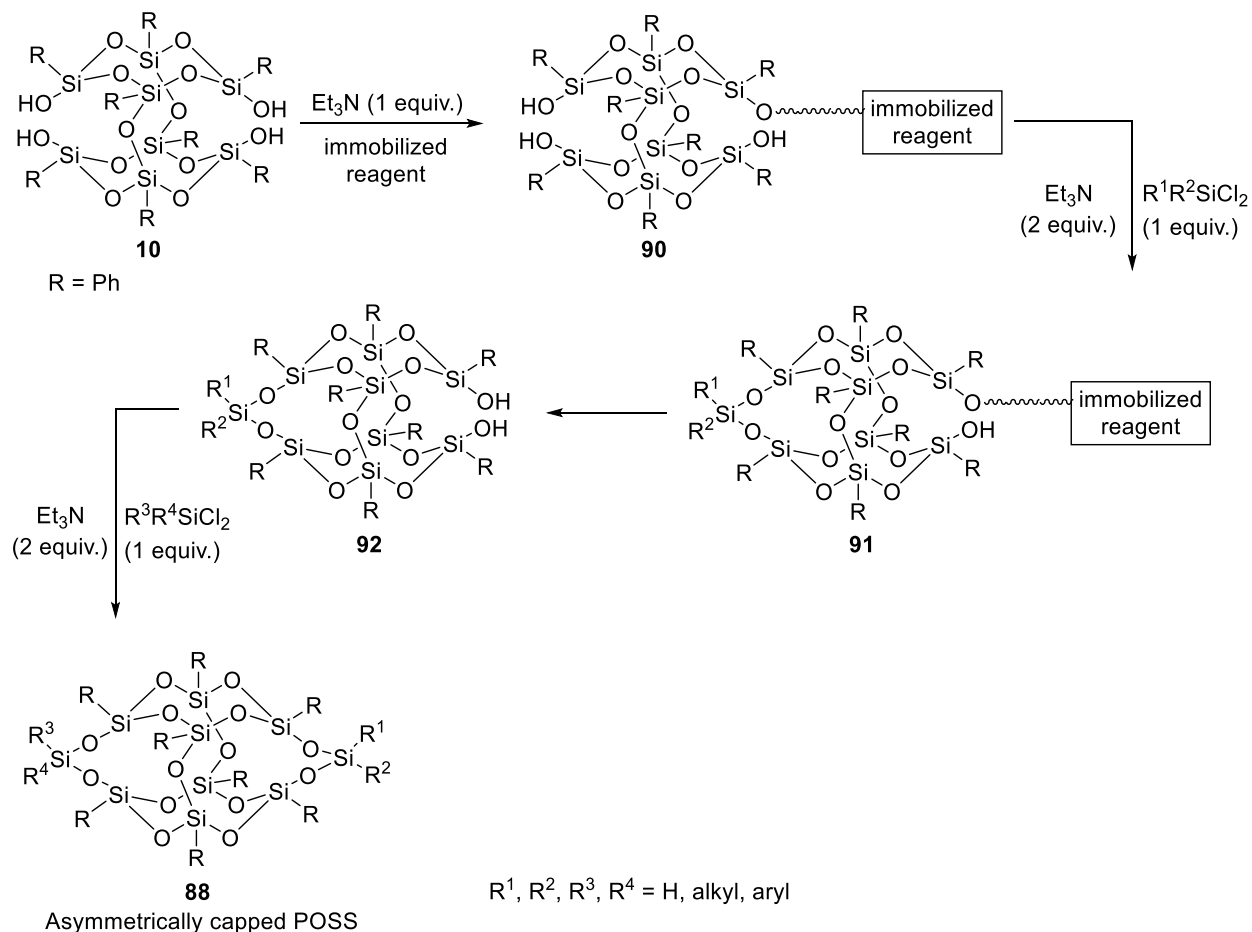
Such a support mechanism can be achieved through grafting (the covalent bond is anchored via the reaction of the reagent with silica surface hydroxyls/silanols to prevent leaching of the grafted moiety) [89(a), Figure 13], or in the case of alkoxy silanes, the use of a ligand as a linker [89(b), Figure 13] through a process called ‘tethering’.<sup>123,124</sup>

**Figure 13: Schematic Representation of some Immobilization Techniques on a (Silica) Support; [89(a)] Grafting, [89(b)] Tethering**



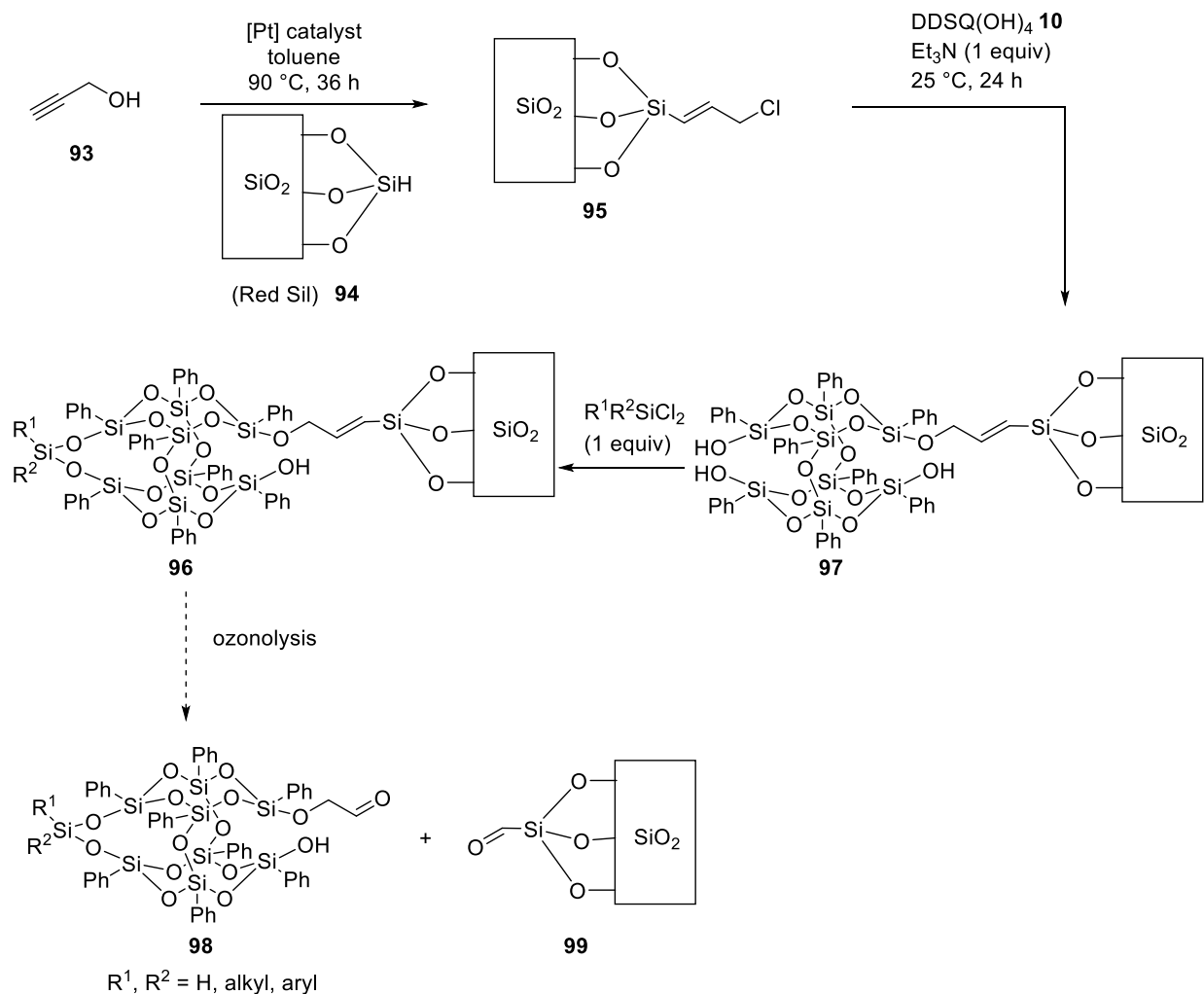
Once the first capping agent has closed one end, the bond on the immobilized surface can be cleaved and a subsequent capping effected using a different dichlorosilane (Scheme 50).

### Scheme 50: Protection of Hydroxyl Groups with Solid Surface Support/Immobilized Reagents



Application of this technique to  $\text{DDSQ(OH)}_4$  **10** was explored in our lab. Attanayake *et al.* achieved significant anchorage of the  $\text{DDSQ(OH)}_4$  to Red Sil but all attempts to detach the solid support by ozonolysis proved futile (**Scheme 51**).<sup>137</sup>

### Scheme 51: Hydrosilylation of Propargylic Chloride with Red-Sil and Reaction of the Resulting Modified Red-Sil Surface with DDSQ(OH)<sub>4</sub>



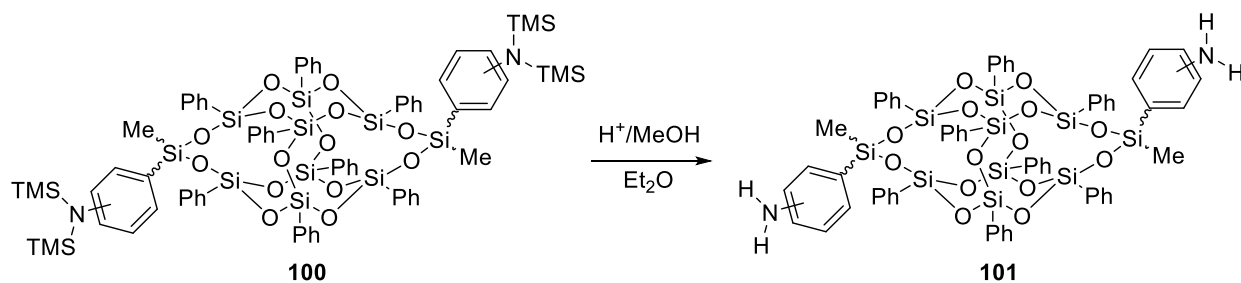
## 3.6 Selective Deprotection Techniques

### 3.6.1 Desilylation of Ph<sub>8</sub>DDSQ(OTMS)<sub>4</sub> to Ph<sub>8</sub>DDSQ(OH)<sub>4</sub>

Functionalized DDSQs and similar structures bearing TMS groups in remote parts of the architecture have been demasked using various techniques.<sup>127–129</sup> Shoen, *et. al.*<sup>127</sup> functionalized DDSQ(OH)<sub>4</sub> with TMS-aniline protected chlorosilane and deprotected the aniline moiety without destroying the cage using acidified methanol (**Scheme 52**).



### Scheme 52: Desilylation of TMS-protected aniline DDSQ with Acidified Methanol



Thus, upon addition of H<sup>+</sup>/MeOH to an Et<sub>2</sub>O mixture of the prefunctionalized (N-trimethylsilyl)<sub>2</sub>-aniline-3-(dichloromethylsilane) DDSQ(OH)<sub>4</sub> **100** and stirring the mixture at 25 °C for 20 h, followed by workup, Schoen obtained the deprotected cis/trans forms of DDSQ(AP)(Me) **101**.

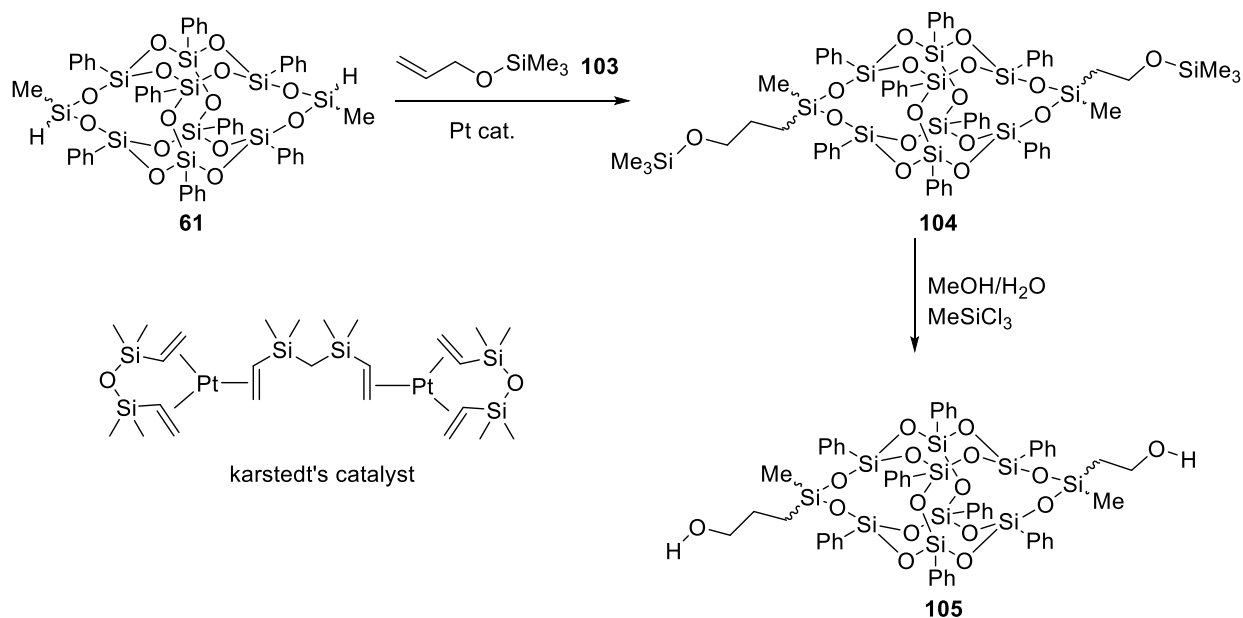
#### 3.6.2 Other TMS Deprotection Techniques

Several other methods for the deprotection of silyl-ethers in organic synthesis have been reported in the literature.<sup>138</sup> Most common of these techniques include the use of: MeSiCl<sub>3</sub>/MeOH, fluoride sources as TBAF, a mixture of AcOH/THF/H<sub>2</sub>O/HCl in various proportions,<sup>139</sup> and so on. However, these approaches have so far been underexplored in silsesquioxane chemistry.

##### 3.6.2.1 Desilylation of 3,13-di(trimethylsilyl)oxypropyl DDSQ for the synthesis of 3,13-dihydroxypropyl DDSQ

Wei *et al.*,<sup>129</sup> in 2015, reported the synthesis of 3,13-dihydroxypropyl DDSQ from the hydrosilylation reaction of a prefunctionalized DDSQ(H)(Me) **61** with a TMS protected allyl alcohol to give the intermediate 3,13-di(trimethylsilyl)oxypropyl DDSQ **104** which was ultimately deprotected with MeSiCl<sub>3</sub> and MeOH (**Scheme 53**).

**Scheme 53: Desilylation of 3,13-di(trimethylsilyl)oxypropyl DDSQ with MeSiCl<sub>3</sub>/MeOH**



Thus, the addition of MeOH followed by dropwise addition of MeSiCl<sub>3</sub> to a stirring solution of 3,13-di(trimethylsilyl)oxypropyl DDSQ in dichloromethane afforded the desilylated cage in quantitative yield. This report was coincident with progresses recorded by a colleague in our lab, Attanayake,<sup>137</sup> using the same reagents and approach as reported by the Zheng group.

## CHAPTER 4: Experimental Section

### 4.1 Materials and Methods

#### 4.1.1 Materials

Except otherwise stated, all operations were done under an inert atmosphere using standard Schlenk techniques. Solvents such as tetrahydrofuran (THF) and toluene were freshly distilled prior to use. Distilled THF was obtained from a still of commercial THF distilled over benzophenone and sodium metal at a temperature of 50 °C under nitrogen. Distilled toluene was obtained from a still of commercial toluene distilled over calcium hydride at a temperature of 120 °C. Other solvents (dichloromethane, diethylether, chloroform, methanol and acetonitrile) were used as purchased without further purification. For a start, octaphenylsilsesquioxane  $[(C_6H_5SiO_{1.5})_8]$  [OPS] was synthesized from phenyltrimethoxysilane  $[C_6H_5Si(OMe)_3]$  following literature procedure by Laine and Roll,<sup>13</sup> Later, all POSS compounds were obtained from Hybrid Plastics (Hattiesburg, MS), chlorosilanes and triethylamine were purchased from Sigma Aldrich. Triethylamine and chlorosilanes were freshly distilled over calcium hydride prior to use.

### 4.2 Analytical Techniques

#### 4.2.1 NMR Spectroscopy

All  $^1H$ -NMR,  $^{13}C$ -NMR and  $^{29}Si$  NMR were recorded on an Agilent DirectDrive2 500 MHz NMR spectrometer equipped with an OneProbe operating at 500 MHz for  $^1H$  NMR, 126 MHz for  $^{13}C$  NMR, and 99 MHz for  $^{29}Si$  NMR  $CDCl_3$  or THF-d and recorded at 25 °C.  $^1H$ -NMR spectra were recorded with 8 scans, a relaxation delay of 1s, and a pulse angle of

45° and referenced to the residual protonated solvent in CDCl<sub>3</sub> (7.24 ppm). <sup>13</sup>C-NMR spectra were collected with 254 scans, a relaxation delay of 0.1 s, and a pulse angle 45°. <sup>29</sup>Si NMR spectra were recorded with either 256 or 512 scans, a relaxation delay of 12 s and a pulse angle of 45°. All 2D experiments were acquired at 25 °C on a Varian UNITY-Inova 600 spectrometer equipped with a 5 mm Pulsed-Field-Gradient (PFG) switchable broadband probe and operating at 599.80 MHz (<sup>1</sup>H) and 119.16 MHz (<sup>29</sup>Si). The <sup>1</sup>H chemical shifts were referenced to that of residual protonated solvent in CDCl<sub>3</sub> (7.24 ppm). <sup>29</sup>Si{<sup>1</sup>H} NMR data were acquired using a recycle delay of 12 s with inverse-gated decoupling, a pulse angle set to 90° and referenced against the lock solvent using vendor supplied lock referencing. Also, <sup>1</sup>H–<sup>29</sup>Si HMBC NOESY correlations were applied to confirm <sup>29</sup>Si NMR and other assignments to compounds synthesized for the first time with the pulse angle set to 45°. Solid-state NMR spectra at 9.4 T (ν<sub>0</sub> = 79.5 MHz (<sup>29</sup>Si) or 100.6 MHz (<sup>13</sup>C)) were recorded at ambient temperature (296 K) on a Bruker Avance 400 spectrometer equipped with a 4 mm MAS probe. All spectra were acquired using magic angle spinning (MAS) at spinning speeds between 9 and 14 kHz, and high power <sup>1</sup>H decoupling was applied during acquisition.

#### **4.2.2 Mass Spectroscopy**

APCI-mass spectra have been recorded on a Finnigan LCQ Deca (ThermoQuest) technologies with LC/MS/MS (quadrupole/time-of-flight) and Waters Xevo G2-XS UPLC/MS/MS inert XL MSD with SIS Direct Insertion Probe.

#### **4.2.3 Infrared Spectroscopy**

IR spectra have been recorded using a JASCO-ATR PROONE FT/IR 6600 spectrometer.

#### 4.2.4 X-Ray Crystallography

X-ray diffraction measurements were performed on a Stoe IPDS2 or a Bruker-AXS SMART APEX 2 CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation. The structures were solved using direct methods (SHELXL-97) and refined by full-matrix least-squares techniques against F<sup>2</sup> (SHELXL-97). Cell parameters were retrieved using the SAINT (Bruker, V8.34A, after 2013) software and refined using SAINT (Bruker, V8.34A, after 2013) on 5941 reflections, 47 % of the observed reflections. Data reduction was performed using the SAINT (Bruker, V8.34A, after 2013) software which corrects for Lorentz polarization.

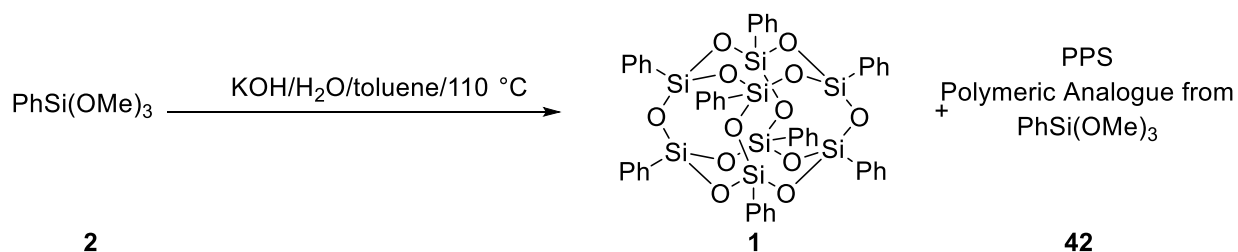
#### 4.2.5 Melting Point Determination

Melting points were measured with a Thomas HOOVER capillary uni-melt melting point apparatus and are uncorrected.

### 4.3 Experimental Procedures

#### 4.3.1 Synthesis of Cubic Octaphenylsilsesquioxane [OPS] from Phenyltrimethoxysilane [PhSi(OMe)<sub>3</sub>]

##### Scheme 54: General Synthetic Scheme of Cubic Octaphenylsilsesquioxane

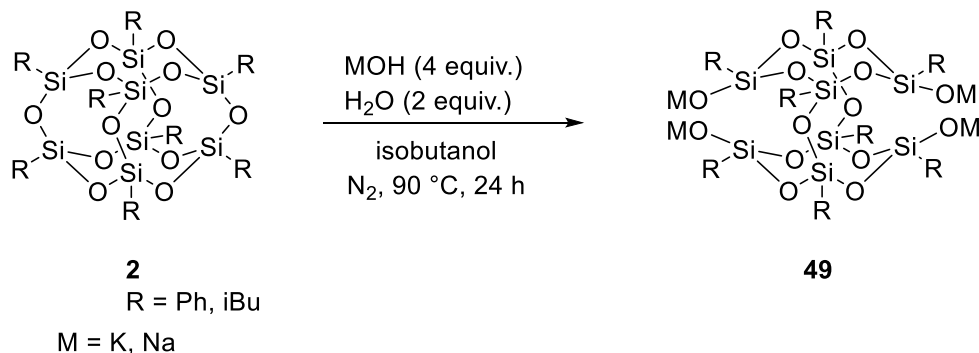


#### 4.3.1.1 Experimental Procedure - Synthesis of Cubic Octaphenyl Silsesquioxane

To an oven-dried, three-necked 250 mL round bottom flask equipped with magnetic stir bar and a cooling condenser, was added  $\text{PhSi}(\text{OMe})_3$  **1** (29 mmol, 5.74 g, 5.41 mL) and KOH (8.91 mmol, 0.50 g). The flask was placed under a nitrogen atmosphere and freshly distilled toluene (50 mL) added to the mixture with a syringe. The mixture was heated to reflux at 110 °C, and deionized water (1.0 mL) slowly added over a period of 30 minutes. The reaction mixture was refluxed for 60 h. The precipitated solid was filtered, washed with methanol (3 x 20 ml) and dried at 70 °C for 12 h to afford a white solid of the completely condensed octaphenyl silsesquioxane  $[\text{Ph}_8\text{T}_8]$  **2** in 2.39 g (64% yield) (**Scheme 54**).<sup>13,32,34,35</sup> The resulting materials were characterized by  $^1\text{H}$  and  $^{29}\text{Si}$  (solid state) NMR spectroscopy.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 – 7.71 (m, 16H), 7.46 – 7.41 (m, 8H), 7.38 – 7.31 (m, 16H).  $^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$ : -79.15 (8Si,  $\text{O}_3\text{SiPh}$ ). mp > 350 °C. Data are consistent with literature report.<sup>13</sup>

#### 4.4 General Procedure for the Synthesis of tetra(sodio)octaorganyl silsesquioxanolate, $[\text{DDSQ}(\text{ONa})_4]$

##### Scheme 55: General Reaction Scheme for the Synthesis of Double Decker Tetrasodium Salts $[\text{DDSQ}(\text{ONa})_4]$



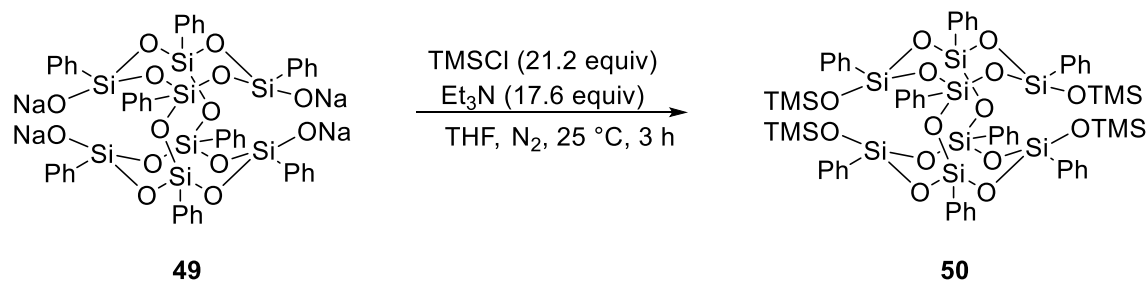
#### 4.4.1 Experimental Procedure - Synthesis of $\text{Ph}_8\text{DDSQ}(\text{ONa})_4$

To a 100 mL round bottom flask equipped with a stir bar was added  $\text{Ph}_8\text{T}_8$  **2** (4.13 g, 4 mmol) and NaOH (0.64 g, 4 equiv.). The reaction mixture was placed under nitrogen and 24 mL of iso-butanol added. Next 0.1 mL (2 equiv.) of water was added, and the mixture stirred at 90 °C for 24 h. The resulting white precipitate was filtered, washed several times with 2-propanol and dried under vacuum at 70 °C for 24 h. Product identification was done by derivatizing the sodium salt **49** to the  $\text{Ph}_8\text{T}_8$  (OTMS)<sub>4</sub> **50** and characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR and MS.

#### 4.4.2 Synthesis of Tetrakis(trimethylsilyl)octaphenyl Silsesquioxane [ $\text{Ph}_8\text{DDSQ}(\text{OTMS})_4$ ]

##### 4.4.2.1 Experimental Procedure - Synthesis of [ $\text{Ph}_8\text{DDSQ}(\text{OTMS})_4$ ]

##### Scheme 56: Synthesis of Tetrakis(trimethylsilyl)octaphenyl Silsesquioxane [ $\text{Ph}_8\text{DDSQ}(\text{OTMS})_4$ ] from [ $\text{Ph}_8\text{DDSQ}(\text{ONa})_4$ ]



$\text{Ph}_8\text{DDSQ}(\text{ONa})_4$  **49** (2.32 g, 2 mmol) was charged into a 100 mL oven-dried round bottom flask equipped with a magnetic stirrer. The flask was purged with nitrogen gas for 30 minutes and THF (30 mL) added to it. Trimethylchlorosilane (42.4 mmol, 21.2 equiv.) was then added followed by dropwise addition of triethylamine (35.6 mmol, 5 mL) for 1 minute (**Scheme 56**). The reaction mixture was stirred at room temperature for 3 h. Deionized water (10 mL) was added to dissolve any NaCl produced and to hydrolyze unreacted

Me<sub>3</sub>SiCl.<sup>113</sup> The organic layer was separated by means of a separating funnel. *n*-Hexane (10 mL) was added, and the organic layer repeatedly washed with deionized water. *n*-Hexane (50 mL) was added to this solution, and the solution left standing at -30 °C in a refrigerator overnight. The precipitated solid was filtered off and dried at reduced pressure to afford **50**, a white solid in 1.78 g (66%), mp. > 340 °C. The product was characterized by <sup>1</sup>H, <sup>29</sup>Si NMR, APCI+ QToF LCMS Measurements. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.62-7.20 (40H, multiplet), 0.2 (s, 36H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 134.24, 133.55, 131.75, 130.07, 129.69, 127.42, 1.88. <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, CDCl<sub>3</sub>, TMS) δ 10.61 (4Si, OSiMe<sub>3</sub>), -75.99 (4Si, O<sub>3</sub>SiPh), 78.82 (4Si, O<sub>3</sub>SiPh). LC/MS QToF (m/z): 1375.28 [M + NH<sub>4</sub>]<sup>+</sup>, calc'd: 1357.25.

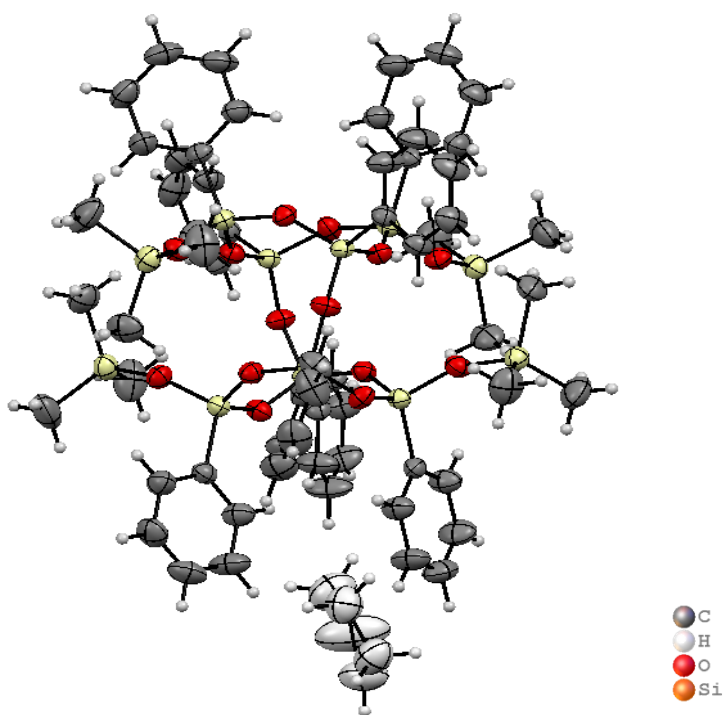
Fine crystals suitable for single X-ray crystallographic analysis were obtained by slow evaporation of a 10 wt% THF/*i*-PrOH solution of the compound according to the procedure described in the literature.<sup>113</sup> ORTEP plot discloses that the compound is tetrakis(trimethylsilylated) “double-decker” octaphenylsilsesquioxane [Ph<sub>8</sub>T<sub>8</sub>(OTMS)<sub>4</sub>] **50** (**Table 1**) and that the crystal structure (**Figure 14**) provided has 2 molecules of THF per molecule of interest.



**Table 1: Crystallographic data for [Ph<sub>8</sub>DDSQ(OTMS)<sub>4</sub>]**

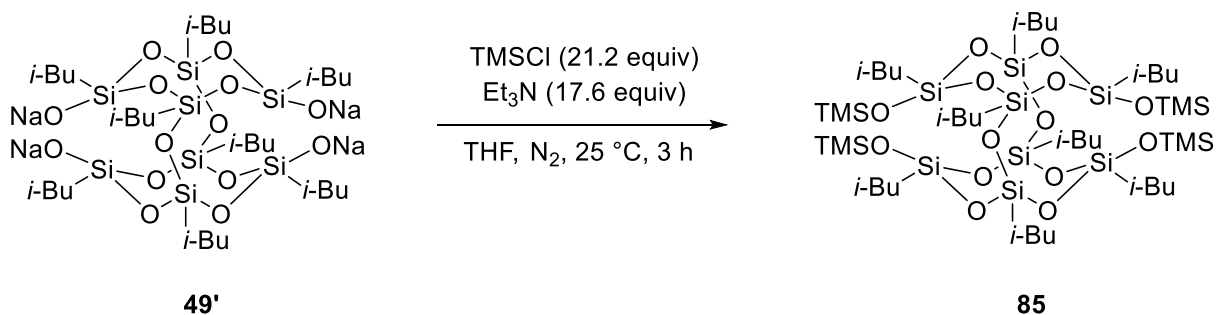
Compound	Ph <sub>8</sub> DDSQ(OSiMe <sub>3</sub> ) <sub>4</sub>
Formula	C <sub>68</sub> H <sub>90</sub> O <sub>16</sub> Si <sub>12</sub> (C <sub>60</sub> H <sub>76</sub> O <sub>14</sub> Si <sub>12</sub> )
Dcalc./ g cm <sup>-3</sup>	1.232
/mm <sup>-1</sup>	0.251
Formula Weight	1500.47 (1357.25)
Colour	colourless
Shape	chunk
Size/mm <sup>3</sup>	0.34×0.23×0.16
T/K	173(2)
Crystal System	monoclinic
Space Group	P2/n
a/Å	12.8383(16)
b/Å	18.587(2)
c/Å	16.957(2)
a/°	90
b/°	91.2290(10)
g/°	90
V/Å <sup>3</sup>	4045.5(9)
Z	2
Z'	0.5
Wavelength/Å	0.710730
Radiation type	MoK
Q <sub>min</sub> /°	1.096
Q <sub>max</sub> /°	25.414
Measured Refl.	64458
Independent Refl.	7458
Reflections Used	5832
R <sub>int</sub>	0.0594
Parameters	439
Restraints	0
Largest Peak	0.556
Deepest Hole	-0.372
GooF	1.048
wR <sub>2</sub> (all data)	0.1594
wR <sub>2</sub>	0.1493
R <sub>1</sub> (all data)	0.0712
R <sub>1</sub>	0.0564

Figure 14: Crystal Structure of [Ph<sub>8</sub>DDSQ(OTMS)<sub>4</sub>] 50



#### 4.4.2.2 Synthesis of *i*-Bu<sub>8</sub>DDSQ(OTMS)<sub>4</sub> from *i*-Bu<sub>8</sub>DDSQ(ONa)<sub>4</sub>

Scheme 57: Reaction scheme for the Synthesis of *i*-Bu<sub>8</sub>DDSQ(OTMS)<sub>4</sub> from *i*-Bu<sub>8</sub>DDSQ(ONa)<sub>4</sub>



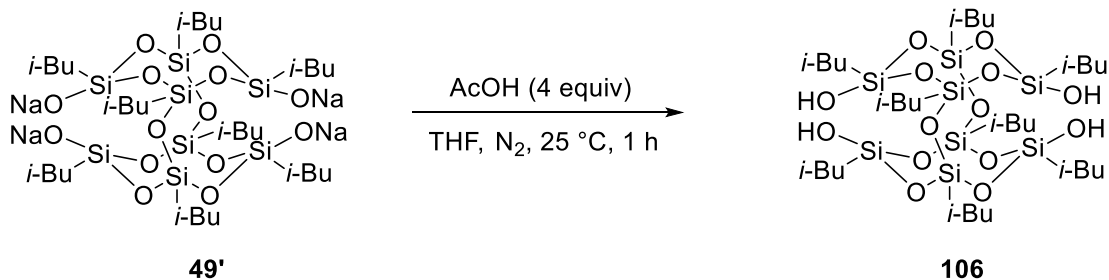
#### Procedure

Into a stirring solution of *i*-Bu<sub>8</sub>DDSQ(ONa)<sub>4</sub> **49'** (2 mmol, 2.0 g) obtained according to the procedure outlined in section 4.2.1 in THF (20 mL) under nitrogen, trimethylchlorosilane (42.4 mmol, 5.4 mL) was added followed by dropwise addition of triethylamine (35.6

mmol, 5 mL) for one minute. The solution was stirred at room temperature for 3 h (**Scheme 57**). Deionized water (10 mL) was then added to dissolve produced sodium chloride and to hydrolyze the unreacted trimethylchlorosilane. The organic layer was separated by means of a separatory funnel.<sup>113</sup> Next, n-hexane (10 mL) was added, and the organic layer repeatedly washed with deionized water. The solvent was evaporated to give a colourless liquid **85** in 1.56 g (66%). The product was characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR measurements. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.83 (dp, *J* = 13.1, 6.7 Hz, 8H), 0.98 – 0.94 (m, 48H), 0.60 – 0.49 (m, 16H), 0.21 – 0.05 (m, 36H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 26.38 – 25.53 (m), 24.93, 24.30, 24.25 – 23.49 (m), 22.48, 2.07 – 1.54 (m). <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>, TMS) δ: -8.70 (4Si, OSiMe<sub>3</sub>), -67.95 (4Si, O<sub>3</sub>Si<sup>*i*</sup>Bu), -68.29 (4Si, O<sub>2</sub>SiOSiMe<sub>3</sub>).

#### 4.4.2.3 Synthesis of *i*-Bu<sub>8</sub>DDSQ(OH)<sub>4</sub> from *i*-Bu<sub>8</sub>DDSQ(ONa)<sub>4</sub>

##### Scheme 58: Synthesis of *i*-Bu<sub>8</sub>DDSQ(OH)<sub>4</sub> from *i*-Bu<sub>8</sub>DDSQ(ONa)<sub>4</sub>



#### Procedure

Acetic acid (0.6 g, 10 mmol) was added dropwise to a THF (20 mL) dispersion of *i*-Bu<sub>8</sub>DDSQ(ONa)<sub>4</sub> **49'** (2.0 g, 2 mmol) under nitrogen atmosphere according to the procedure described in the literature by Kawakami and Lee.<sup>113</sup> The reaction mixture was stirred at room temperature for 1 h. The solution was then neutralized with a saturated aqueous sodium hydrogen carbonate (10 mL) and washed with deionized water (10 mL).

The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvent evaporated by rotary evaporation. The resulting liquid was washed with acetonitrile to obtain a colorless oily product **106** in 1.06 g (58%). The product was characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR, APCI+ QToF LCMS Measurements.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.89 – 1.82 (m, 8H), 0.98 – 0.94 (m, 48H), 0.59 (tdd,  $J = 11.1, 8.4, 5.6$  Hz, 16H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  25.78, 25.74, 25.65, 23.93, 23.90, 23.09, 23.03, 22.78, 22.35, 14.08.  $^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ )  $\delta$  -58.54 (4Si, *i*-BuSiO<sub>3</sub>), -68.52 (4Si, *i*-BuSiO<sub>2</sub>OH).

## 4.5 Synthesis of Symmetric POSS Cages

### 4.5.1 Corner-Capping of Double Decker Oligomeric Silsesquioxanes (DDSQs)

#### 4.5.1.1 General Experimental Procedure for the Synthesis of Tetramethyloctaphenyl silsesquioxane [ $\text{Me}_2\text{SiPh}_8\text{DDSQSiMe}_2$ ] and Dimethyldihydrodoctaphenylsilsesquioxane, $\text{MeHSiPh}_8\text{DDSQSiMeH}$ from $\text{Ph}_8\text{DDSQ(ONa)}_4$

[ $\text{Ph}_8\text{DDSQ(ONa)}_4$ ] **49** (2 mmol, 2.3 g) and THF (30 mL) were charged into a pre-dried flask bearing a magnetic stir bar. The flask was immersed into an ice bath, purged with highly pure nitrogen (nitrogen passed through a pad of silica) and stirred vigorously for 1 h. Next, a suitable capping agent ( $\text{R}^1\text{R}^2\text{SiCl}_2$ , 2 equiv.) in 5 mL THF was added dropwise over a period of 30 minutes. The reaction mixture was stirred at 0 °C for 4 h and at room temperature for 20 h. The insoluble solid was removed by filtration, and the solvent together with other volatiles by rotary evaporation to obtain a white solid. The solid was washed with MeOH (3 x 20 mL) and dried in vacuo at 40 °C for 24 h (**Schemes 59 and 60**). Products in yields of 1.53 g (65%); mp. = 272 °C and 1.68 g, (72%), mp. = 254 °C for

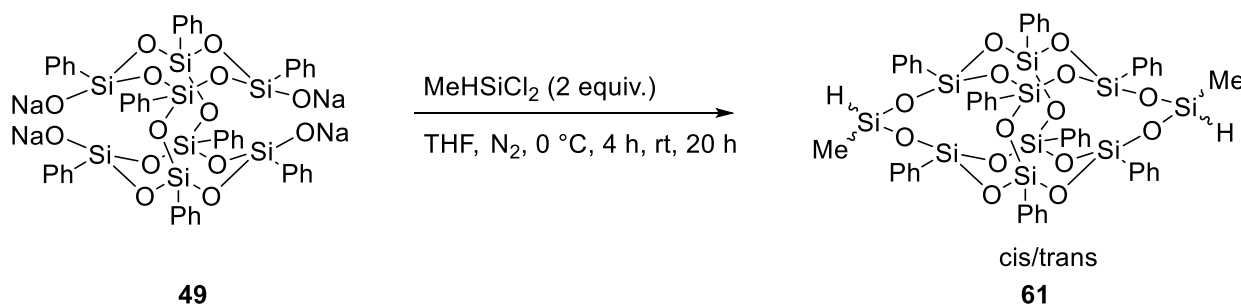
[Me<sub>2</sub>SiPh<sub>8</sub>DDSQSiMe<sub>2</sub>] **60** and [MeHSiPh<sub>8</sub>DDSQSiMeH] **61** respectively were characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR and MS.

**Scheme 59: The Synthesis of Tetramethyloctaphenyl Silsesquioxane, Me<sub>2</sub>SiPh<sub>8</sub>DDSQSiMe<sub>2</sub>**



**Spectral data:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.17 (m, 40H), 0.30 (s, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 134.03, 130.35, 127.74. <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>) δ -16.54 (2Si, O<sub>2</sub>SiMe<sub>2</sub>), -78.60 (4Si, O<sub>3</sub>SiPh), -79.59 (4Si, O<sub>3</sub>SiPh). LC/MS QTof (m/z): 1182.11 Da [M + H]<sup>+</sup>, (calc'd: 1181.82 Da).

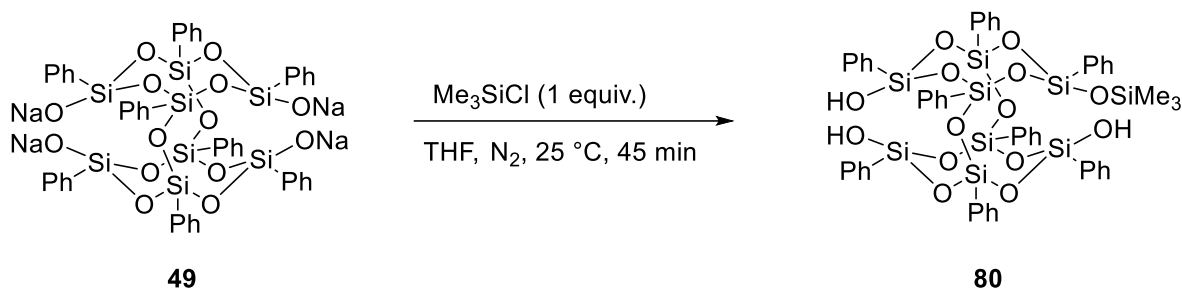
**Scheme 60: Synthesis of Dimethyldihydridoctaphenyl Silsesquioxane, MeHSiPh<sub>8</sub>DDSQSiMeH**



**Spectral data:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.16 (m, 40H), 5.00 (s, 2H), 0.38 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 134.08 – 133.87 (m), 130.44, 127.84 – 127.59 (m), 0.62. <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>) δ -32.76 (2Si, MeHSiO<sub>2</sub>), -77.80 (4Si, PhSiO<sub>3</sub>), [-79.08 (1Si, s), -79.28 (2Si, s), -79.48 (1Si, s)] (cis/trans isomers). Spectral data are consistent with the structures of the compounds and the spectral data reported by Zheng *et. al.*<sup>126</sup>

## 4.6 Synthesis of Asymmetric POSS cages by Monoprotection (One-Pot Approach)

### Scheme 61: Attempted Monoprotection of $\text{DDSQ}(\text{ONa})_4$ with $\text{Me}_3\text{SiCl}$ as Protecting Group

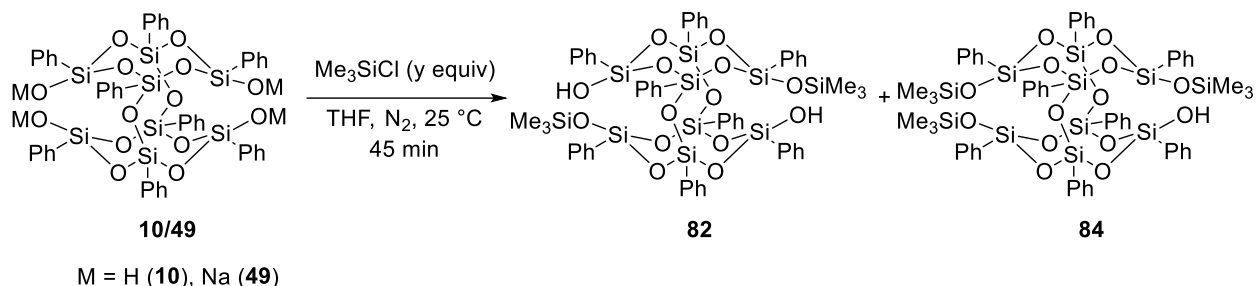


#### 4.6.1 General Experimental Procedure

To a 100 mL pre-dried round bottom flask equipped with a stir bar, was added  $\text{Ph}_8\text{DDSQ}(\text{ONa})_4$  **49** (2 mmol, 2.32 g) and THF (20 mL). The flask was purged with highly pure nitrogen (nitrogen passed through a pad of silica), and after vigorous stirring for 10 min,  $\text{Me}_3\text{SiCl}$  (1 equiv., 0.22 g, 0.25 mL) was added dropwise (**Scheme 61**). The solution was stirred for a further 45 minutes at  $25^\circ\text{C}$  and then poured into  $\text{Et}_2\text{O}$  (25 mL), washed with 10%  $\text{K}_2\text{CO}_3$  (5 mL) and brine solution (5 mL).<sup>119</sup> The mixture was then dried with anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. Attempts to further purify the resulting crude mixture were unsuccessful and no useful spectroscopic information could be obtained.

## 4.7 Tris- and Bis-protection of DDSQ(OM)<sub>4</sub> with Trimethylsilylchloride

### Scheme 62: Condition Screening for the Optimal Production of Tris-(Me<sub>3</sub>Si)-Ph<sub>8</sub>DDSQ(OH)



#### 4.7.1 General Procedure for Tris-Protection and Bis-Protection with TMSCl

Into a 100 mL pre-dried round bottom flask equipped with a magnetic stirrer, was added Ph<sub>8</sub>DDSQ(ONa)<sub>4</sub> **49** (2 mmol, 2.32 g) or Ph<sub>8</sub>DDSQ(OH)<sub>4</sub> **10** (2 mmol, 2.14 g) and THF (20 mL). The flask was placed under nitrogen and the reaction mixture stirred vigorously for 10 minutes. Next, Me<sub>3</sub>SiCl (y equiv.) was added and stirring continued at 25 °C for 45 min.<sup>119</sup> The mixture was poured into Et<sub>2</sub>O (25 mL), washed with 10% K<sub>2</sub>CO<sub>3</sub> (5 mL) and brine solution (5 mL), dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. Products were purified by flash column chromatography (hexanes:ethylacetate = 30:1) and solvent evaporated to give two white solids (Table 2). The products were characterized individually by <sup>1</sup>H, <sup>29</sup>Si NMR, HMBC, NOESY, APCI+ QToF LCMS Measurements. Fine crystals suitable for single X-ray crystallographic analysis were obtained by slow evaporation of a 10 wt% THF/i-PrOH solution of both compounds.<sup>113</sup>

#### **Ph<sub>8</sub>DDSQ<sub>8</sub>(SiMe<sub>3</sub>)<sub>3</sub>(OH) 84**

**Spectral data:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.06 (m, 40H), 4.99 (s, 1H), 0.13 (s, 9H), 0.11 (s, 9H), -0.01 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 134.44, 134.38, 134.26,

134.35, 134.28, 134.18, 134.01, 127.64, 127.53, 127.51, 127.49, 1.90, 1.48.  $^{29}\text{Si}$  NMR (99 MHz,  $\text{CDCl}_3$ )  $\delta$  15.60 (1Si, OSiMe<sub>3</sub>), 11.41 (1Si, OSiMe<sub>3</sub>), 11.27 (1Si, OSiMe<sub>3</sub>), -68.51 (1Si, O<sub>2</sub>Si(OH)Ph), -72.67 (1Si, O<sub>3</sub>SiPh), -76.11 (1Si, O<sub>3</sub>SiPh), -76.15 (1Si, O<sub>3</sub>SiPh), -78.22 (2Si, O<sub>3</sub>SiPh), -79.29 (2Si, O<sub>3</sub>SiPh).  $^1\text{H}$ - $^{29}\text{Si}$  HMBC NMR (100 MHz,  $\text{CDCl}_3$ ) showing cross peaks.  $^1\text{H}$ - $^1\text{H}$  NOESY NMR (100 MHz,  $\text{CDCl}_3$ ). APCI+ QToF LCMS (m/z): [M + H]<sup>+</sup> 1285.21 Da, (calc'd: 1285.21 Da). mp. 167 – 171 °C. These data correlate with the crystal structure obtained for Tris-TMS Ph<sub>8</sub>T<sub>8</sub>(OH).

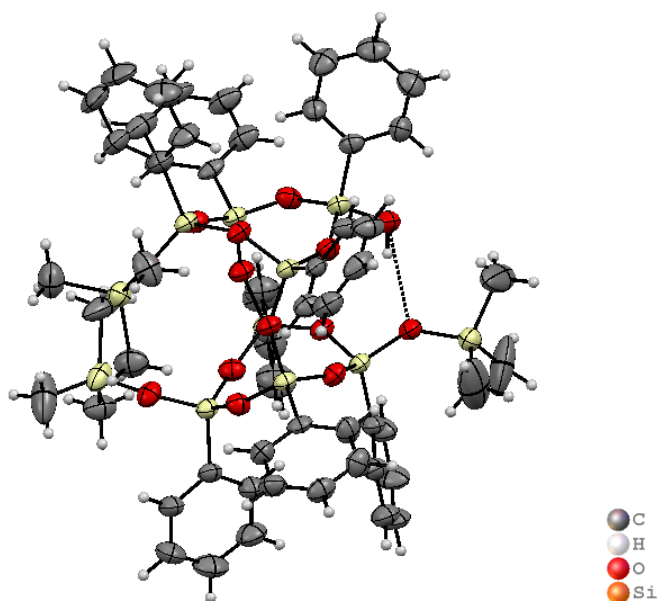
**Crystallographic Data:** ShelXT/ORTEP plot was determined by single-crystal X-ray diffraction for Crystal Data. C<sub>57</sub>H<sub>69</sub>O<sub>14</sub>Si<sub>11</sub>, MW = 1287.11, monoclinic, P21/c (No. 14), a = 21.347(3) Å, b = 14.0292(19) Å, c = 22.671(3) Å,  $\beta$  = 96.019(2)°,  $\alpha$  =  $\gamma$  = 90°, V = 6752.0(16) Å<sup>3</sup>, T = 173(2) K, Z = 4, Z' = 1,  $\mu(\text{MoK}\alpha)$  = 0.270, 12519 reflections measured, 12519 unique (Rint = .) which were used in all calculations. The final  $wR_2$  was 0.1616 (all data) and  $R_1$  was 0.0688 ( $I > 2(I)$ ). This data represents the crystallographic structure of tris-TMS protected cage (Me<sub>3</sub>Si)<sub>3</sub>Ph<sub>8</sub>DDSQ(OH) (**Table 3**) (**Figure 15**).



**Table 2: Crystallographic Data for Tris-TMS Ph<sub>8</sub>DDSQ(OH) 84**

Compound	Ph <sub>8</sub> DDSQ(OTMS) <sub>3</sub> (OH)
Molecular Formula	C <sub>57</sub> H <sub>69</sub> O <sub>14</sub> Si <sub>11</sub>
Dcalc./ g cm <sup>-3</sup>	1.266
m /mm <sup>-1</sup>	0.270
Formula Weight	1287.11
Colour	colourless
Shape	block
Size/mm <sup>3</sup>	0.26×0.24×0.07
T/K	173(2)
Crystal System	monoclinic
Space Group	P21/c
a/Å	21.347(3)
b/Å	14.0292(19)
c/Å	22.671(3)
a/°	90
b/°	96.019(2)
g/°	90
V/Å <sup>3</sup>	6752.0(16)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoKa
Q <sub>min</sub> /°	1.710
Q <sub>max</sub> /°	25.452
Measured Refl.	12519
Independent Refl.	12519
Reflections Used	8312
R <sub>int</sub>	.
Parameters	750
Restraints	0
Largest Peak	0.463
Deepest Hole	-0.311
GooF	1.019
wR2 (all data)	0.1616
wR2	0.1410
R1 (all data)	0.1155
R1	0.0688

Figure 15: Crystal Structure of  $[\text{Ph}_8\text{DDSQ}(\text{OTMS})_3(\text{OH})]$  **84**



**$\text{Ph}_8\text{DDSQ}(\text{OH})_2(\text{OSiMe}_3)_2$  **82****

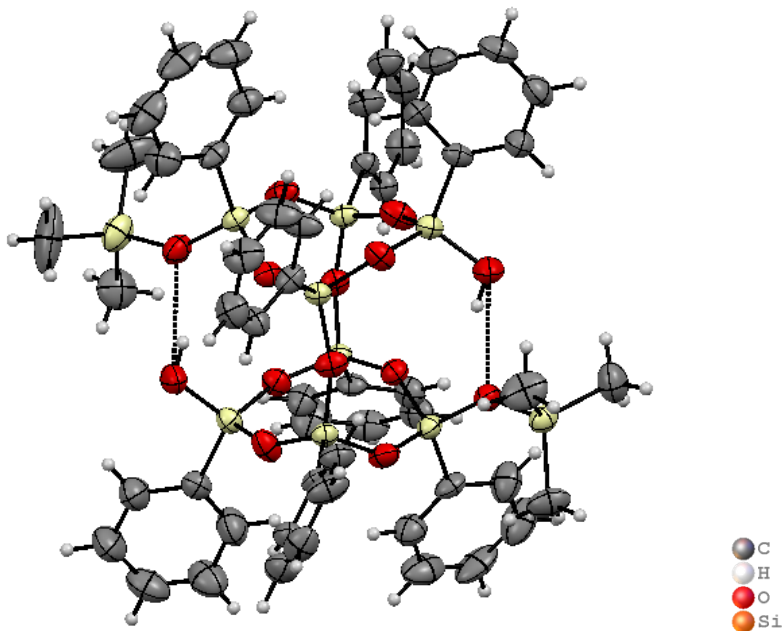
Spectral Data:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.16 (m, 40H), 4.75 (d,  $J$  = 10.9 Hz, 2H), 0.18 – 0.03 (m, 18H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  134.41, 134.38, 134.30, 134.13, 134.06, 131.62, 130.59, 130.45, 130.38, 130.29, 127.74, 127.66, 127.58, 1.51.  $^{29}\text{Si}$  NMR (99 MHz, Chloroform- $d$ )  $\delta$  16.07 (1Si,  $\text{OSiMe}_3$ ), 15.68 (1Si,  $\text{OSiMe}_3$ ), -69.06 (1Si,  $\text{O}_2\text{Si}(\text{OH})\text{Ph}$ ), -69.28 (1Si,  $\text{O}_2\text{Si}(\text{OH})\text{Ph}$ ), -73.23 (1Si,  $\text{O}_3\text{SiPh}$ ), -77.44 (1Si,  $\text{O}_3\text{SiPh}$ ), -78.27 (1Si,  $\text{O}_3\text{SiPh}$ ), -79.26 (1Si,  $\text{O}_3\text{SiPh}$ ). APCI+ QToF LCMS ( $m/z$ ): 1213.17 Da [ $\text{M} + \text{H}$ ] $^+$ , (calc'd 1213.17 Da). m.p. 190 – 201  $^\circ\text{C}$ . The  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and MS spectral data are consistent with X-ray crystal structure of  $\text{Ph}_8\text{DDSQ}(\text{OH})_2(\text{OSiMe}_3)_2$  **82**.

**Crystallographic Data:**  $C_{54}H_{60}O_{14}Si_{10}$ ,  $M_r = 1213.92$ , tetragonal,  $I-4$  (No. 82),  $a = 29.6068(4)$  Å,  $b = 29.6068(4)$  Å,  $c = 14.0465(2)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 12312.6(4)$  Å<sup>3</sup>,  $T = 173(2)$  K,  $Z = 8$ ,  $Z' = 1$ ,  $\mu(\text{CuK}\alpha) = 2.524$ , 46831 reflections measured, 11753 unique ( $R_{int} = 0.0968$ ) which were used in all calculations. The final  $wR_2$  was 0.1849 (all data) and  $R_1$  was 0.0681 ( $I > 2(I)$ ). (Table 3, Figure 16).

**Table 3: Crystallographic Data for Bis-TMS Ph<sub>8</sub>DDSQ(OH)<sub>2</sub> 82**

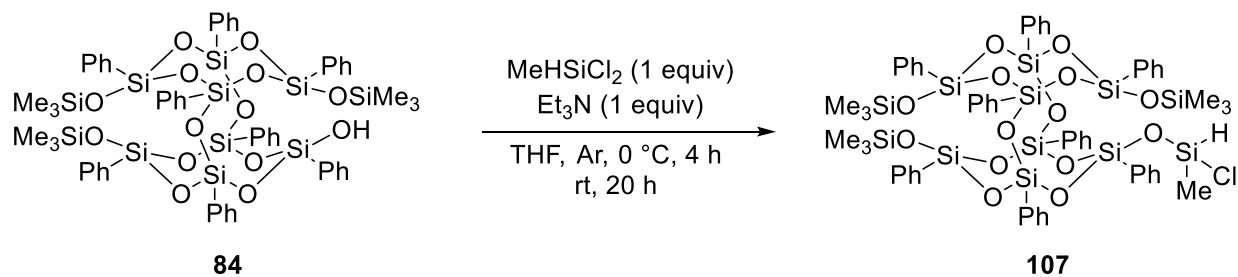
Compound	Ph <sub>8</sub> DDSQ(OTMS) <sub>2</sub> (OH) <sub>2</sub>
Formula	C <sub>54</sub> H <sub>60</sub> O <sub>14</sub> Si <sub>10</sub>
Dcalc./ g cm <sup>-3</sup>	1.310
<i>m</i> /mm <sup>-1</sup>	2.524
Formula Weight	1213.92
Colour	colourless
Shape	needle
Size/mm <sup>3</sup>	0.42×0.08×0.07
T/K	173(2)
Crystal System	tetragonal
Flack Parameter	-0.035(18)
Hooft Parameter	-0.6(5)
Space Group	I-4
<i>a</i> /Å	29.6068(4)
<i>b</i> /Å	29.6068(4)
<i>c</i> /Å	14.0465(2)
<i>a</i> /°	90
<i>b</i> /°	90
<i>g</i> /°	90
<i>V</i> /Å <sup>3</sup>	12312.6(4)
<i>Z</i>	8
<i>Z'</i>	1
Wavelength/Å	1.541838
Radiation type	CuK
<i>Q</i> <sub>min</sub> /°	2.110
<i>Q</i> <sub>max</sub> /°	72.184
Measured Refl.	46831
Independent Refl.	11753
Reflections Used	9250
<i>R</i> <sub>int</sub>	0.0968
Parameters	712
Restraints	0
Largest Peak	0.620
Deepest Hole	-0.421
GooF	1.006
<i>wR</i> <sub>2</sub> (all data)	0.1849
<i>wR</i> <sub>2</sub>	0.1692
<i>R</i> 1 (all data)	0.0880
<i>R</i> 1	0.0681

Figure 16: Crystal Structure of  $[\text{Ph}_8\text{DDSQ}(\text{OTMS})_2(\text{OH})_2]$  **82**



#### 4.8 Functionalization of $\text{Ph}_8\text{DDSQ}(\text{OH})(\text{OTMS})_3$ with $\text{MeHSiCl}_2$

Scheme 63: Functionalization of  $\text{Ph}_8\text{DDSQ}(\text{OH})(\text{OSiMe}_3)_3$  **84** with  $\text{MeHSiCl}_2$



#### Procedure

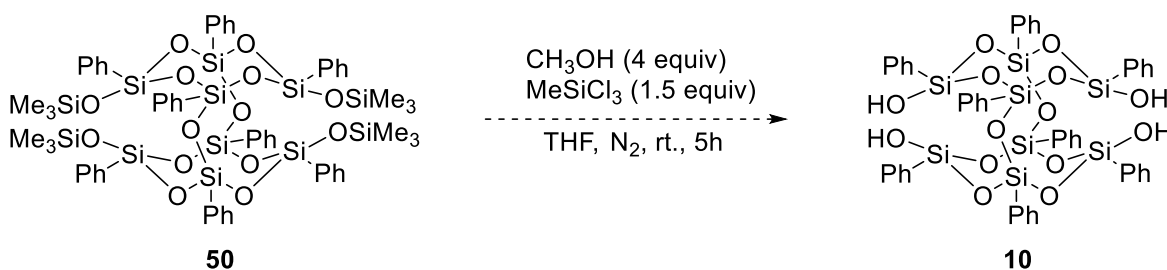
$[\text{Ph}_8\text{DDSQ}(\text{OSiMe}_3)_3(\text{OH})]$  **84** (1 mmol, 1.29 g) was charged into a pre-dried round bottom flask bearing a magnetic stir bar. THF (10 mL) was added to the flask. The flask was immersed into an ice bath and the reaction mixture stirred vigorously under argon for 1 h.

MeSi(H)Cl<sub>2</sub> (1 equiv., 0.12 g, 0.11 mL) in 5 mL THF was added followed by dropwise addition of triethylamine (1 mmol, 0.14 mL) over a period of 30 minutes. The reaction was stirred at 0 °C for 4 h and at room temperature for 20 h. The suspension was filtered through a glass frit and the filter cake washed with THF (3 x 5 mL). The filtrate was evaporated by rotary evaporation to afford a white solid. The crude product was purified by flash column chromatography (hexane: ethylacetate = 30:1) to afford **107** in 0.98 g (73%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.07 (m, 40H), 4.99 (d, *J* = 0.8 Hz, 1H), 3.74 (s, 1H), 0.13 (s, 9H), 0.11 (s, 9H), 0.02 (s, 3H), -0.01 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 134.43, 134.28, 134.16, 134.10, 134.02, 131.37, 131.15, 130.34, 130.27, 130.12, 130.08, 129.91, 129.81, 127.62, 127.59, 127.57, 127.54, 127.48, 1.87, 1.46. <sup>29</sup>Si NMR (99 MHz, Chloroform-*d*) δ 15.61 (1Si, OSiMe<sub>3</sub>), 11.42 (1Si, OSiMe<sub>3</sub>), 11.28 (1Si, OSiMe<sub>3</sub>), -55.34 (1Si, -OSiMe(H)(OH)), -68.50 (1Si, O<sub>3</sub>SiPh), -76.10 (1Si, O<sub>3</sub>SiPh), -76.15 (1Si, O<sub>3</sub>SiPh), -78.21 (2Si, O<sub>3</sub>SiPh), -79.28 (2Si, O<sub>3</sub>SiPh). IR(KBr): 3491 (Ph-OH), 3073-3027 (C-H aromatic), 2968 (C-H aliphatic) 1594 - 1430 (Si-Ph), 1252 - 571 (Si-O-Si), cm<sup>-1</sup>. APCI+ QTof LCMS (m/z): 1345.1748 Da [M + H]<sup>+</sup>, (calc'd: 1345.2102 Da). mp > 320 °C.

## 4.9 Attempts at TMS Deprotection

### 4.9.1 Desilylation of Ph<sub>8</sub>DDSQ(OSiMe<sub>3</sub>)<sub>4</sub> **50** to Ph<sub>8</sub>DDSQ(OH)<sub>4</sub> **10**

#### Scheme 64: Attempted Desilylation of Ph<sub>8</sub>DDSQ(OSiMe<sub>3</sub>)<sub>4</sub> with MeOH and MeSiCl<sub>3</sub>



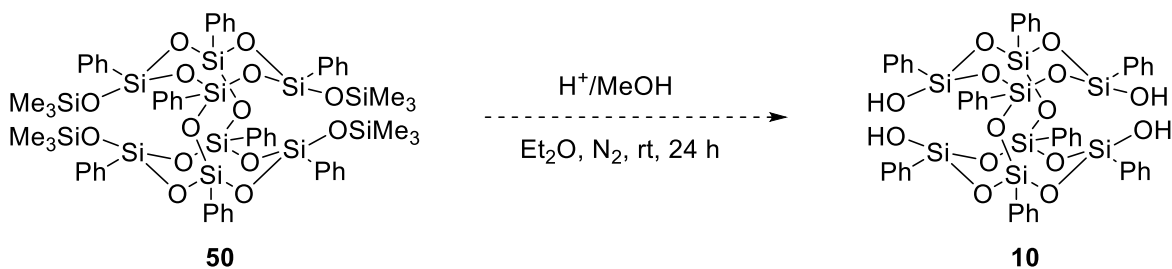
## Procedure

$\text{Ph}_8\text{DDSQ}(\text{OSiMe}_3)_4$  **50** (0.2 mmol, 0.27 g) and THF (5 mL) were added to a flask equipped with a magnetic stir bar. Methanol (4 equiv, 0.2 mmol, 2 mL) was added to the flask with vigorous stirring. Next, methyltrichlorosilane (1.5 equiv, 0.075 mmol, 0.045 g, 40  $\mu\text{L}$ ) dissolved in 60  $\mu\text{L}$  THF was added dropwise over a period of 30 minutes using a syringe. The reaction mixture was stirred at room temperature for 5 h (**Scheme 64**). The excess methyltrichlorosilane and solvent were removed by rotary evaporation and the resulting solid product recrystallized from a mixture of THF/hexane (10/10 by volume).<sup>37</sup> The crude product was dried under vacuum at 40 °C for 24 h and analyzed by  $^{29}\text{Si}$  NMR.  $^{29}\text{Si}$  NMR (99 MHz, Chloroform-*d*)  $\delta$  -38.68, -47.75, -47.97, -64.65, -78.50. See Screening results (**Table 4**)

In a different approach from the conditions above, desilylation was also attempted using conditions as reported Lee et al (**Scheme 56**).<sup>127</sup>

### 4.9.2 Desilylation with Acidified MeOH in Ether

#### Scheme 65: Attempted Desilylation of $\text{Ph}_8\text{DDSQ}(\text{OSiMe}_3)_4$ **50** with Acidified MeOH



## Procedure

$\text{Ph}_8\text{DDSQ}(\text{OSiMe}_3)_4$  **50** (0.2 mmol, 0.27g) and THF (2 mL) [or  $\text{Et}_2\text{O}$  (2 mL)] were added to a 50 mL round bottom flask equipped with a magnetic stir bar. The flask was placed

under nitrogen at room temperature. Next, 1 mL of acidified methanol ( $H^+/MeOH$ ) was added dropwise within 1 minute and the reaction mixture stirred at room temperature for 24 h. The heterogenous mixture was filtered and the retentate dried in an oven at 90 °C for 5 h.<sup>108</sup> The crude product was characterized by  $^{29}Si$  NMR (**Table 5**).  $^{29}Si$  NMR (99 MHz, Chloroform-*d*)  $\delta$  7.28, 3.30 [Appendix 38 (mineral acids). (acetic acid)].

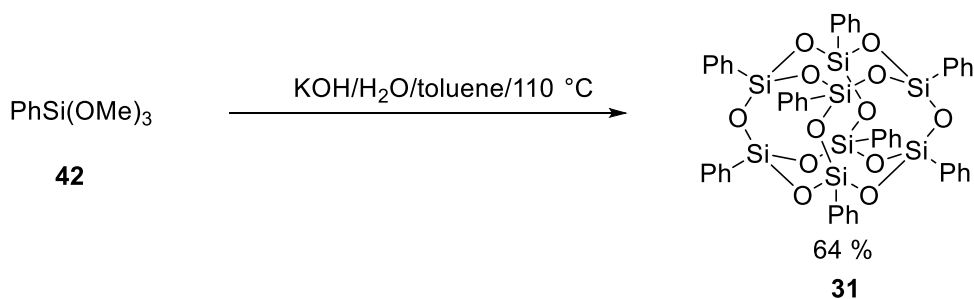


## CHAPTER 5 Results and Discussion

### 5.1 Cubic OPS [ $\text{Ph}_8\text{T}_8$ or $\text{T}_8$ ] **31**

Section 4.3.1.1 describes the transformation of commercial  $\text{PhSi}(\text{OMe})_3$  into octaphenyl $\text{T}_8$ ; the compound that is used as starting material for the attempted synthesis of the asymmetric POSS compounds. Like the Laine group<sup>106</sup> where  $\text{PhSi}(\text{OEt})_3$  was used as starting material, hydrolysis and polycondensation of  $\text{PhSi}(\text{OMe})_3$  under identical conditions afforded the cubic OPS,  $\text{Ph}_8\text{T}_8$  **31** target (Scheme 66). Spectral data were in good agreement with those of the Laine team. In addition to the fully condensed cage, polyphenylsilsesquioxane was also obtained as a byproduct in line with their observations.

#### Scheme 66: Synthetic Scheme of Cubic Octaphenyl Silsesquioxane (OPS)



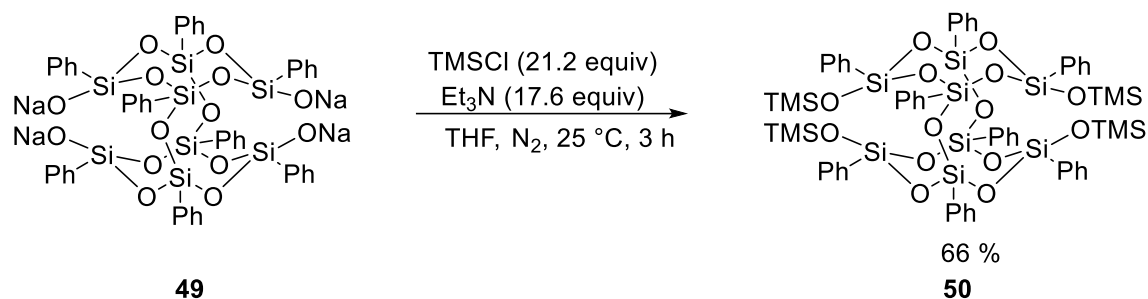
#### 5.1.1 Tetra(sodio)octaorganyl silsesquioxanolate, $[\text{DDSQ}(\text{ONa})_4]$ and its TMS

##### Derivatives

The selective cleavage of two Si-O-Si linkages of the synthesized OPS in Section 4.3.1.1 following the Kawakami route<sup>125</sup> is illustrated in Sections 4.4.1 – 4.4.2. Hydrolysis of OPS with NaOH afforded  $[\text{Ph}_8\text{DDSQ}(\text{ONa})_4]$  **49**, which was characterized by conversion into

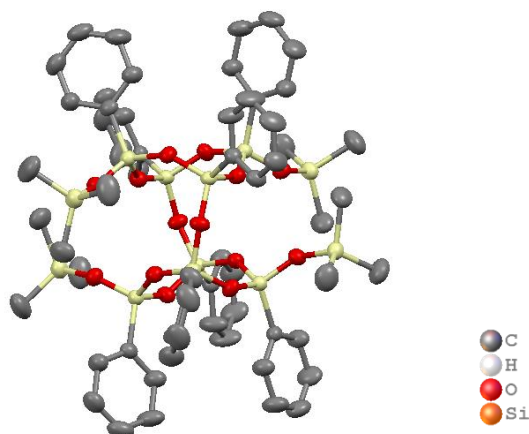
the TMS derivative (**Scheme 67**).  $[\text{Ph}_8\text{DDSQ}(\text{OSiMe}_3)_4]$  **50** was isolated in gram scale as a white crystalline solid (66%), mp > 340 °C.

**Scheme 67: Synthesis of Tetrakis(trimethylsilyl)octaphenyl Silsesquioxane  $[\text{Ph}_8\text{DDSQ}(\text{OTMS})_4]$**



Spectral data discloses 36 methyl-protons and 40 phenyl-protons by  $^1\text{H}$  NMR and three kinds of Si atoms (each integrating to four (4)), characteristic of the structure of the target compound. This is consistent with the literature report<sup>13</sup> and matched the crystal structure of the compound (**Figure 17**).

**Figure 17: Crystal Structure of  $[\text{Ph}_8\text{DDSQ}(\text{OTMS})_4]$**



Unlike  $[\text{Ph}_8\text{DDSQ}(\text{OTMS})_4]$ , **50** several attempts including silylation with TMSCl,  $\text{PhHSiCl}_2$ ,  $\text{Ph}_2\text{SiCl}_2$ , and stannation with  $\text{SnCl}_4$  to derivatize  $[\textit{i}\text{-Bu}_8\text{DDSQ}(\text{ONa})_4]$  **49'** into

crystalline organic products were unsuccessful. In all attempted cases, the products obtained were oily. However, the spectral data obtained for both [*i*-Bu<sub>8</sub>DDSQ(OTMS)<sub>4</sub>] **85** and [*i*-Bu<sub>8</sub>DDSQ(OH)<sub>4</sub>] **106** perfectly matched the respective structures (**Figures 18–21**).

**Figure 18: <sup>1</sup>H NMR of [*i*-Bu<sub>8</sub>DDSQ(OTMS)<sub>4</sub>] **85****

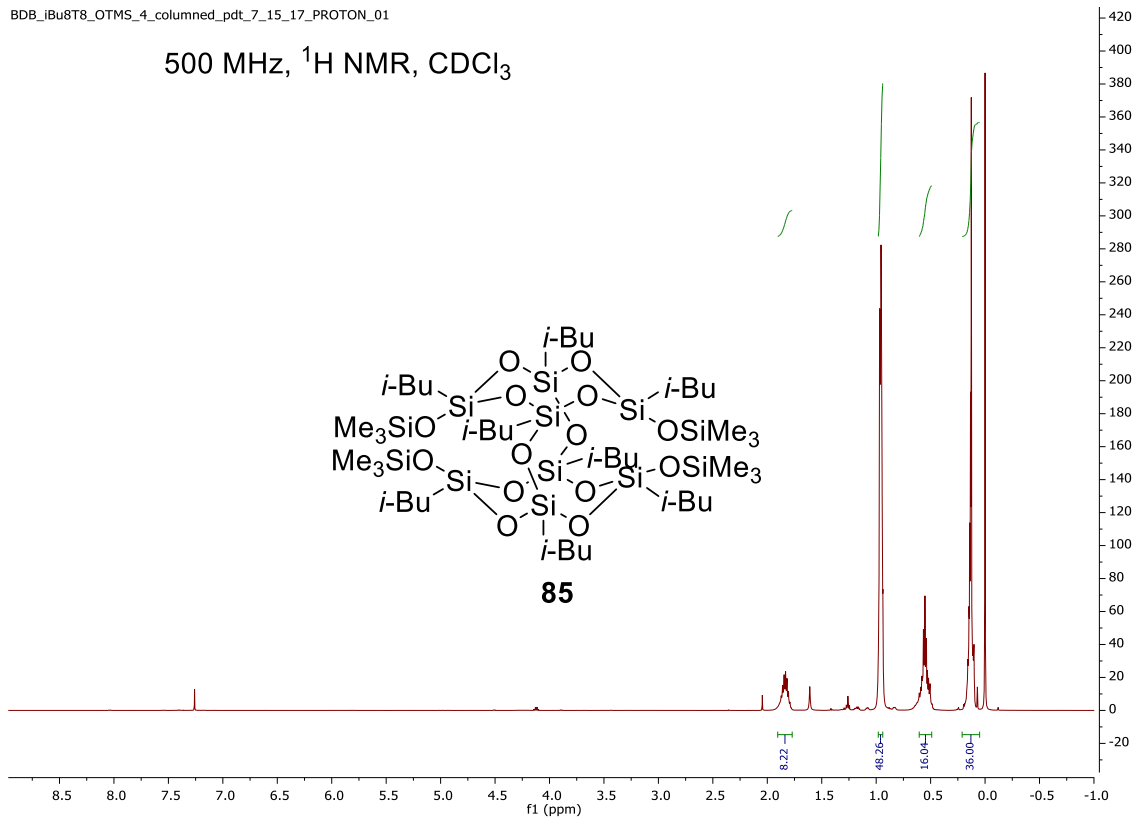
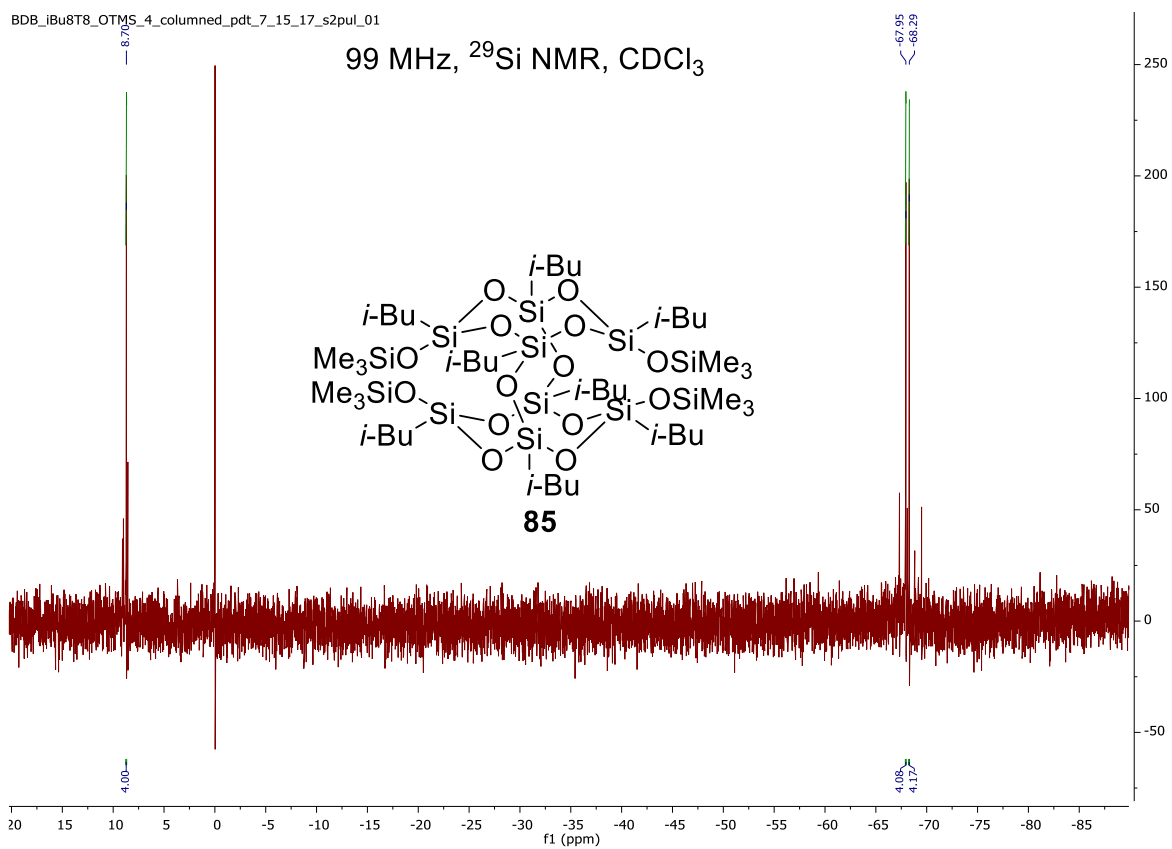


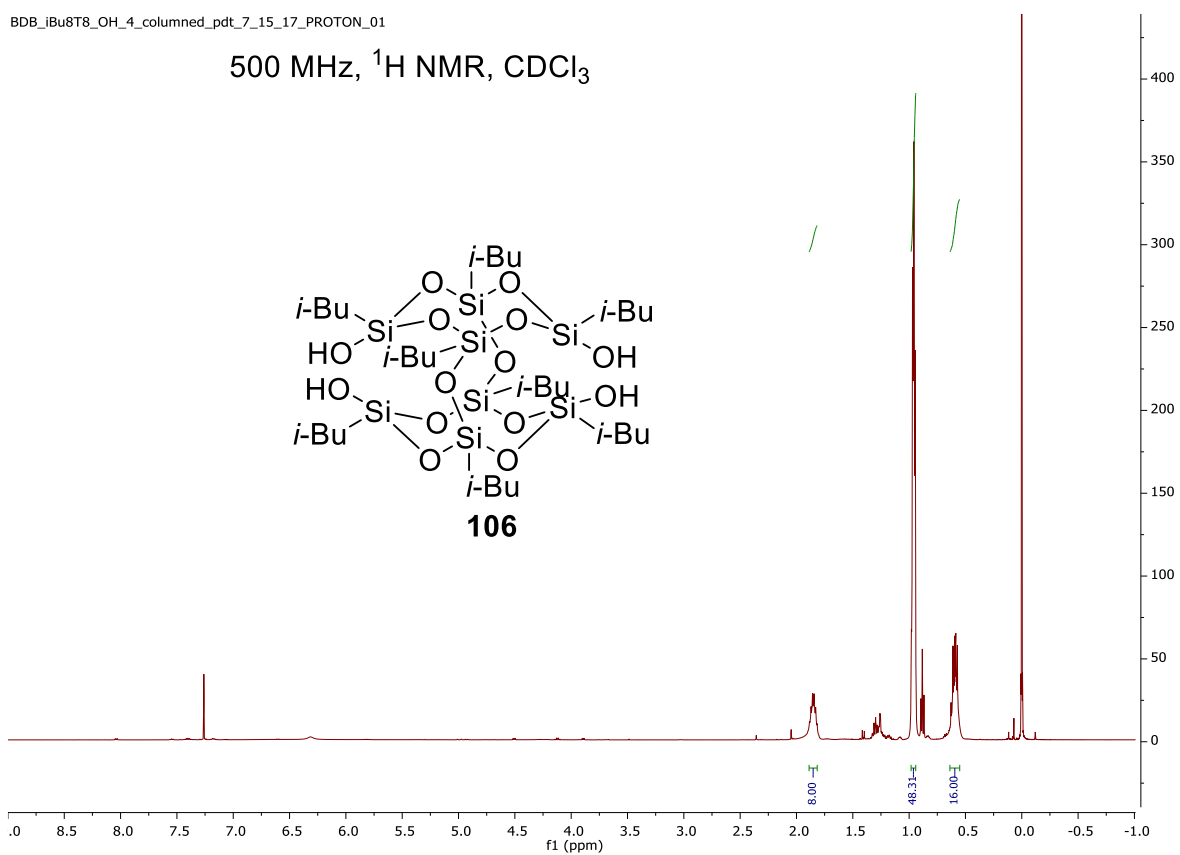
Figure 19:  $^{29}\text{Si}$  NMR of [i-Bu<sub>8</sub>DDSQ(OTMS)<sub>4</sub>] 85



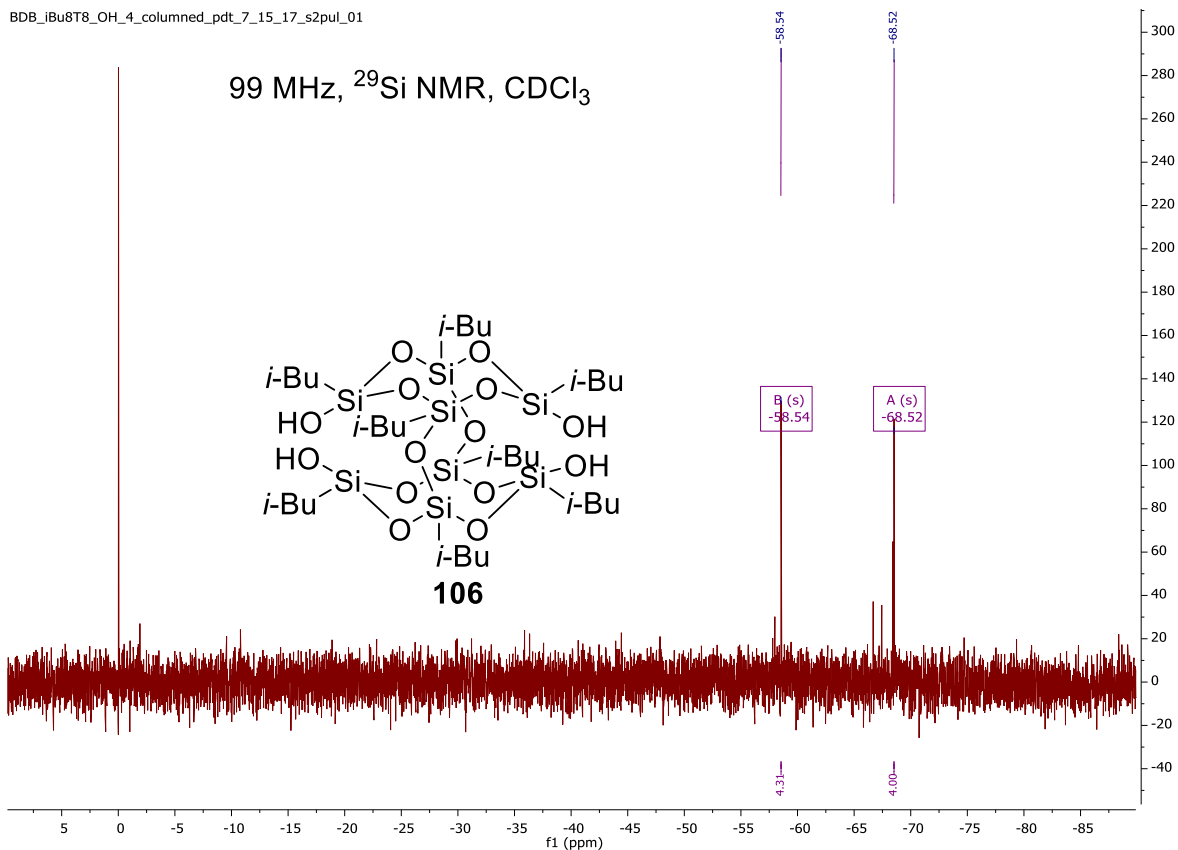
**Figure 20:  $^1\text{H}$  NMR of [*i*-Bu<sub>8</sub>DDSQ(OH)<sub>4</sub>] 106**

BDB\_iBu8T8\_OH\_4\_columned\_pdt\_7\_15\_17\_PROTON\_01

500 MHz,  $^1\text{H}$  NMR,  $\text{CDCl}_3$



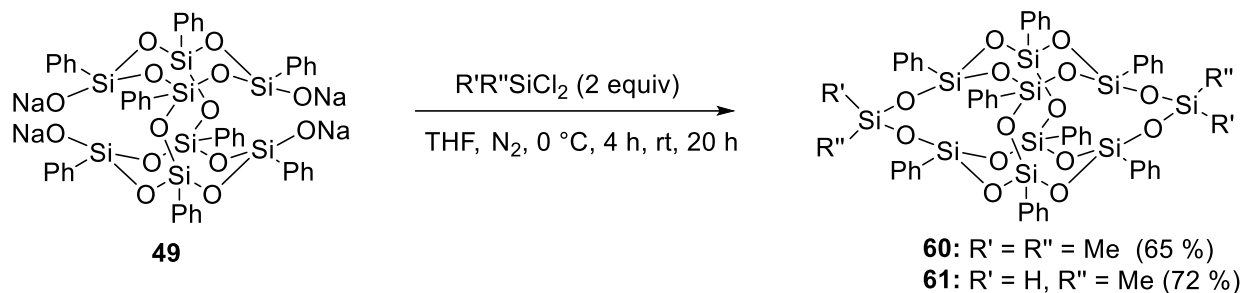
**Figure 21:  $^{29}\text{Si}$  NMR of [*i*-Bu<sub>8</sub>DDSQ(OH)<sub>4</sub>] 106**



## 5.2 Symmetric POSS Cages

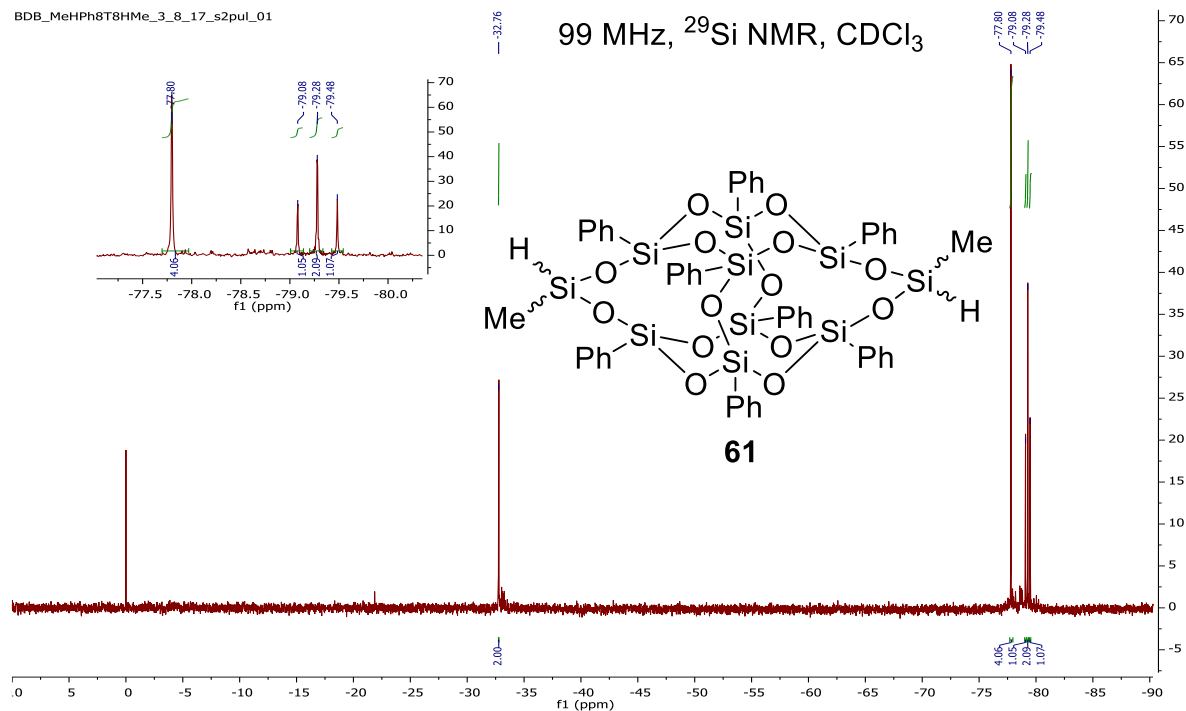
The procedure for corner capping DDSQ(ONa)<sub>4</sub> for the synthesis of symmetrically functionalized DDSQs is outlined (**Scheme 68**). Functionalization of the open ends with suitable di-functional chlorosilanes ( $\text{RR}'\text{SiCl}_2$ ) affords the symmetrically capped POSS cages.

**Scheme 68: Corner-Capping of Octaphenyl Silsesquioxane Tetrasodium Salt [DDSQ(ONa)<sub>4</sub>] 49**



With  $\text{Me}_2\text{SiCl}_2$  (or any capping agent with two identical R groups on the chlorosilane), only a single product **60** was obtained. However, with two different R-substituents on the chlorosilane (e.g.  $\text{MeHSiCl}_2$ ), **61** was isolated as its geometric isomers (*cis* and *trans*). Clearly, unlike **60**, the  $^{29}\text{Si}$  NMR spectrum for **61** shows further splitting of signals in the -77 to -80 ppm range. Thus, the resonances in the -32.76 (2Si,  $\text{MeHSiO}_2$ ), -77.80 (4Si,  $\text{PhSiO}_3$ ) and -79.28 (4Si,  $\text{PhSiO}_3$ ) ppm are assigned to the *trans* isomer, and those at -32.76 (2Si,  $\text{MeHSiO}_2$ ), -77.80 (4Si,  $\text{PhSiO}_3$ ), -79.08 (2Si,  $\text{PhSiO}_3$ ), and -79.48 (2Si,  $\text{PhSiO}_3$ ) ppm denote the silicon nuclei for the *cis* configuration (**Figure 22**). Thus, the *cis*-isomer exhibits two pairs of signals in a 1:1 ratio for the internal silicons of the tetracyclosiloxane rings linked by two oxygen atoms with unique resonances at -79.08 (2Si) and -79.48 (2Si).

**Figure 22:  $^{29}\text{Si}$  NMR Spectrum Showing Signals for *cis/trans* Isomers of MeHSiDDSQSiMeH **61****

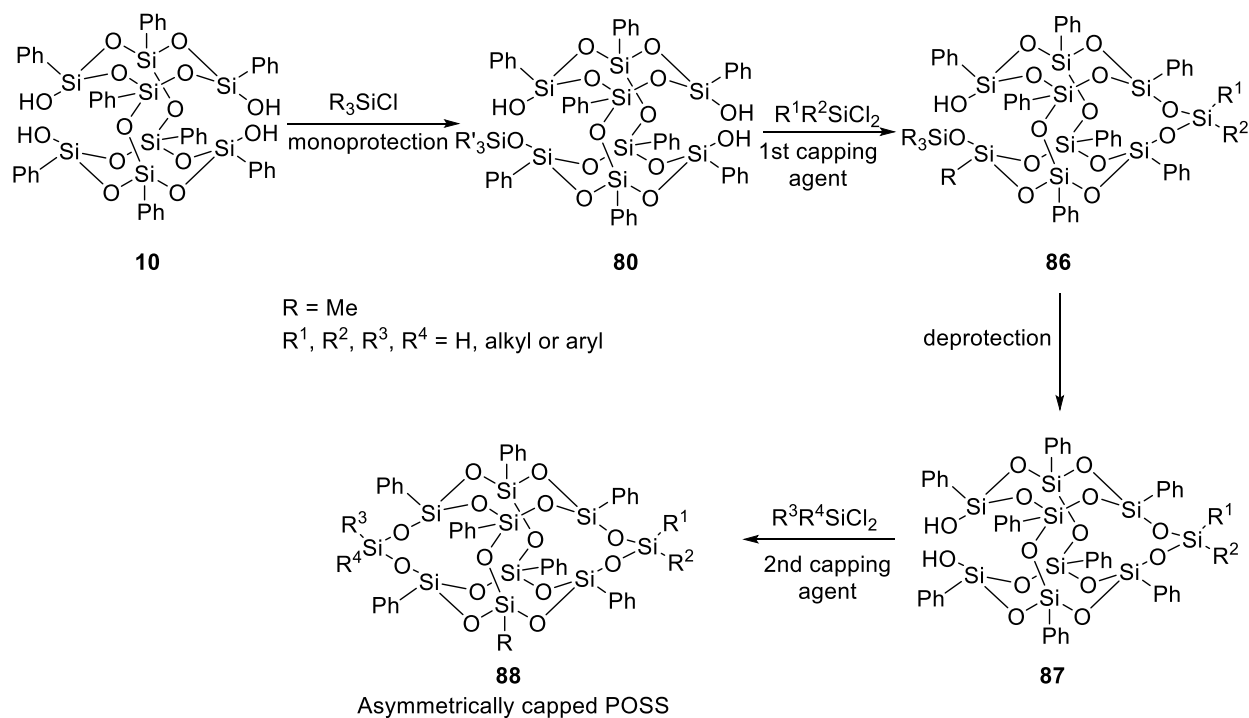


These results are in good agreement with the chemical shifts reported by Wang et al.<sup>126</sup>  $\text{Me}_2\text{SiPh}_8\text{DDSQSiMe}_2$  **60** was isolated as a single white compound in 65% yield; mp = 272 °C and  $\text{MeHSiPh}_8\text{DDSQSiMeH}$  **61** as a white geometric isomer (*cis* and *trans*) in 72% yield; mp = 254 °C.



### 5.3 Selective Protection of DDSQ(OH)<sub>4</sub> 10 with TMSCl

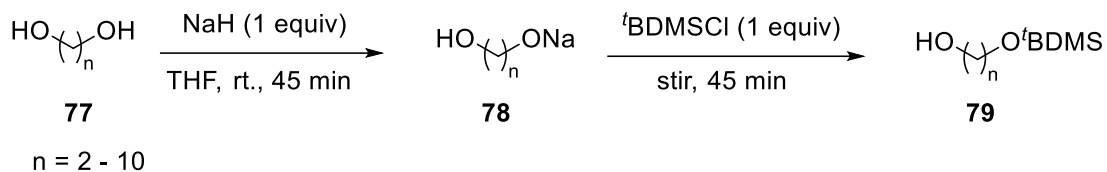
#### Scheme 69: Synthesis of Asymmetric POSS Cage via Monoprotection



In our attempts at synthesizing asymmetric POSS cages from the highly symmetrical DDSQ precursor, we turned to protection chemistry. As described in the literature, monosilylation and desilylation have been achieved for the protection of various organic functionalities like the OH group. McDougal and coworkers,<sup>119</sup> for instance demonstrated the selective monosilylation of symmetric 1,n-diols at room temperature and attributed the source of selectivity to the properties of the monosodium salt of the diol (**Scheme 70**). These properties are based on the solubility of the sodium salt in the reaction solvent and the kinetics of silylation and proton transfer. The McDougal team claimed that the rate of silylation of the sodium salt precursor is faster than that for the proton transfer from the

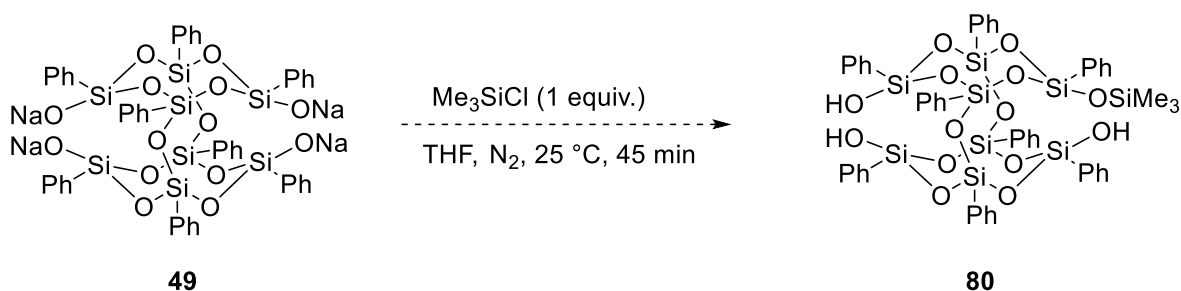
alkoxide to the already silylated product. Thus, upon addition of the silylating agent the small amount of the sodium salt that dissolved in the solvent is immediately silylated.

### Scheme 70: Monosilylation of Symmetric 1,n-diols



The starting materials for most asymmetric product are symmetrical precursors. Bifunctional products of type X CH<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>CH<sub>2</sub>Y can result from the selective protection of one hydroxyl group in (HO)CH<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>CH<sub>2</sub>(OH) (**Scheme 70**). Achieving selective protection from such precursors is therefore crucial; especially for cases where all the hydroxyl groups in the molecule are identical (all primary, or secondary or tertiary). In our attempt to extend this concept to our DDSQ(ONa)<sub>4</sub> precursor, the procedure as outlined below was followed and reaction progress monitored by <sup>29</sup>Si NMR (**Scheme 71**).

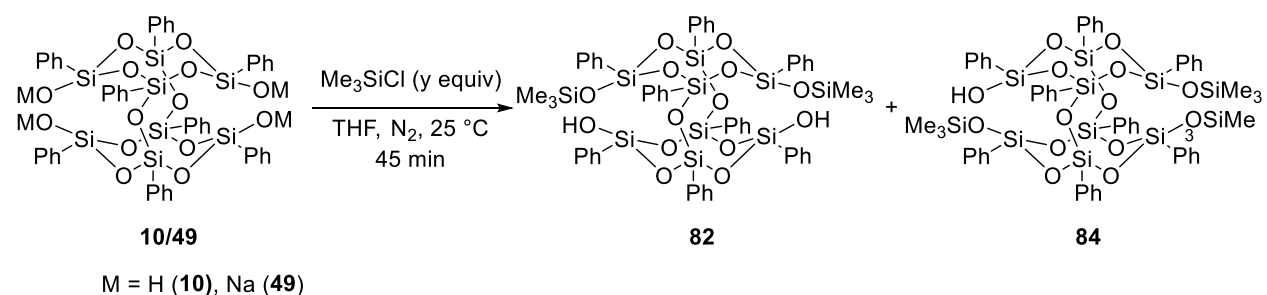
### Scheme 71: Attempted Monoprotection of DDSQ(ONa)<sub>4</sub> with Me<sub>3</sub>SiCl



The sodium salt precursor was obtained from the sodium hydroxide hydrolysis of OPS **2** (Sections 4.4.1 – 4.4.2). The voluminous white precipitate that resulted from this reaction was believed to be DDSQ(ONa)<sub>4</sub> **49**. Silylation of **49** with sub-stoichiometric amounts will unavoidably afford a statistical mixture of the unreacted tetrasodium salt, monosilylated, bis silylated, tris-silylated and tetra-silylated products. In this vein, selective silylation of

our substrate, DDSQ(ONa)<sub>4</sub> **49** with TMSCl was carried out with the hope of achieving some partial protections (**Scheme 70**). <sup>29</sup>Si NMR of the crude product showed a complex mixture with no indication of the mono-protected product. Attempts to purify the products by either column chromatography or recrystallization/precipitation proved futile. This drove us to elaborate the protocol by setting up a series of reactions to examine whether increasing the amount of TMSCl could enable us to achieve some partial protections (**Scheme 72**).

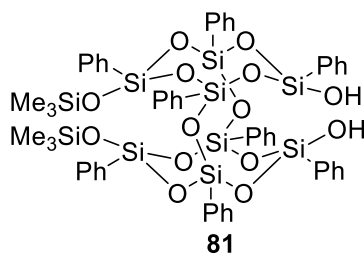
**Scheme 72: Condition Screening for the Optimal Production of Ph<sub>8</sub>DDSQ(OH)(OSiMe<sub>3</sub>)<sub>3</sub>**



Results from the screening process are given in Table 4. Interestingly, NMR data indicates some multiple protection. From the crude material, both Ph<sub>8</sub>DDSQ<sub>8</sub>(OSiMe<sub>3</sub>)<sub>3</sub>(OH) **84** and Ph<sub>8</sub>DDSQ(OSiMe<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> **82** were isolated in their pure forms by flash column chromatography. Surprisingly, the bis-protected cage with the two TMS groups on the same side of the molecule (**Figure 23**) was not observed.

Probably, compared to **81** (**Figure 23**), formation of the bis-TMS cage of type **82** is energetically the most favorable - the one that requires the least energy for formation.

**Figure 23: Ph<sub>8</sub>DDSQ (OSiMe<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> **81** with the TMS groups on the same side**



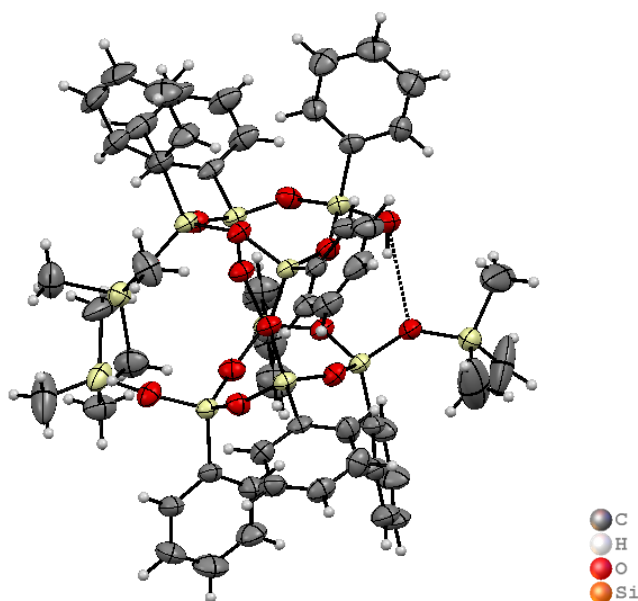
**Table 4: Substrate screening for optimal yield of Ph<sub>8</sub>DDSQ(OSiMe<sub>3</sub>)<sub>3</sub>(OH) **84** and Ph<sub>8</sub>DDSQ(OSiMe<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> **82****

Entry	Substrate	TMSCl (y equiv.)	Yield (%)	
			Ph <sub>8</sub> DDSQ(OSiMe <sub>3</sub> ) <sub>3</sub> (OH) <b>84</b>	Ph <sub>8</sub> DDSQ(OSiMe <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub> <b>82</b>
1	Ph <sub>8</sub> T <sub>8</sub> (ONa) <sub>4</sub>	3	1.05 g (41)	0.44 g (18)
2	Ph <sub>8</sub> T <sub>8</sub> (ONa) <sub>4</sub>	4	1.23 g (48)	0.58 g (24)
3	Ph <sub>8</sub> T <sub>8</sub> (OH) <sub>4</sub>	3	1.18 g (46)	0.51 g (21)
4	Ph <sub>8</sub> T <sub>8</sub> (OH) <sub>4</sub>	4	1.31 g (51)	0.69 g (28)

Reactions were run on a 2 mmol scale of starting materials, THF (20 mL), room temperature, 1 h. Percent yields are given in parenthesis.

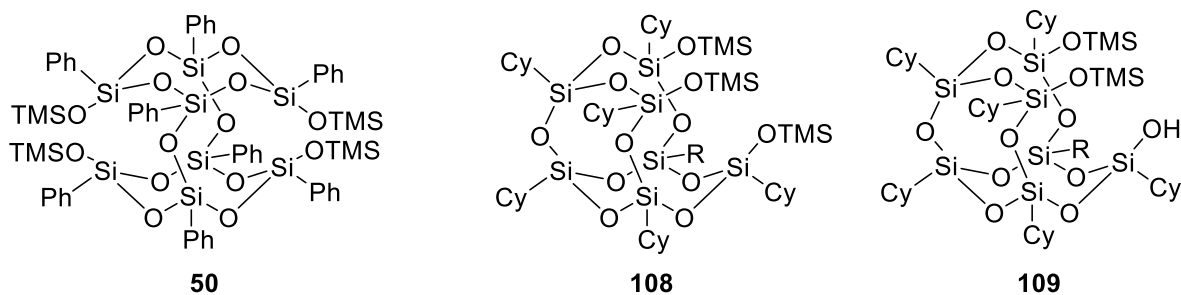
Maximal yields for both **82** and **84** (entry 4) were obtained with 4 equivalents Me<sub>3</sub>SiCl using DDSQ tetrasilanol as precursor. The X-ray crystallographic data for the tris-product (Table 3, Chapter 4) shows that the compound is the tris-protected cage, Ph<sub>8</sub>DDSQ(OTMS)<sub>3</sub>(OH) **84** (Figure 15). Within the framework of our design (**Scheme 69**), it is unlikely that **84** can get us to the target asymmetric DDSQs. This is so because any attempts to react the remaining silanols with chlorosilanes and subsequent deprotection can invariably afford symmetrically functionalized DDSQs. Nevertheless, the structure of **84** is still noteworthy as it has the potential to undergo further interesting transformations.

**Figure 15: Crystal Structure of [Ph<sub>8</sub>DDSQ(OTMS)<sub>3</sub>(OH)] **84****



The structure of **84** is not only novel but also very interesting. This is so because, so far, reports regarding general modification of POSS silanols and silnolates with chlorosilanes to give incompletely condensed silsesquioxane derivatives are scarce. The few available examples are limited to the complete substitution of the tetrasilanol-POSS, the trisilanol POSS or one or two such groups in trisilanol POSS (**Figure 24**).

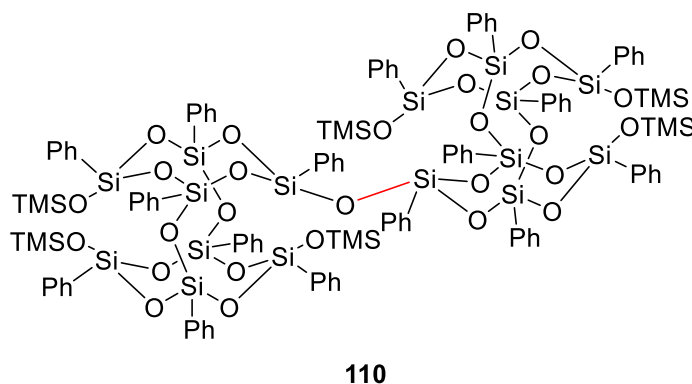
**Figure 24: Structures of Some POSS Compounds with Silyl Protecting Groups**



With structures **82** and **84**, introduction of certain moieties (eg. vinyl silyl moieties) on to the remaining hydroxyl groups can make them very versatile templates for further

chemical modifications. Thus, the silanol group in  $\text{Ph}_8\text{DDSQ}(\text{OSiMe}_3)_3(\text{OH})$  **84** is likely to undergo self-condensation to yield a tris-TMS-DDSQ(OH) cage dimer **110** with a new Si-O-Si linkage or surface functionalization via cross condensation with a silane coupling partner.

**Figure 24: Tris-TMS-DDSQ-OH [ $\text{Ph}_8\text{DDSQ}(\text{OSiMe}_3)_3(\text{OH})$ ] Dimer**



Also, the acidity of the silanol group can allow this compound to form hydrogen bonds to organic compounds containing suitable hydrogen bonding sites. The free hydroxyl group can also be functionalized in ways that can open the opportunity to introducing a wide variety of functional groups into this type of organosilicon compounds. For instance, metal catalyzed O-silylation of the Si-OH in  $\text{Ph}_8\text{DDSQ}(\text{OSiMe}_3)_3(\text{OH})$  **84** with substituted-allylsilanes for the synthesis of functionalized POSS used in electronic devices.

Similarly, the crystallographic data for the bis-product (**Table 4, Chapter 5**) shows that the compound is the bis-protected cage,  $\text{Ph}_8\text{DDSQ}(\text{OTMS})_2(\text{OH})_2$ . **82** Interestingly, the crystal structure for this compound shows that the free hydroxyl groups are on alternating ends of the two cyclic cyclosiloxane rings (**Figure 16**). Like the tris-protected TMS cage,  $\text{Ph}_8\text{DDSQ}(\text{OTMS})_2(\text{OH})_2$  **82** could also be an important industrial intermediate in silicone industries. However, unlike  $\text{Ph}_8\text{DDSQ}(\text{OTMS})_3(\text{OH})$  **84**, the presence of two silanols in

$\text{Ph}_8\text{DDSQ}(\text{OTMS})_2(\text{OH})_2$  **82** makes it more multifunctional by providing the opportunity for it to undergo many more transformations. Thus, this compound can be potentially functionalized on the two ends with either the same or different functional groups. It can tether two polymer chains to give POSS-cage containing polymers that can lower the chain mobility of the polymer and also, surface modification via condensation or silylative coupling can, for instance, afford either the polymeric form or products that can undergo further functionalization. Their structure makes them ideal candidates for the synthesis of metalized polyhedral oligomeric silsesquioxane structures that are known to be very suitable for use as catalysts. Metalized POSS compounds have, for instance, been used as cure promoters, catalysts, and as alloying agents that can strengthen polymer microstructures, such as coils, domains, chains, and segments, at the molecular level.<sup>140</sup>

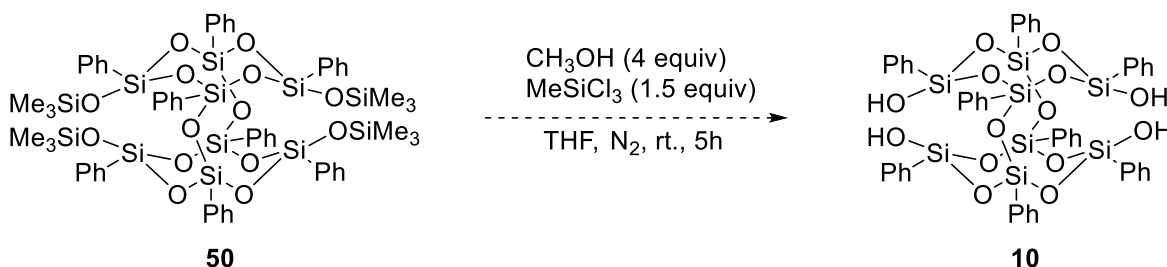
#### **5.4 Attempted Removal of the TMS Protecting Group from $\text{Ph}_8\text{DDSQ}(\text{OTMS})_4$ **50** with $\text{MeSiCl}_3$ and $\text{MeOH}$**

The TMS-masked  $\text{DDSQ}(\text{OH})_4$  is predominantly composed of Si-O-Si linkages throughout its structure. This architecture has the potential of making the search for reagents and conditions that are selective for the removal of the TMS silicons a serious challenge. In our pursuit for ideal deprotection conditions, the tetrakis-TMS DDSQ cage **5a** was chosen as a model substrate for two reasons, viz: Its structure is composed of Si-O-Si linkages, including the new bonds resulting from protection of its silanols with TMSCl and it is much easier to prepare than our preferred intermediate, tris-TMS-DDSQ(OH) **84** and bis-TMS-DDSQ(OH)<sub>2</sub> **82**. However, attempts made with **50** following various literature procedures<sup>127–129</sup> and in some case with some modifications, have been unsuccessful. All routes and conditions explored were either not efficient or, in most



cases, rupture the inner core siloxy ethers completely. For instance, in our initial attempts to desilylate **50** to **10** using MeSiCl<sub>3</sub> and MeOH ruptured the cage completely (**Scheme 73**). Table 5 below displays some of our trial results.

**Scheme 73: Attempted Desilylation of Ph<sub>8</sub>DDSQ(OSiMe<sub>3</sub>)<sub>4</sub> **50** with MeOH and MeSiCl<sub>3</sub>**



**Table 5: Conditions screening for the desilylation of Ph<sub>8</sub>DDSQ(OSiMe<sub>3</sub>)<sub>4</sub> **50** to Ph<sub>8</sub>DDSQ(OH)<sub>4</sub> **10****

Entry	Reaction Solvent	MeOH (x equiv)	MeSiCl <sub>3</sub> (y equiv)	Product (from NMR of crude material)
1.	CH <sub>2</sub> Cl <sub>2</sub>	4	2	CD
2.	CH <sub>2</sub> Cl <sub>2</sub>	4	1.5	CD
3.	CH <sub>2</sub> Cl <sub>2</sub>	2	2	CD
4.	THF	4	2	CD
5.	THF	4	1.5	CD
6.	THF	2	4	CD

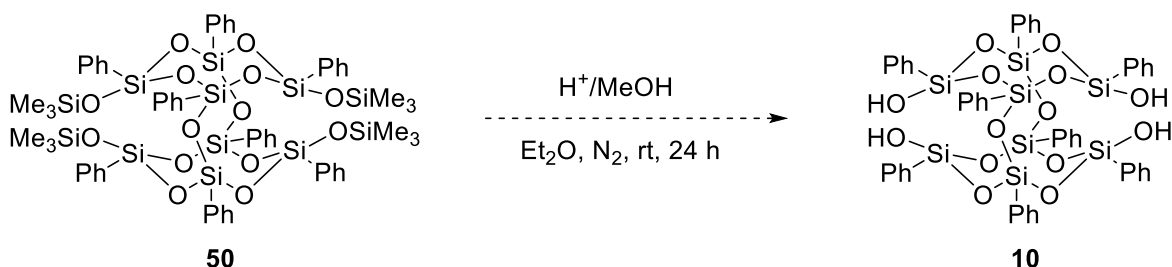
**Substrate: Ph<sub>8</sub>DDSQ(OSiMe<sub>3</sub>)<sub>4</sub>, CD = Cage Decomposed**

Reactions were followed by <sup>29</sup>Si NMR spectroscopy. Signals in the -76 to -79 ppm region symbolic of the POSS cage and also the silanol peaks at the -68 ppm region for all conditions screened were absent. The crude <sup>29</sup>Si NMR signal peaks in the -37 to -47 region symbolizes D-silicon – silicons bound to two oxygen atoms only. This result thus discloses a completely broken cage.

## 6.5 Attempted Removal of the TMS Protecting Group from Ph<sub>8</sub>DDSQ(OTMS)<sub>4</sub> **50** with H<sup>+</sup>/MeOH

In a different approach from the conditions above, desilylation was also attempted using conditions reported by Schoen *et. al.*<sup>127</sup> With Schoen, the precursor was a functionalized DDSQ which is structurally different from mine. While she desilylated a prefunctionalized N-TMS DDSQ (closed cage) with acidified MeOH, our trials were based on an open-caged TMS-functionalized double decker silsesquioxane. This structural difference might be the reason for the susceptibility of all the silo ether oxygens in **50** to attack by the acidified MeOH. Results from exploring her conditions to our system were therefore not surprising, albeit the use of other acids with different pka values (**Scheme 74**). Results of our trials are shown in Table 6.

### Scheme 74: Attempted Desilylation of Ph<sub>8</sub>DDSQ(OSiMe<sub>3</sub>)<sub>4</sub> 50 with Acidified MeOH



**Table 6: Conditions screening for optimal deprotection of Ph<sub>8</sub>DDSQ(OSiMe<sub>3</sub>)<sub>4</sub> 50 with acidified MeOH**

Entry	Acid (mol/dm <sup>3</sup> )	MeOH (mL)	Product (from crude NMR)
1	0.1M AcOH	2	NR
2	0.5M AcOH	2	NR
3	1M AcOH	2	NR
4	0.1M HCl	2	CD
5	0.1M H <sub>2</sub> SO <sub>4</sub>	2	CD

Substrate: Ph<sub>8</sub>DDSQ(OSiMe<sub>3</sub>)<sub>4</sub>, NR = No Reaction; CD = Cage Decomposed

Reactions were followed by Si-NMR, and like in **Scheme 73**, results also disclosed completely ruptured cages for the most part (entries 4 and 5). However, with acetic acid, the starting material was recovered (entries 1-3).

The deprotection above was one that was applied by Shoen<sup>127</sup> (**Scheme 52**) in removing the TMS group from her aniline-capped DDSQ. Interestingly, both her precursor (cis/trans functionalized DDSQ) and targets are completely different from ours. However, in addition to trying her conditions several other modifications were explored for amenability to our target. Thus, a number of acids with different pka values were investigated in pursuance

of appropriate conditions for deprotecting the tetrakis-TMS protected DDSQ (**Scheme 74**, **Table 6**). Results were similar to trial 1 for the most part. NMR data either showed a completely ruptured cage (**Table 6**, entries 4 and 5) or indicated no reactions (entries 1-3).

## CHAPTER 6: Conclusions and Future direction

### 6.1 Conclusions

This dissertation explored opportunities to selectively assemble asymmetric POSS compounds starting from cubic octaphenyl silsesquioxane  $\text{Ph}_8\text{T}_8$ , **31** the double decker tetrasilanol  $\text{Ph}_8\text{DDSQ}(\text{OH})_4$  **10** or its sodium salt  $\text{Ph}_8\text{DDSQ}(\text{ONa})_4$  **49**. Literature reports for the synthesis of symmetrically functionalized  $\text{Ph}_8\text{DDSQ}(\text{OH})_4$  **10** or its sodium salt **49** were replicated. Synthesis of the cubic silsesquioxane from  $\text{PhSi}(\text{OMe})_3$  and subsequent fission of Si-O-Si linkages to give the double decker product was also established. Importantly also, preliminary results from our efforts to synthesize other double decker silsesquioxanes including the *i*-Bu<sub>8</sub>DDSQ(OH)<sub>4</sub> and Ph<sub>12</sub>DDSQ(OH)<sub>4</sub> from their corresponding cubic precursors have been encouraging. However, desymmetrization of these molecules has been daunting to date. Like any other nascent discoveries, our approach stumbled into some difficulties, yet novel partial silylations were realized using protection techniques. From our proposed route, key potential intermediates were isolated and their crystal structures secured. This progress was constrained by the challenge to uncover the right reagents and conditions that could selectively and efficiently demask the protected DDSQ cage and hence provide the opportunity to introduce the second capping agent.

Thus, our initial attempts to access an asymmetric DDSQ via the McDougals' selective monoprotection failed for double decker silanol or silanolate as precursors. The platform for subsequent bridging upon monoprotection was not realized, likely due to the presence

of unprotected functionalities in the octaphenyl POSS cages or the plausible presence of the diprotected species on opposite ends of the cage. This presumption, and possibly other yet unidentified dynamics playing within the reaction vessel, should be further explored to reveal the cause for the failure in monoprotection. However, with some modifications on the technique, the tris-TMS-protected cage was synthesized and isolated. This development was inspiring as it would have provided entry into the asymmetric POSS cage only if deprotection had not crumbled our cage. Potentially though, the tris-TMS DDSQ(OH) **84** being reported for the first time could be utilized in forming particularly metal containing silsesquioxanes as new catalyst systems for both homogeneous and heterogeneous catalysis. This can not only broaden the metallasilsesquioxanes library but will also promote the commercialization of silsesquioxane-based catalytic materials for industrial applications.

## **6.2 Future Directions**

The progress recorded this far with the search for selective protocols for entry into asymmetric POSS compounds is noteworthy. A non-selective approach developed by a colleague in our lab has resulted in the generation of the asymmetric A/B POSS cages, albeit with other side products and yields that are no more than 50%. With such developments, a selective approach would ideally provide more scalable atom-efficient chemistry and afford better yields of functionalized asymmetric double deckers. Progress with the tris-protection route by way of being able to isolate and characterize various intermediates are encouraging. The concept surrounding the observed selectivity may be useful for entry into the desired target. This chemistry should therefore be further explored. However, this notwithstanding, and based on the current challenges faced so

far, prospective alternatives using other protecting groups and solid state supports described above are worthy of exploration. Focus should particularly be given to use of protecting groups that can result to the formation of other ethers that can exhibit a chemistry (at the capping sights) different from the Si-O-Si linkages that dominates silsesquioxanes architecture. Thus, formation of, for instance, Si-O-C, Si-O-B, Si-O-Sb, Si-O-Sn bonds as against Si-O-Si bonds should be given due considerations. Success on the foregoing could open a new area of research in silsesquioxane chemistry and will allow a great many new nanostructured compounds to be synthesized. With such anticipated glaring prospect, extension of the techniques to other variations of POSS cages including [Ph<sub>12</sub>T<sub>12</sub>], [Ph<sub>10</sub>T<sub>10</sub>], [*i*-Bu<sub>8</sub>T<sub>8</sub>] and other phenyl functionalized cages will invariably provide a basis for future exploration. This explains why exploration of this chemistry is to be encouraged to expand on the number of functionally useful double deckers for both research and engineering purposes. The physical and mechanical properties of the potential POSS compounds resulting from the above might match those of Ph<sub>8</sub>DDSQ(OH)<sub>4</sub> or even be superior.

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