Silsesquioxane lego chemistry : catalytic receptor ensembles for alkene epoxidation

Silsesquioxane Lego Chemistry: Catalytic receptor ensembles for alkene epoxidation

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Contents

Chapter 1

General introduction and the scope of this thesis

***Abstract**: The history and the latest developments in silsesquioxane chemistry are reviewed. Especially the state of the art of the application of metal-containing silsesquioxane derivatives in catalysis is provided. The scope of this thesis is revealed and relates to bio-inspired, silsesquioxane-based catalytic ensembles, enabling more sustainable epoxidation chemistry.*

1.1 Introduction

As reported by Sprung and Günther in 1955, silsesquioxanes appeared as white precipitates in silane polymerizations.[1] The name silsesquioxane, (in which 'sil' stands for silicon, 'sesqui', comes from Latin *semisque*, "and a half", and 'oxane' refers to any saturated oxygen compound) refers to any compound in which the ratio of Si to O is 1.5, meaning that silicon is trivalent towards oxygen, leaving its fourth valency to another substituent, typically H or an organic group. This results in a general formula of $(RSiO_{1.5})_n$ (for integer oxygen numbers, n must be an even number). This also includes polymeric and resinous materials. The most interesting class are molecular silsesquioxanes, also referred to as POSS^{TM} (Polyhedral Oligomeric SilSesquioxanes, a trademark of Hybrid Plastics Inc.). The POSS compounds can be divided into completely condensed structures, (Fig. 1.1), corresponding with $(RSiO_{1.5})_n$ (n = 4, 6, 8, 10, 12), and incompletely condensed silsesquioxanes, containing silanol groups and being of a more complex genral formula (Fig. 1.2).[2]

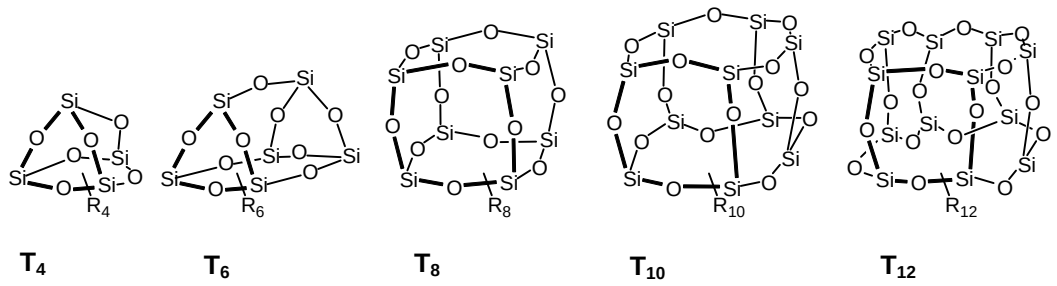

Fig. *1.1* *Completely condensed silsesquioxane structures*

An easier notation for silsesquioxanes is T_n, for completely condensed structures and $T_n(OH)_m$ for OH-containing structures. The T stands for a corner silicon atom, bonded to three oxygen atoms. Though n and m are dependent, for a quick recognition, they are treated as independent. So T_4 stands for $R_4Si_4O_6$.

Tetrameric silsesquioxanes are only known with R = *i*-C_3H_7 and *t*-C_4H_9[3], whereas hexamers are known for R = *c*-C_5H_9 and *c*-C_6H_{11}[4], though the scope has been expanded more recently with *i*-C_4H_9, n-octyl, Ph, $(CH_2)_2CMe_2CH_2CO_2Me$[5]. Octameric silsesquioxanes are encountered more generally with a variety of alkyl, substituted alkyl, cycloalkyl and aromatic organic groups. The isobutyl group, has a strong tendency to form octamer T_8. Larger aggregates T_{10} and T_{12} are generally known for R = H, Me, Vinyl and Phenyl.

Incompletely condensed silsesquioxanes have two origins: Like completely condensed silsesquioxanes, a) direct synthesis through hydrolytic condensation of silane starting materials, such as trialkoxysilanes $(RSiOR')_3$ or trichlorsilanes $(RSiCl_3)$ under appropriate conditions or b) silyl ether opening of completely condensed silsesquioxanes.

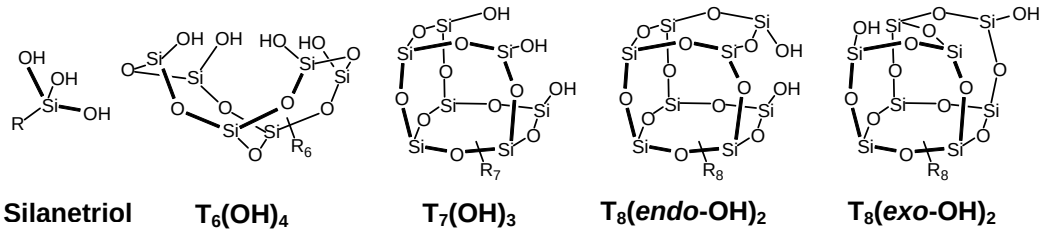

Fig.1.2 *Incompletely condensed silsesquioxane structures*

1.2 Metal-containing silsesquioxanes

Feher et al. initiated the research towards the use of silsesquioxane molecules as ligands for main group and transition metals at the end of the 1980s,[6] considering silsesquioxanes as models for industrially used silica supports. The resemblance of silsesquioxanes to silica supports is not only apparent from the molecular structure, but the electronic properties of silsesquioxane silanol groups mimic the behavior of silica as well. Important characteristics which can be replicated in silsesquioxane chemistry include electron withdrawing bonding sites,[7] interactions with adjacent oxygen donors[8] which contribute to the stability of clusters grafted onto surfaces,[8] and a defined orientation of surface hydroxyl groups which can dictate the selectivity by which reagents react with the surface. For example, the considerably enhanced alkene metathesis activity of surface carbene complexes over those of their homogeneous analogues, has been similarly exhibited in silsesquioxane chemistry.[9]
In Figure 1.3, a few important structural similarities between silsesquioxanes and schematized silica surfaces are depicted. First of all, the defined orientation of the silanol groups, which is also present in silsesquioxanes, may ensure
a strong multi-dentate bonding to metals. Furthermore, silsesquioxanes have enough residual siloxane bridges to resemble the silica surface and these residual siloxane bridges can interact with the metal.

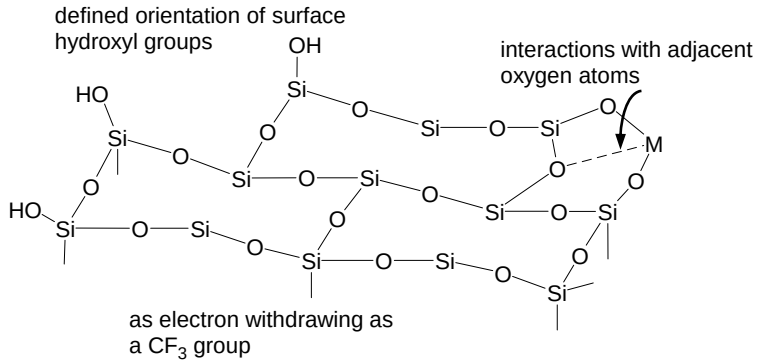

Fig. 1.3 *Schematic overview of a silica-based catalyst support, indicating important surface properties*

Since the discovery of silsesquioxanes, a rich coordination chemistry has been developed with metals and metalloids throughout the periodic table; at present, these involve: Li, Na, K, Be, Mg, Sc, Y, La, U, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Ru,

Os, Co, Rh, Pt, Cu, Au, Zn, Al, Ga, Tl, Ge, Sn, Pb, As, Sb, Bi. Metal-containing silsesquioxanes have been subject to several reviews.[10]

1.3 Catalysis with metal-containing silsesquioxanes

Metal-containing silsesquioxane derivatives provide new catalysts with both homogeneous and heterogeneous applicability. The steric and electronic properties of silsesquioxane silanolate ligands render metal centers more Lewis acidic than conventional alkoxide or siloxide ligands do. This concept has been exploited in newly developed catalysts for alkene metathesis[7], polymerization, epoxidation, and Diels-Alder reactions of enones.

There has been considerable research recently on heterogenization of homogeneous catalysts due to the ease of separation and purification of the products and the recovery of the catalysts. Thus, development of active heterogeneous catalysts with predefined active sites by immobilizing metal POSS compounds on insoluble supports appears promising.[11]

1.4 Silsesquioxane titanates as homogeneous epoxidation catalysts

In 1994, our group started a search for non-leaching heterogeneous liquid phase epoxidation catalysts. At that time detailed studies how the catalytically active metal species are bound to the support were rare. As today, usually more attention was paid to the performance of the catalyst, rather than to the fundamental question whether the catalyst is truly heterogeneous or not. In fact, many catalysts consisting of a metal oxide on an inert carrier owe their catalytic activity to rapid leaching of the metal from the surface to form active homogeneous catalysts, a fact that the designers of the original catalysts clearly did not have in mind.

In order to approach this issue at a molecular level, Abbenhuis first reported in 1997, on epoxidations catalyzed by model systems, titanium silsesquioxanes. Soon, Maschmeyer *et al.* followed with their own findings, as did leading industrial researchers from Shell.[12]

In these silsesquioxane titanates, exemplified in Fig. 1.4, the metal site is incorporated *via* spatially oriented siloxy bonds (Ti–O–Si) which structurally resemble surface sites

that have been purportedly identified on silica surfaces. Heterogeneous titanium catalysts are very important in oxidation processes but at the same time have been reported to undergo some leaching in liquid-phase applications. For instance, the highly active Shell titanium/silica epoxidation catalyst used in the SMPO process for propylene oxide, becomes only truly heterogeneous after a certain time on stream.[13] Similar materials, that were reported as the result of grafting silica[14] or MCM-41 mesoporous silica[15] with titanium derivatives, or even novel titanosilicates[16], might therefore be only partially heterogeneous when applied in liquid-phase oxidation reactions.

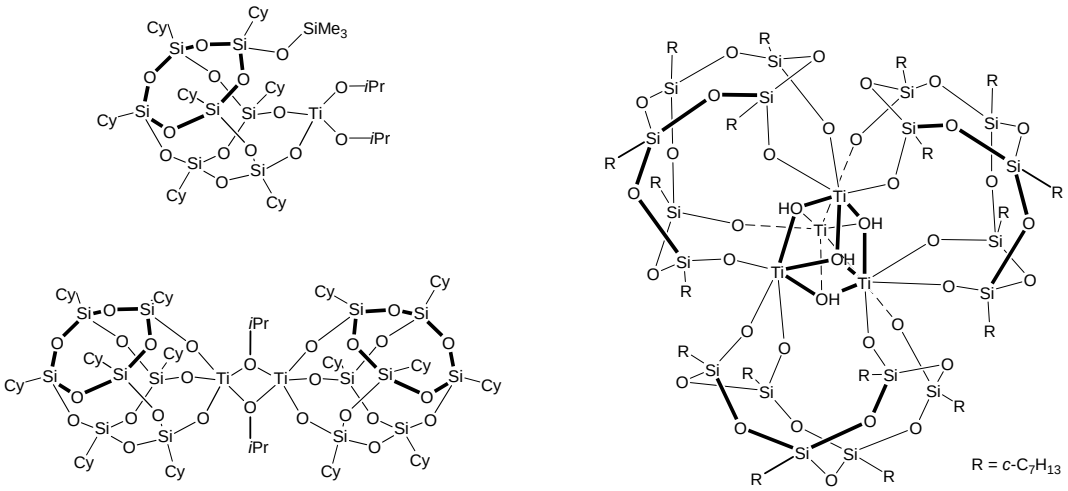

Fig. 1.4 *Silsesquioxane titanates provide models for industrial epoxidation catalysts*

With silsesquioxane model systems, Abbenhuis *et al.* proved that liquid-phase, silica-supported titanium epoxidation catalysts are accessible and active in many cases but will be truly heterogeneous only when stringent conditions are met.[5a] Particularly, the titanium site should be incorporated in a silanol nest rendering at least terdentate silanolate coordination. These findings are consistent with a mechanism for alkene epoxidation in which reversible hydrolysis of a titanium siloxy function occurs. This supports the now firmly established mechanism of heterogeneous alkene epoxidation by titanium silicalites proposed by Clerici, Ingallina, Sheldon and Van Doorn (Fig. 1.5).[17]

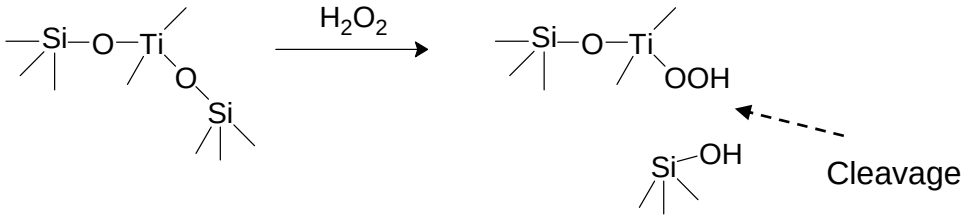

Fig. 1.5 *Part of the epoxidation pathway proposed by Clerici and Sheldon in which the peroxide reacts with the titanium site to form an active species for epoxidation. Clearly, multidentate bonding is required to prevent leaching of titanium.*

Still, the debate of catalyst stability has not ended. For certain, dentacity of siloxy chelation is the factor that determines whether a titanium silsesquioxane catalyst is stable in protic media. For silica-supported titanium sites, this statement is further corroborated by computional work, for instance, of Hillier,[18] However, when a water-containing medium for the epoxidation reaction is used, the dentacity is not the only factor that determines the stability of the catalyst. In addition, the intermolecular surrounding of the titanium site should then be hydrophobic enough to assist in further protecting the site against irreversible hydrolysis.

1.5 The quest for molecularly defined catalytic materials

In the mid 1990s, the major hurdle for the use of silsesquioxanes, not even to mention the impossibility to turn them into heterogeneous catalysts, was the long preparation time (ranging from a few weeks to 36 months) and the limited scope of the organic side groups on the silicon atoms (non-reactive groups unsuitable for ligand immobilization). Since then, new developments have shortened the preparation times and broadened the scope considerably. Starting with Maschmeyer, the use of high-throughput experimentation and synthesis robots have accelerated the optimization of synthesis conditions.[19] Recently, base-catalyzed polycondensation reactions have proven to be an excellent way to prepare large quantities of silsesquioxanes. Parallel, and in synergy with Lichtenhan, we have applied for patents on the preparation of completely condensed and incompletely condensed silsesquioxanes with isobutyl and isooctyl side-groups that can be prepared on large scales in a short time.[20] Until recently, functionalization of silsesquioxane silanols has been limited to either corner-capping of trisilanols with a trihaloorganosilane moiety, leaving no further reactive silanol groups, or reaction of the trisilanol with mono- or dihaloorganosilane

reactants, leaving two or one silanol groups, respectively. In the first case, a large number of possible side groups can be introduced, ranging from simple alkyl groups to reactive alcohols, amines and alkenyl groups. These groups allow the silsesquioxane cores to be included in polymeric materials. Furthermore, there was a substantial interest in octafunctional silsesquioxanes where all the side groups on the silicon atoms are identical and reactive. In these cases the functionality ranges from alkyls, alcohols, amides and carboxylates to halides, nitrates and phosphanes.[21] These can even be used as building blocks for dendrimers, as shown by Cole-Hamilton et al. for use in catalytic hydroformylation reactions.[22] The latest development involves the synthesis of functionalized silsesquioxane trisilanols. With these, homogeneous catalysts like our titanium-based epoxidation catalysts can be converted into molecularly defined catalytic materials. In fact, we believe so strongly in the inherent nanotech innovation that we recently founded the company “Hybrid Catalysis” to further commercialize silsesquioxane-derived catalytic materials.[23]

With homogeneous silsesquioxane-based epoxidation catalysts in hand, Abbenhuis started to work on their immobilization. An exciting first lead was that immobilization could be achieved by exploiting the strong adsorption of a silsesquioxane titanium complex in all silica MCM-41 channels.[24] The resulting self-assembled materials are active, truly heterogeneous, and recyclable catalysts for alkene epoxidation in the liquid phase. Essential for an irreversible adsorption of the silsesquioxane complex proved the use of somewhat hydrophobic, aluminium-free MCM-41.
Somewhat disappointing was the finding that none of the epoxidation catalysts developed so far were active in applications with aqueous hydrogen peroxide. Also the commercially employed Shell SMPO catalyst has this drawback. Clearly, just having a robust, accessible titanium site was not enough, nor was every combination of just such a site with any support.

1.6 Why water kills the cat

That the scope of catalytic epoxidation with silsesquioxanes did not include aqueous hydrogen peroxide was a puzzle that needed to be solved! Solvay started funding our research in the late 1990s and as a major producer of hydrogen peroxide they were not too pleased with catalysts that refused to work with their oxidant.

Little help came from the observation that few catalysts have been truly efficient in alkene epoxidation with aqueous hydrogen peroxide. Development of such catalysts is so important as only air is more sustainable than this oxidant.[25] Still rather unbeatable, the best catalyst in this field is the synthetic titanium-containing zeolite, titanium silicalite-1 (TS-1),[26] which is active for a wide range of oxidation reactions, including epoxidation.[27] For TS-1, activity seems to originate from a combination of a robust active Ti(OSi)n site (n = 3, 4),[28] and its location in a hydrophobic channel or cavity in the MFI (ZSM-5) structure.[29] The resulting catalytic ensemble prevents poisoning of the active site by water as well as unproductive decomposition of the oxidant.

Through our previous work on homogeneous epoxidation catalysis, we knew that we had robust silsesquioxane titanium derivatives in hand. The next challenge was to convert these compounds into materials that would add a hydrophobic environment, if not to dream of defined pores and cavities, to the active site.

Profiting from advances in silsesquioxane ligand synthesis, Abbenhuis *et al.* were able to make titanium derivatives with a function suitable for ligand tethering. Such a function was provided by a vinyl-, resp. styryl-containing silsesquioxane ligand that could be grafted on inorganic or organic supports. Subsequently, we were very excited when we found that some of these catalytic materials could indeed be used in heterogeneous epoxidation with aqueous hydrogen peroxide, albeit with limited activity and low total turn over numbers.[30]

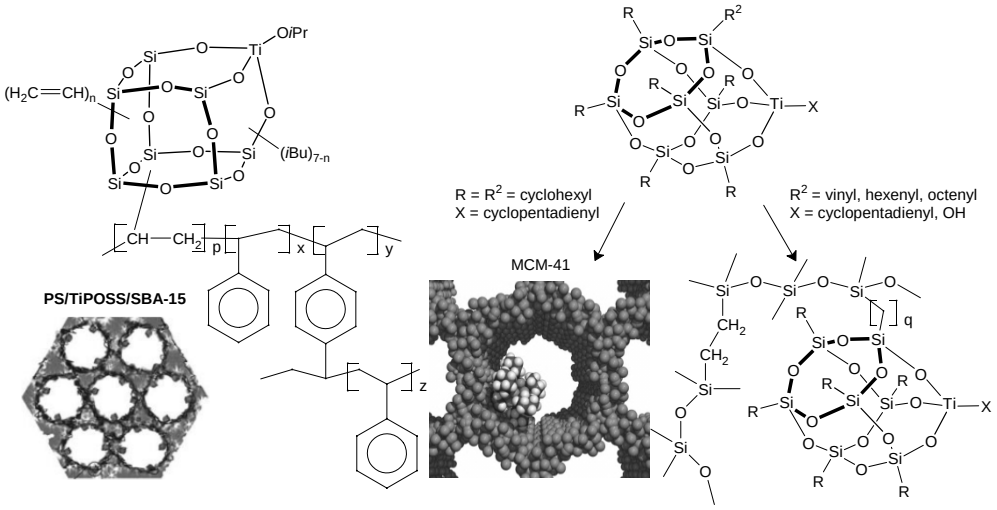

Fig. 1.6 *Approaches to catalytic materials for epoxydation: functionalized styryl POSS immobilized on SBA-15 (left);*[5] *physisorbed POSS in all silica MCM-41 (middle);*[15] *3D-netted silicone grafted POSS (right) which presents the first silsesquioxane-based catalyst that works with aqueous hydrogen peroxide.*[21]

1.7 Aim and scope of this thesis

First results with silsesquioxane immobilization demonstrated that grafting of functionalized titanium silsesquioxanes on polysiloxanes provided a way to realize the formation of a catalytic ensemble that was capable of performing epoxidation with aqueous hydrogen peroxide.[24] Clearly, the entire system was capable of outperforming the sum of its parts; it is the synergy between active site and its environment that allows hybrid catalysts, and likewise TS-1, or even metalloenzymes to achieve their desirable performance.

Aim of this thesis is to provide a clear technology push for enabling immobilization of silsesquioxane metal complexes. In order to meet this goal, new routes to silsesquioxane ligands have to be developed, in particular new organofunctionalized trisilanol ligands.

This thesis aims to further improve silsesquioxane catalysed epoxidation with aqueous hydrogen peroxide. To meet this goal, attempts are made to include functional groups

that may act as a receptor for aqueous hydrogen peroxide. In a attempt to follow Nature's concepts, the ultimate goal of this thesis is to tailor silsesquioxane baes, catalytic ensembles with regard to active site, cavity size and substrate recognition.

For useful receptors, urea derivatives will be aimed at. The fact that urea forms a very stable adduct with hydrogen peroxide while it does not complex water provides a first indication that such receptors can be made. Its structure has been determined by X-ray[31] and neutron diffraction[32]. We and others[33] already performed DFT calculations on hypothetical urea adducts.

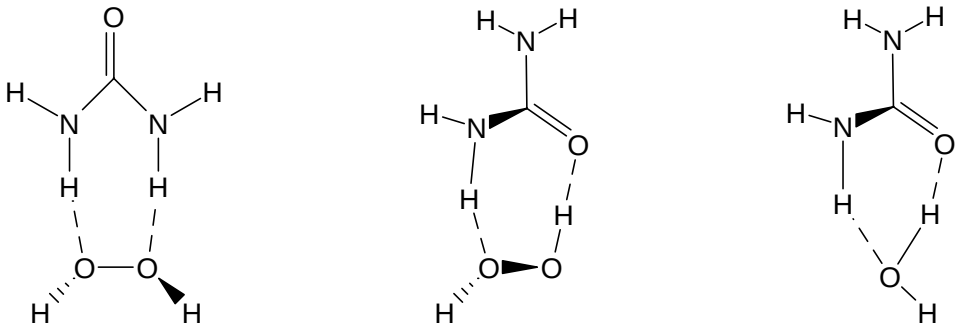

Fig. 1.7 *Structures of urea with hydrogen peroxide as in crystal structure (**a**), the most stable structure according to DFT (**b**), and the most stable complex with water (**c**)*

The structure of the urea hydrogen peroxide adduct as it has been determined by neutron diffraction, involving an N_2-H_2O_2 (**a**) interaction could be accurately reproduced by DFT computational methods; the binding energy for this adduct was calculated to be 6.3 kcal/mol, though the structure may be more stable due to intermolecular interations in the solid. The calculation of the interaction of urea with water[34] results in a different structure involving a urea NO-H_2O (**c**) interaction, though the similar H_2O_2 complex (**b**) is more stable. Interestingly, water does not occupy the preferable position of H_2O_2 although the geometry optimization was started from such a point. These findings already provide some justification for the hypothesis that selective receptors for H_2O_2 can be designed, made and exploited in catalytic epoxidation.

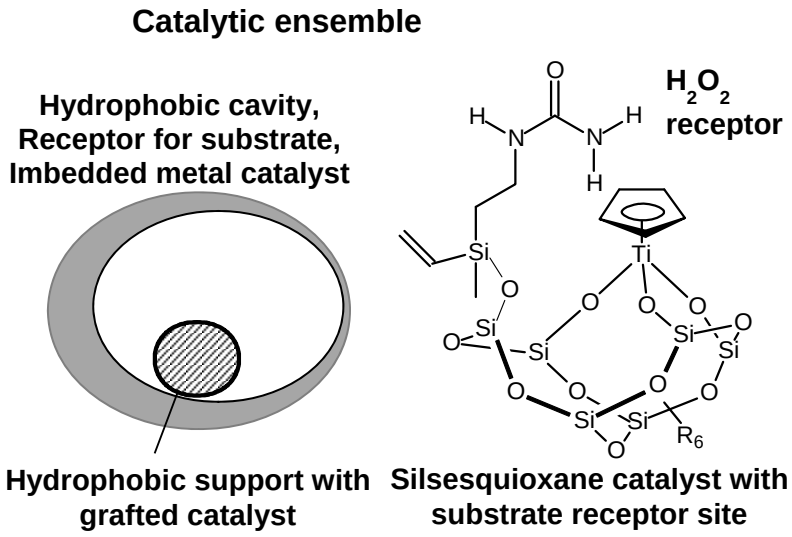

Fig. 1.8 *Following Nature's concepts, aim of this thesis is to tailor catalytic ensembles with regard to actve site, cavity size and precise, substrate recognition.*

Chapter 2 deals with the synthesis of different kinds of silsesquioxanes, including a tetrasilanol in large scale, as well as an alternative route to trisilanols under basic conditions. An optimized route for monofunctionalized T8-compounds will be given, using relatively cheap trialkoxysilanes. The partial silylation of tetrasilanol was investigated as well.

In ***chapter 3***, the scope of the functionalization of the tetrasilanol parent compound to monofunctionalized trisilanols is investigated, and it turned out that relatively small non-polar side chains give the highest yields, whereas amino groups and derivatives thereof give gels, consisting of many different species. The products were characterized using ^{1}H, ^{13}C and ^{29}Si-NMR, infrared and MALDI-TOF-MS. Furthermore, functionalization of silsesquioxanes, containing unsaturated side chains are subjected to hydroformylation to produce aldehydes, and a modified Wacker oxidation to create ketone functions.

In ***chapter 4***, the titanium complex of doubly disilylated tetrasilanol is described. The crystal structure shows an ideally tetrahedrally surrounded titanium atom with highly

distorted ligands. This complex contains four unsaturated side groups per titanium, and is utilized in the synthesis of titanium macrocycles. The functionalized trisilanols described in chapter 3 are transformed into cyclopentadienyl titanium complexes. The hydrolytic stability of new complexes is investigated.

Chapter 5 describes the epoxidation of simple olefins with *tert*-butyl hydroperoxide (TBHP) and aqueous hydrogen peroxide. Novel silsesquioxane titanates are the catalysts used here. Epoxidation activity is correlated to the mode of silsesquoxane or macrocycle chelation and encapsulation. The extent to which organofunctionalized silsesquioxane ligands acts as molecular substrate receptors seems to be limited,

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Chapter 2

Practical routes to functionalized silsesquioxane compounds

***Abstract**: The synthesis of a fully condensed, prismatic silsesquioxane compound, (c-$C_6H_{11})_6Si_6O_9$, was optimized to afford 150 gram batches within days. This material can be converted to a versatile tetrasilanol, (c-$C_6H_{11})_6Si_6O_7(OH)_4$, for which the selective silylation was studied. Base-catalyzed hydrolytic condensation of trialkoxysilanes was employed to develop routes to other functionalized silsesquioxane derivatives including corner-capped compounds, silanols and silanolate metal complexes.*

2.1 Introduction

The chemistry of organo-functionalized silsesquioxanes has emerged as a fascinating new field of modern nanotechnology.[1] Nanostructured polyhedral oligomeric silsesquioxane (POSS) compounds have been used to design novel hybrid nanocomposites now used in a variety of material applications.[2] Altogether, silsesquioxanes present well-defined, three-dimensional nano-sized building blocks that can create unique hybrid inorganic / organic materials, where a precise control of nanostructure and properties is needed.[3]

Incompletely condensed silsesquioxanes (Fig. 2.1) have two origins: (i) Direct synthesis through hydrolytic condensation of silane starting materials or (ii) silyl ether opening of completely condensed silsesquioxanes.

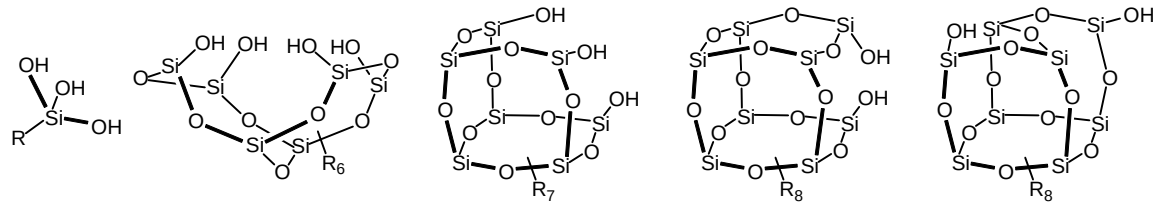
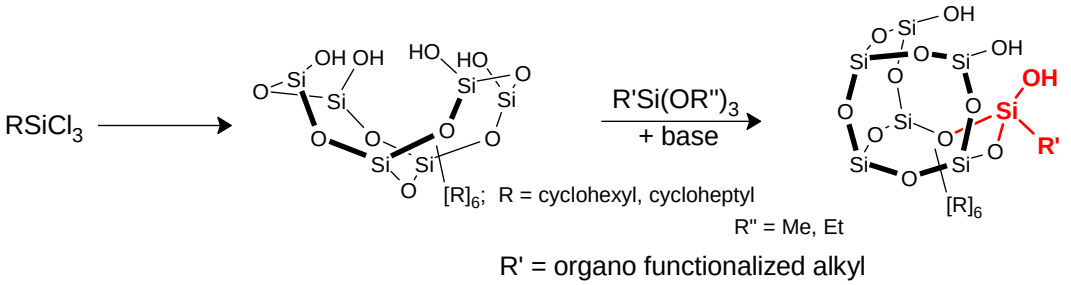


Fig. 2.1 *Incompletely condensed silsesquioxane structures*

In this chapter, both possible synthetic routes to incompletely condensed silsesquioxanes will be explored. Emphasis is on the large-scale synthesis of a particularly desirable tetrasilanol that will be further exploited in the context of catalyst development (Scheme 2.1).



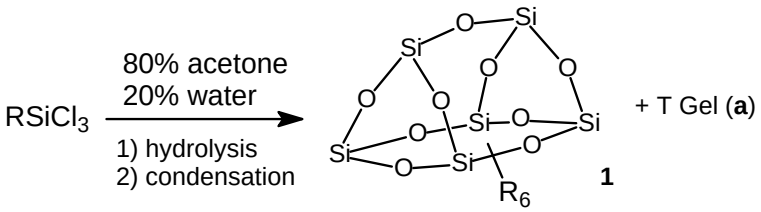
Scheme 2.1 *Main synthetic targets: improved route to tetrasilanols and their conversion to organofunctionalized trisilanols.*

2.2 Results and Discussion

2.2.1. Large-scale synthesis of trisilanol and tetrasilanol silsesquioxanes.

The reaction of *c*-$C_6H_{11}SiCl_3$ (1.5 kg, 7 mol) with water (0.78 L) and acetone (4.71 L) is very vigorous and believed to give the T_1 cyclohexylsilanetriol *c*-$C_6H_{11}Si(OH)_3$, instantaneously.[4] Addition could be done within five minutes using a double walled glass reactor with a water circulation cooling. After addition of two thirds of the trichlorosilane reagent, phase separation occurred, forming a bottom “organic” layer consisting mainly of silicon-based products and acetone, with a top “aqueous” layer, consisting of concentrated hydrochloric acid in acetone, which becomes brown due to acid-catalysed polycondensation of acetone. The heat generated by the hydrolysis of

the trichlorosilane reagent brought the reaction temperature to ca 50 ^{o}C, after which this temperature was kept constant.

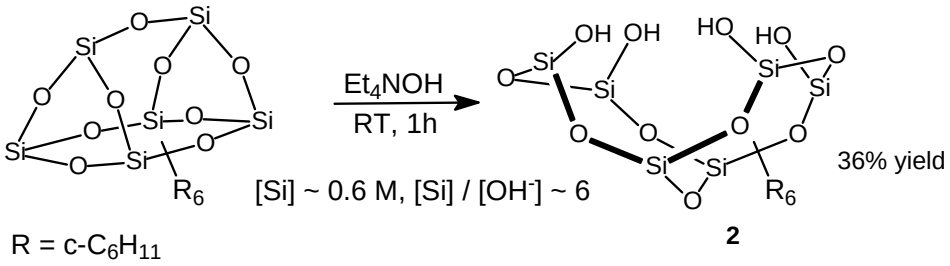


[Si] = 0.2 M: R = c-C_6H_{11} 7 % yield after 3 months
R = c-C_5H_9 0 % yield
[Si] = 1.25 M: R = c-C_6H_{11} 17 % yield after 1 night (kg scale process)
R = c-C_5H_9 13 % yield after a few days
R = i-Bu 0 % yield

Scheme 2.2 *Synthesis of $R_6Si_6O_9$ (**1**) from $RSiCl_3$ (R = c-C_6H_{11}) by hydrolytic condensation at high concentrations; T-gels (**a**), are highly soluble polycondensates*

Formation of (*c*-C_6H_{11})$_6Si_6O_9$ **1** (cyclohexyl-T_6) by hydrolysis of cyclohexyltrichlorosilane in aqueous acetone occurs mainly in the first hours and is most favorite at elevated temperatures[5]. The maximum yield of **1** was obtained after around 12 h. After this period side products may be formed as well, like (*c*-C_6H_{11})$_7Si_7O_9(OH)_3$ **3** which under our conditions is suppressed; (no further solid formation was found later) but polycondensates of acetone gradually hamper product isolation through filtration. Isolation of **1** at earlier periods is also hampered by the high viscosity of the reaction mixture, possibly due to larger oligomeric chain structures in the by-products. The formation of **1** is mainly governed by entropy, as it is the smallest stable silsesquioxane with *c*-C_6H_{11} groups, its low solubility in acetone being the driving force in its production, and hampering its breakdown. The OH-groups may give hydrogen bonds between molecules, and the lack of them also imparts in entropy. In our case we were able to recover 17 %, calculated from cyclohexyltrichlorosilane. Although more recently, an anhydrous method[6], using DMSO as source for O-atoms is developed for T_6 silsesquioxanes, the reported yields being no better than ours.

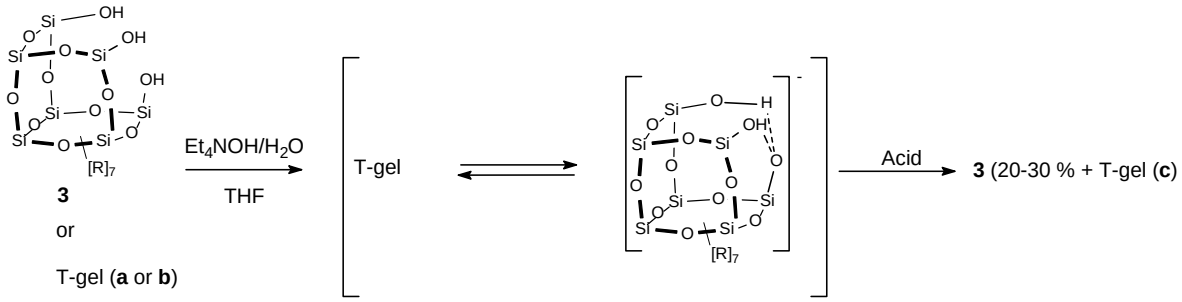
This prismatic compound contains two strained 6-membered rings, and as a result can be ring-opened by tetraalkylammonium hydroxide to form tetrasilanols of which only isomer **2**, with *endo*-hydroxyl groups is known (see scheme 2.3). Although yields of tetrasilanol $(c\text{-}C_6H_{11})_6Si_6O_7(OH)_4$ **2** have been reported as high as 70 %, when performed in one gram scale, this dropped to 64 % at 10 g scale[7] and to around 30-40 % when upscaled to eighty gram of **1**.[8] An explanation to this is hardly to be given, as the reaction produces no significant amount of heat.



Scheme 2.3 *Synthesis of tetrasilanol **2** from T_6 **(1)***

The formation of prismatic compound $(c\text{-}C_6H_{11})_6Si_6O_9$ **1** and tetrasilanol **2** is still accompanied by formation of by-products, which we refer to as T-gels. These materials are highly soluble in acetone and have a fluffy appearance when dry. MALDI-TOF-MS investigation gave a molecular mass range of 900-3000, in which the species have a polymerization grade of $(c\text{-}C_6H_{11}SiO_{1.5})_a(H_2O)_{0.5b}$ a = 6-22 with b = 0-6, with highest intensities in the range a = 10-15. Submission of T-gel **a** to reaction with 35 % aqueous $Et_4N^+OH^-$ in THF in the ratio [Si]:[OH^-] = 7:1 with [Si] = 100 mM gave trisilanol **3** in 15-25 % yield after 30 days. Heating to reflux did not improve this yield, although the product could be obtained after 1 week. The residue **b** obtained was again submitted to reaction with quaternary base under equal conditions to give another batch with the same yield, which also worked the third time. Evidence that this process is an equilibrium reaction is obtained from the fact that pure $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ **3** gave a recovery of trisilanol of 30 % with the remainder gels **c** giving equal MALDI-TOF-MS spectra (see scheme 2.4). In all cases, the reaction mixtures were homogeneous, indicating that crystallization cannot be the driving force; the only driving force imaginable is the high acidity of the trisilanol, reported to

have a pKa in THF of 8-10,[9] which would thus form the most stable salt with the quaternary base, of which a crystal structure of a tetrabutylammonium salt has been reported.[10] Quick addition of acid to ensure fast protonation of all silsesquioxane species present would freeze out the equilibrium.



Scheme 2.4 *Equilibrium reaction of trisilanol* ***3*** *(R = c-C_6H_{11}) and T-gels in THF solution in the presence of aqueous $Et_4N^+(OH)^-$. Ratio $Et_4N^+(OH)^-$:* ***3*** *is 1:7.*

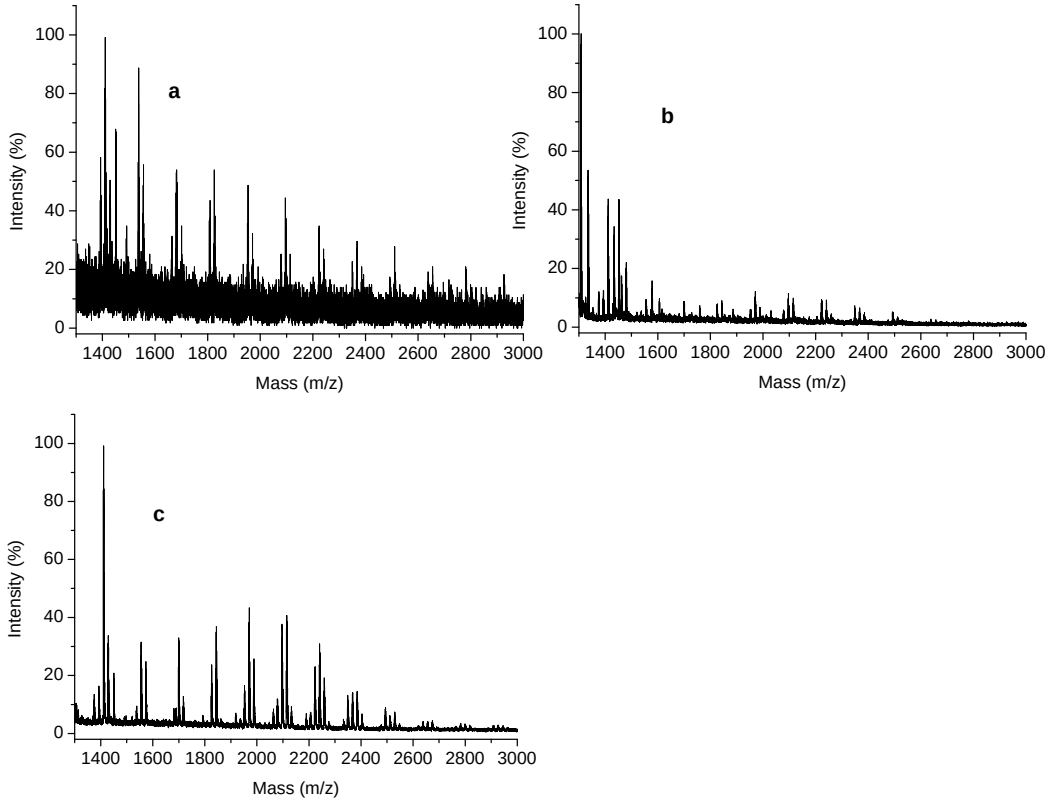


Fig. 2.2 *MALDI-TOF-MS analysis of T-gels formed in silsesquioxane synthesis: T gel from (c-C_6H_{11})$_6Si_6O_9$ synthesis (**a**), T-gel (**b**) obtained after reaction of **a** with Et_4NOH after isolation and T-gel (**c**) after reaction of (c-C_6H_{11})$_7Si_7O_9(OH)_3$ with Et_4NOH after removing equilibrium trisilanol.*

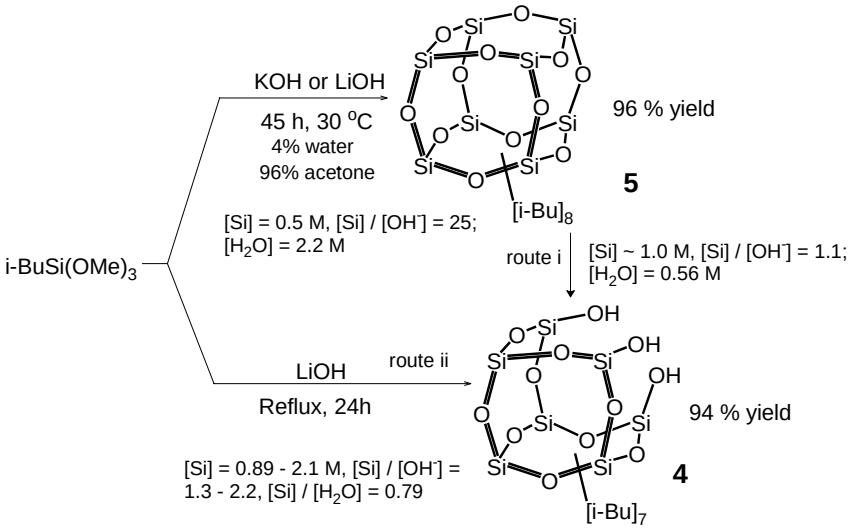
From Fig. 2.2, it is clear that all T-gels show molecular weights corresponding to the number of T groups, with variable degrees of hydration. This way, one would think that this method would make it possible to create trisilanols from all kind of feedstocks with different R-groups, which is unfortunately not the case, as the R-groups still play a major role in the selectivity of silsesquioxane formation.

However, the reaction of cyclohexyltrimethoxysilane with quaternary base under the same conditions did not work out. The same holds for the other R-groups, like vinyl, allyl, chloromethyl, giving gels, which in the case of vinyl also contains traces of completely condensed octasilsesquioxane T_8.

2.2.2 Optimization of (Isobutyl)$_7$Si$_7$O$_9$(OH)$_3$ and (Isobutyl)$_8$Si$_8$O$_{12}$ Synthesis

Two alternative routes have been investigated to the silsesquioxane trisilanol (i-$C_4H_9)_7Si_7O_9(OH)_3$ (**4**, Scheme 2.5). Route 1 involves base catalyzed rearrangement of silsesquioxane oligomers or T-resins for which an octasilsesquioxane T_8, [(i-$C_4H_9)_8Si_8O_{12}$] (**5**) was used as a typical starting material. Route 2 involves base catalyzed hydrolytic condensation of (i-C_4H_9)Si(OMe)$_3$, a bulk chemical which is generally used for crosslinking of silicones and to create hydrophobic surfaces on concrete and other construction materials. Initially, both routes were demonstrated to work but the acetone used as a solvent did deteriorate due to basic reaction conditions. Therefore other solvents were tested.

Several routes to octasilsesquioxane T_8, have been described in the literature, the best methods involve hydrolytic condensation of trialkoxysilanes using tetra(n-butyl)ammonium fluoride. Using this method, Bassindale reported a moderate yield of 26 % for the synthesis of [(i-$C_4H_9)_8Si_8O_{12}$] (**5**).[11] Surprisingly, we discovered that simple hydrolysis of (i-C_4H_9)Si(OMe)$_3$ catalyzed by a trace of KOH affords **5** in a few days with 96% isolated yield (Scheme 2.5). Using higher concentrations of base, the reaction generally results in the formation of T gel resins. An exception is LiOH which at high concentration leads to the formation of trisilanol **4** (Scheme 2.5, route 2).



Scheme 2.5 *Selective synthesis of isobutyl silsesquioxane from isobutyltrimethoxy silane (R = i-C_4H_9), by use of different bases*

Table 2.1 Route 1, influence of different solvents in the conversion of **5** to **4** by lithium hydroxide[a]

Entry	Solvent	[Si] / [OH^-]	[Si] / [H2O]	(i-C_4H_9)$_8$$Si_8O_{12}$ **5** (mmol)	Conversion to **4** (%)
1	MeOH	1.14	1.78	28.6	0
2	EtOH	1.14	1.78	28.6	20
3	2-propanol	1.14	1.78	28.6	80
4	Acetone	1.14	1.78	28.6	80
5[b]	Acetone, MeOH	1,17	1.78	63	96

[a] Conditions: Suspension of (i-C_4H_9)$_8$$Si_8O_{12}$ **5** (25 g, 28.6 mmol) in solvent (225 mL), LiOH.H_2O, T = 60 °C, the reactors were stirred magnetically overnight. Workup by addition to 250 mL of 1 M HCl. Product was obtained by filtration or decanting, washed with MeOH (50 mL) and dried at 40 °C in vacuo. [b] Acetone (420 mL), MeOH (80 mL), anhydrous LiOH used, T = 55°C, workup with double amounts of HCl and MeOH as *a*, In both cases [i-C_4H_9Si] ~ 1.0 M, [OH^-] = 0.87 M, [H_2O] = 0.56 M, [i-C_4H_9Si]/[OH^-] = 1.1

Base catalyzed rearrangement of T_8 compound **5** to the trisilanol **4** (Scheme 2.5, route 1) was previously reported by Lichtenhan *et al.*[12] We could optimize this route to afford **4** in near to quantitative yield. The solvent that works best, however, is acetone / methanol which is not inert under reaction conditions employing base. Attempts to perform the reaction in alcohol solvent as MeOH, EtOH or iPrOH largely failed (Table 2.1) due to incomplete conversion.

In the case of lithium hydroxide-mediated reactions, trisilanol **4** seems in any case to be the thermodynamic product: hydrolysis of closed cage **5** gave a maximum yield of 96 % by silicon (table 2.1), which means that not just decornering to **4**, which would correspond to 88 % yield on Si, but also polymerization of the postulated single corner [*i*-$C_4H_9Si(OH)_3$] into **4**.

Table 2.2 Route 2, influence of different bases in the hydrolytic condensation of (*i*-C_4H_9)$Si(OMe)_3$ to silsesquioxane trisilanol **4**[a]

Entry	Base (mmol))	Water (mmol)	OH peak (IR)	Product	Yield (g)
1	$LiOH.H_2O$ (55)	91 [b]	Yes	**4** [c]	6.61
2	NaOH (55)	91	Yes	T gel	5.25
3	C_2H_5ONa (55)	146	Yes	T gel	6.23
4	KOH 85% (55)	91	Yes	T gel	5.98
5	Et_4NOH (55)	18	n.d.	T gel	n.d.

[a] Conditions: Ethanol (70 mL), + water, T = 60°C, *i*-$C_4H_9Si(OMe)_3$ (14 mL, 13.0 g, 73 mmol), the reactors were stirred magnetically overnight. Workup by addition to 30 mL of 1 M HCl. Product was obtained by filtration or decanting, washed with MeOH and dried at 40 °C in vacuo, after which IR and melting points were recorded. [b] Including crystal water. [c] mp = 147 °C.

Secondly, we also studied the direct synthesis of trisilanol **4** from *i*-$C_4H_9Si(OMe)_3$, As such, selective base-catalyzed hydrolysis of *i*-$C_4H_9Si(OMe)_3$, was investigated varying solvents and bases (Tables 2.2 – 2.3). First a profound difference in the nature of the base utilized in the formation of **4** from the trimethoxysilane (Table 2.2) was found.

From Table 2.2 it is evident that the bases NaOH, KOH and hydroxides of quaternary ammonium ions tend to form T gels at relatively high silane concentrations, whereas lithium hydroxide surprisingly gives silsesquioxane trisilanol (*i*-$C_4H_9)_7Si_7O_9(OH)_3$ (**4**) on acidic work-up. Under optimized reaction conditions, the [Si] / [Li] ratio is in the range of 1.3 / 2.2. In principle, this could account for the formation of **4** in the form of a lithium silanolate, even a trisilanolate is possible. Perhaps in the case of lithium this structure could be of profound stability. Subsequent addition of acid sets the trisilanol **4** free, which was then filtered off. Unfortunately, we were not able to isolate crystals of the lithium salt suitable for X-ray crystallography.

Table 2.3 Route 2, influence of solvent and silane concentration in the formation of silsesquioxane trisilanol **4** by lithium hydroxide [a]

Entry	Solvent	[*i*-$C_4H_9Si(OMe)_3$] / resp. [LiOH] (M)	[Si] / [OH^-]	Yield (%)	Product
1	Acetone	0.89 / 0.67	1.3	67	4
2 [b]	Acetone, MeOH	0.89 / 0.39	2.2	94	**4**
3	MeOH	0.89 / 0.67	1.3	73	**5**
4	EtOH	0.89 / 0.67	1.3	64	**4**
5	EtOH	1.5 / 1.1	1.4	90	**4**
6	EtOH	2.4 / 1.8	1.3	98	**4**
7	EtOH	2.9 / 2.3	1.3	98	**4**
8	EtOH	3.1 / 2.4	1.3	0 [c]	T gel
9	2-propanol	0.89 / 0.67	1.3	57	**4**
10	2-propanol	1.5 / 1.1	1.4	0 [c]	T gel
11	2-propanol	2.4 / 1.8	1.3	0 [c]	T gel

[a] Conditions: *i*-$C_4H_9Si(OMe)_3$ in solvent (150 mL), $LiOH.H_2O$, and H_2O in ratio [*i*-C_4H_9Si]/[OH^-] = 1.4, [*i*-C_4H_9Si]/[H_2O] = 0.79, T = 60°C, the reactors were stirred magnetically overnight. Workup by addition to 250 mL of 1 M HCl. Product was obtained by filtration or decanting, washed with MeOH (50 mL) and dried at40 °C in vacuo, [b] Data taken from WO2001/010871, [c] sticky solid.

The influence of solvent and silane concentration of the formation of trisilanol **4** is listed in Table 2.3. Clearly, ethanol is the best solvent found in this study so far which allows shorter reaction times and tolerates higher concentrations of the starting material (*i*-C_4H_9)$Si(OMe)_3$. Under optimized conditions, the reaction proceeds with 98% yield of high purity trisilanol **4.**

Of the tested solvents, methanol, remarkably, gave closed cage compound **5**, according to its melting point and lack of OH-groups. The other solvents brought about almost pure trisilanol **4**, though we did not measure the exact composition.

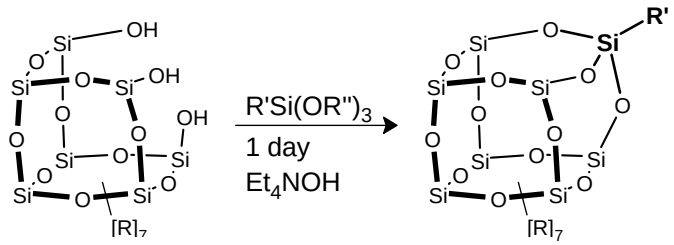
Concentration of the reaction mixture is another parameter, which may influence the outcome of the hydrolytic condensation of *i*-$C_4H_9Si(OMe)_3$. We varied the concentration of the silane, base and water in ethanol and isopropanol respectively, keeping the reactant ratios constant, as shown in Table 2.3.

It seems that at higher silane concentration, the reaction only works in ethanol, whereas the less polar 2-propanol did not give defined products. Concentration of the reaction mixture is hardly important when ethanol is used. However at very high concentrations a sudden drop in yield occurs. An explanation may be the fact that the vast amount of trimethoxysilane reagent changes the polarity and solvent properties of the reaction mixture.

2.2.3 New routes for corner-capping reactions of trisilanols with trialkoxysilanes

Corner-capping of trisilanols is normally performed by using trichlorosilanes[13]. These compounds react with trisilanols or other silanol functionalities instantly, but require one equivalent of base, mostly a tertiary amine or pyridine, for each chloride ligand substituted. This produces lots of waste chloride salts, which form thick suspensions, and they also have environmental impact, as we found that a high amount of solvent is required to obtain good yields. Moreover the silylation process must be performed in an anhydrous environment, as residual water immediately reacts with trichlorosilanes in the presence of amines.

A practical route for corner-capping of trisilanols was developed using the base-catalyzed reaction utilizing trialkoxysilanes R'Si(OR")$_3$, with R" generally being Me Et. The only waste products formed are alcohols (R"OH). As shown in table 2.4, the reaction needs water to occur, though in the equation it is not consumed. This implies that the trialkoxysilane reagent must first be hydrolyzed partially or fully to the silanetriol RSi(OH)$_3$, which subsequently condenses with the trisilanol, releasing water.



4 R = *i*-C_4H_9

5 R' =

a *i*-C_4H_9 **d** $H_2C=C(Me)C(=O)O(CH_2)_3$

b Vinyl **e** $H_2N(CH_2)_3$

c $Cl(CH_2)_3$ **f** $H_2N(CH_2)_2NH(CH_2)_3$

Scheme 2.6 *Corner-capping of trisilanol **4** with trialkoxysilanes catalyzed by aqueous quaternary base.*

Table 2.5 Corner-capping of trisilanol **4** with trialkoxysilanes with different conditions

Entry	Base (mmol)	Water (mmol)	Solvent (mL)	R'Si(OMe)$_3$	Yield (%)
1	-	-	acetone (100)		n.r.
2	Et_3N (10)	-	acetone (100)	*i*-C_4H_9	n.r.
3	Pyridine (10)	-	acetone (100)	*i*-C_4H_9	n.r.
4	Et_4NOH (1.2)	18	acetone (100)	*i*-C_4H_9	n.r.[b]
5	Et_4NOH (1.2)	18	THF (40)	*i*-C_4H_9	Sticky paste
6	Et_4NOH (1.2)	18	THF (20)	*i*-C_4H_9	**5a** 40
7	Et_4NOH (1.2)	18	THF (20)	$Cl(CH_2)_3$	**5c** 50
8	Et_4NOH (1.2)	18	THF (20)	Vinyl	**5b** 55
9	Et_4NOH (1.2)	18	THF (20)	$H_2N(CH_2)_3$	**5e** 25
10	Et_4NOH (1.2)	18	THF (20)	$H_2N(CH_2)_2NH(CH_2)_3$	**5f** 5
11	Et_4NOH (1.2)	18	THF (20)	methacryloxypropyl	**5d** 32
12[c]	Et_4NOH (12)	180	THF (80)	methacryloxypropyl	**5d** 64

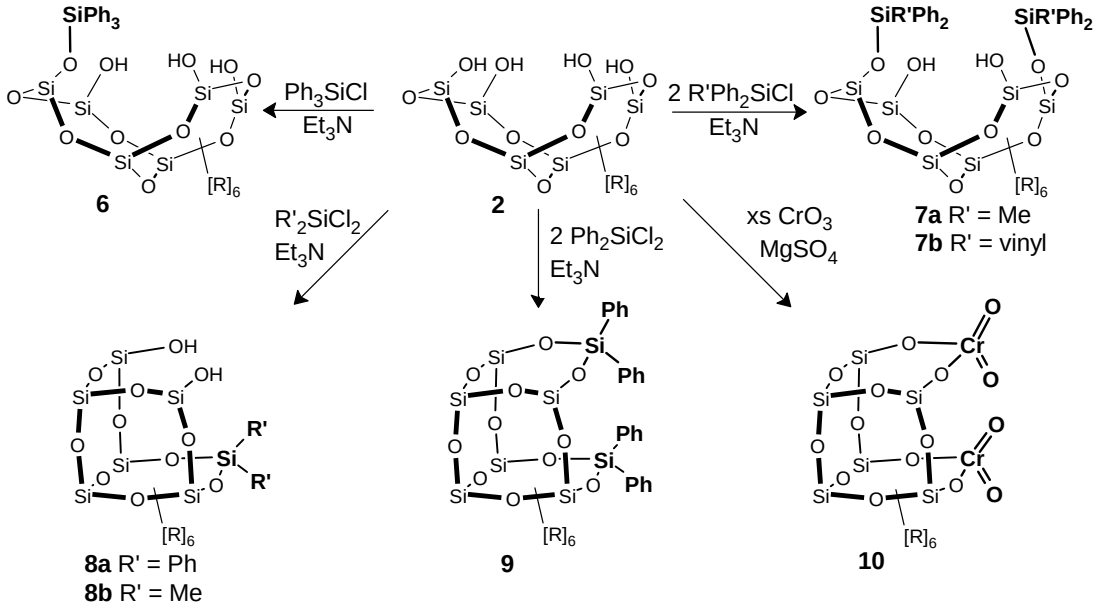
[a] Conditions: 10.0 g trisilanol **4** (10.0 g, 12.6 mmol), RSi(OMe)$_3$ (13.0 mmol), Workup by partial evaporation and addition of methanol, washing with acetone, purity checked by NMR [b] trialkoxysilane formed insoluble precipitate.

Also a self-catalyzed reaction was found. Amine-containing substrates can also be added in without the help of additional base. Using commercial THF (containing traces of water), we were able to increase the yield of product **5e** to 95 % yield. This tells that the base needs not to be strong, but just aids in hydrolyzing the trialkoxysilane moiety and forming of Si-O-Si bonds. As no quaternary salts are to be

removed, evaporation of the reaction mixture yields practically pure corner-capped product.

*2.2.4 Partial silylation of cyclohexyl tetrasilanol (c-$C_6H_{11})_6Si_6O_7(OH)_4$ (**2**).*

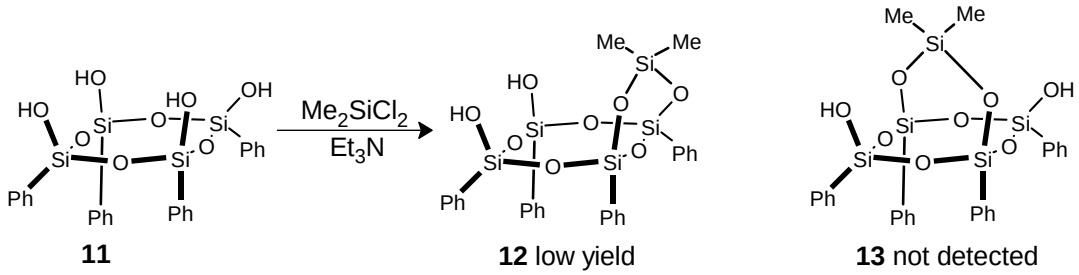
Reaction of tetrasilanol (*c*-$C_6H_{11})_6Si_6O_7(OH)_4$ **2** with chlorosilanes and an amine was studied to selectively form partially silylated compounds. As the only well-defined product of **2** with Me_3SiCl is the tetrasilylated compound, we decided to test the silylation behavior with more bulky agents (scheme 2.7). The most bulky silylating agent, Ph_3SiCl gave the monosilylated compound **6**, in 50 % selectivity.



***Scheme 2.7** Selective reactions of tetrasilanol **2** (R = c-C_6H_{11})*

Due to the bulkiness of Ph_3SiCl, the reaction is quite slow, formation of the ammonium salt being noticed after one hour. Unlike tetrasilanol **2**, trisilanol (*c*-$C_6H_{11})_7Si_7O_9(OH)_3$ **3** shows no activity at all towards Ph_3SiCl. Product **6** could be crystallized from hexane. Its six different methine signals in ^{13}C-NMR and silicon signals in ^{29}Si-NMR are in accordance with the postulated structure of **6**. Unfortunately, we could not obtain crystals, suitable for X-ray analysis, but like for trisilanols, we expect a dimeric structure, which was revealed with vapor pressure osmometry. With less bulky $Ph_2R'SiCl$ (R = Me, C_2H_3) we could not obtain a monosilylated product, instead full conversion to disilylated products **7a** (R' = Me)

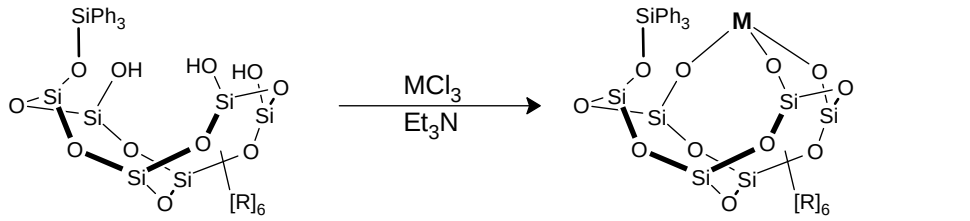
and 7**b** (R' = C_2H_3) was attained when the amine-mediated silylation was performed in the ratio **2** : $Ph_2R'SiCl$ = 1 : 2. Although **7a-b** are reasonably pure, these compounds could be obtained only as an oil. Structural proof came from a methylgallium complex, which shows disubstitution across the diagonal. Changing R' = H, no selective partial silylation was found, which also holds for substitution beyond two groups; instead only mixtures with 2, 3 and 4 substituents were obtained. Thus, the substitution behaviour seems to be fully governed by steric bulk. When difunctional silylating agents, like Ph_2SiCl_2, were used in one equivalent, full conversion to disilanol **8a**, with the formation of an 8-membered ring rather than a 6-membered or 10-membered ring. Reaction with the smaller Me_2SiCl_2 yielded the disilanol **8b** in ca 50 % yield. A second equivalent of Ph_2SiCl_2 to **8a** or two equivalents of Ph_2SiCl_2 to **2** gave the bis-disilylated silsesquioxane **9**. The feature of formation of 8-membered rings over 6-membered rings is also reflected in metallation. Reaction of chromium trioxide with **2** gave the bischromate **10**[14] whereas a recently prepared bis-titanium-cyclopentadienyl complex ((*c*-$C_6H_{11})_6Si_6O_{11}(TiCp)_2O$[15] shows similar features. This rule, however, has exceptions, as reaction of tetrasilanol *cis-cis-cis* $(PhSi(OH)O)_4$ (**11**) with Me_2SiCl_2 yields **12** only, albeit in low yields[16]. An 8-membered ring structure **13** was not detected at all (see scheme 2.8). An explanation could be the rupture of a hydrogen bond in the diagonally silylated product. Larger bridging reagents, e.g. $(Me_2ClSi)_2O$, or $(Me_2ClSiO)_2SiMe_2$, gave only intractable mixtures when reacted with tetrasilanol **2**.



Scheme 2.8 *Reaction of dimethyldichlorosilane with cis-cis-cis (PhSi(OH)O)4 (**11**)*

*2.2.5 Chemistry of (c-C_6H_{11})$_6Si_6O_7(OH)_3OSiPh_3$ (**6**)*

Trisilanol **6** behaves greatly as a normal trisilanol, like **3** in its reaction with tripodal reagents (scheme 2.9), like PCl_3, $MeGeCl_3$ and Cp^*TiMe_3 to form their products **14-16** in quantitative yield. We were not able to crystallize any of these compounds, possibly because of the lack of symmetry and intermolecular forces. The ^{31}P-NMR-spectrum of **14** shows a single peak at δ = 104.31 ppm ($CDCl_3$), compared to 86.12 ppm for (c-$C_6H_{11})_7Si_7O_{12}P$ (benzene-d6). Unfortunately, the reaction of **6** with $CpTiCl_3$ did not give a well-defined product, here the difference with normal trisilanols is reflected, as in all products from trisilanol **6**, one 6-membered ring is introduced, unlike trisilanol **3**, which forms only 8-membered rings on metallation or corner-capping.



6 M = P (**14**), GeMe(**15**), TiCp* (**16**)

***Scheme 2.9** Reactions of trisilanol **6** (R = c-C_6H_{11}) with different trichlorides*

*2.2.6 Characterization and chemistry of (c-$C_6H_{11})_6Si_6O_7(OH)_2(OSiR'Ph_2)_2$ (**7a-b**)*

Compounds **7a** and **7b** show in their ^{13}C-NMR three methine peaks and in its ^{29}Si-NMR spectrum two silsesquioxane resonances at - 67.6 and - 68.0 ppm with the silanol being - 59.4 ppm. Infrared spectra of **7a-b** in CCl_4 typically give a sharp peak at 3590 and a broader peak at 3445 and 3453 cm^{-1} respectively, indicating an isolated OH group and an internally hydrogen bonded OH-group, comparable to bulky disilanols like (c-$C_5H_9)_7Si_7O_9(OH)_2OSiMePh_2$, giving 3592 and 3453 cm^{-1} respectively[17]. Reaction of **7a** with trimethylgallium revealed a monomethylgallium complex of which the crystal structure deduces the symmetry of the ligand. The compound is a dimeric monomethylgallium complex, containing both unsymmetrical ligands to form a centrosymmetric unit.

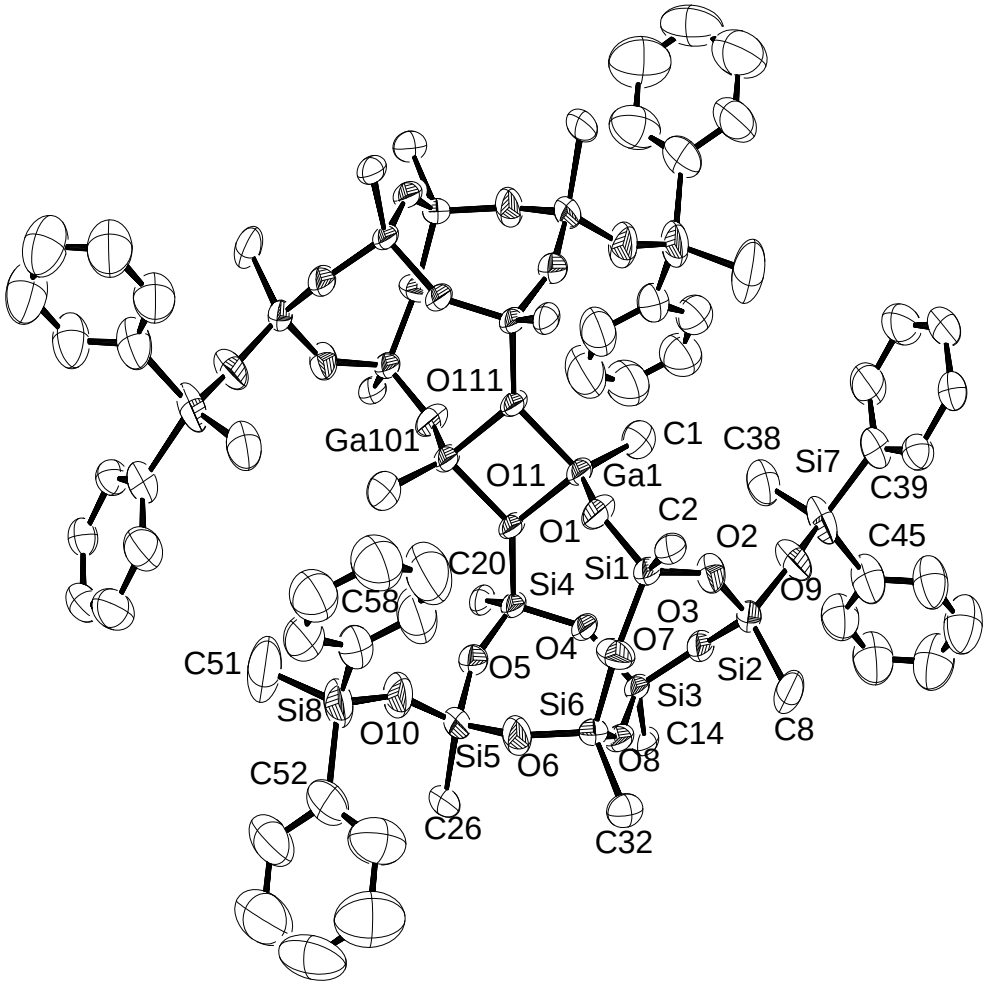


Fig. 2.3 *Molecular structure and labeling scheme of* $[(Ph_2MeSiO)_2(C_6H_{11})_6Si_6O_7O_2GaMe]_2$***(17); displacement ellipsoid drawing (50% probability). The cyclohexyl groups, except for the ipso carbon have been omitted for clarity.***

The bond distances observed in the gallium complex **17** are comparable in a similar complex, dimeric $(c\text{-}C_6H_{11})_7Si_7O_9(OH)O_2GaMe$.[18]

Ideally, the diagonal oxygen atom distances O1-O11 and O9-O10 should be equal, but in this structure the atomic distance O1-O11 has shortened whereas O9-O10 has lengthened considerably. The skeletal silicon distances are 4.675 Å for Si1-Si4 and 6.580 Å for siloxy-substituted silicons Si2-Si5. As the Ga-O and Si-O distances have not dramatically changed, we must conclude that the cages possess a very high degree of flexibility, which is also found in the later prepared titanium complex, which was synthesized by reacting two equivalents of disilanol **7b** with $Ti(O^iPr)_4$, (see chapter 4) although it took a long time to start crystallization.

Table 2.6 Selected Bond Lengths (Å) and Angles (deg) for $[Ph_2MeSiO)_2(c\text{-}C_6H_{11})_6Si_6O_9GaMe]_2$ (**17**)

Bond Lengths			
Ga1-μ^2O1	1.801(4)	Si5-O6	1.618(5)
Ga1-μ^3O11	1.938(3)	Si5-O10	1.609(5)
Ga1-μ^3O111	1.934(3)	Si5-C26	1.835(10)-1.920(9)
Ga1-C1	1.907(8)	Si6-O6	1.622(5)
Si1-μ^2O1	1.591(4)	Si6-O7	1.606(4)
Si4-μ^3O11	1.637(3)	Si6-O8	1.627(3)
Si1-O2	1.626(4)	Si6-C32	1.845(5)
Si1-O7	1.621(4)	Si7-O9	1.632(7)
Si1-C2	1.867(5)	Si7-C38	1.856(14)
Si2-O2	1.615(4)	Si7-C39	1.883(10)
Si2-O3	1.621(5)	Si7-C45	1.846(10)
Si2-O9	1.593(5)	Si8-O10	1.636(5)
Si2-C8	1.865(9)	Si8-C51	1.868(10)
Si3-O3	1.617(5)	Si8-C52	1.821(5)
Si3-O4	1.629(3)	Si8-C58	1.861(5)
Si3-O8	1.629(3)	Spatial distances	
Si3-C14	1.855(4)	O1-O11	3.013
Si4-O4	1.622(4)	O9-O10	9.063
Si4-O5	1.611(4)	Si1-Si4	4.675
Si4-C20	1.854(5)	Si2-Si5	6.580
Si5-O5	1.616(4)		
Bond Angles			
C1-Ga1-O1	124.5(3)	Ga1-O1-Si1	138.5(2)
C1-Ga1-O11	115.3(3)	Ga1-O11-Si4	128.43(19)
C1-Ga1-O111	115.6(2)	Ga1-O11-Ga101	98.12(14)
O1-Ga1-O11	107.31(18)	Ga101-O11-Si4	133.3(2)
O1-Ga1-O111	104.72(15)	Dihedral Angle	
O11-Ga1-O111	81.88(13)	O11-Ga1-O111-Ga101	0.02(14)

*2.2.7 Characterization and chemistry of $(c\text{-}C_6H_{11})_6Si_6O_7(OH)_2O_2SiR'_2$ (**8a-b**)*

Similar to the disilanols **7a-b**, silsesquioxane **8a** also behaves as a bulky disilanol, with comparable infrared absorptions at 3591 (sharp) and 3458 cm^{-1}. The latter absorption is somewhat shifted toward higher wavenumbers, indicating stronger hydrogen bonding. ^{1}H-NMR shows the two phenyl groups, one pointing outwards and

the other towards the OH groups, which are split up by 72 Hz. This splitting is less in the OH free compound **7** (32 Hz). The smaller dimethyl derivative **8b** shows two IR bands at 3445 and 3279 cm^{-1}, indicating intermolecular and strong intramolecular hydrogen bonding.

2.3 Conclusions

The synthesis of tetrasilanol (c-$C_6H_{11})_6Si_6O_7(OH)_4$ involves a hydrolytic condensation of c-$C_6H_{11}SiCl_3$ forming prismatic silsesquioxane (c-$C_6H_{11})_6Si_6O_9$ in 17 % yield. The latter can be hydrolyzed with a quaternary ammonium hydroxide to form the terasilanol in 40-50 % yield. Waste materials obtained during synthesis are hydroxylated oligomers of (c-$C_6H_{11}SiO_{1.5})_a(H_2O)_{0.5b}$ a = 6-22 and b = 0-6. This oligomer mixture is in equilibrium with (c-$C_6H_{11})_7Si_7O_9(OH)_3$ as the monoanion when treated with quaternary base, and 20-30 % of the silsesquioxane could be obtained after acid workup.

Base-catalyzed condensation works well for isobutyl substituted silsesquioxanes:
A base-catalyzed route for isobutyl substituted trisilanol (i-$C_4H_9)_7Si_7O_9(OH)_3$ in ethanol using lithium hydroxide gives near to quantitative yield. Selective synthesis of silsesquioxanes strongly depends on the nature and concentration of the base employed. New selective silylation reactions have been found for cyclohexyl tetrasilanol silsesquioxane

2.4 Experimental Section

General considerations. All reactions with air- or moisture-sensitive materials were carried out under argon using standard Schlenk techniques[19]. Freshly distilled, dry and oxygen-free solvents were used throughout. The silsesquioxanes (c-$C_6H_{11})_6Si_6O_7(OH)_4$ and (c-$C_7H_{13})_6Si_6O_7(OH)_4$ were obtained by synthesis methods described in the literature and through improved methods reported in this chapter.[20, 21] ^1H (400 MHz) and ^{13}C (100.6 MHz)-NMR were recorded on a Varian Mercury 400 spectrometer, ^{29}Si-NMR (99.3 MHz) was recorded on a Varian Inova 500 spectrometer, MALDI-TOF-MS analysis was performed on a

Voyager-DE™ STR Biospectrometry™ Workstation with *trans*-2-[3-(4-Butylphenyl)-2-methyl-2-propenylidene]malononitrile as matrix and sodium trifluoroacetate as Na^+ source

Large scale preparation of (c-$C_6H_{11})_6Si_6O_9$ (**1**).

Cyclohexyltrichlorosilane (1516 g, 6.9 mol) was added in about 10 min. to a stirred mixture of acetone (4.71 L) and water (0.78 L) at room temperature. The temperature rose to 50°C, after which the reaction mixture was stirred for 7 hours. The bottom layer was drawn off, diluted with acetone (1L), and filtered. The filter residue was washed with more acetone and dried in an oven to give **1** in 17% yield (150 g). Analytical data are in accordance with literature. The filtrate was evaporated to dryness to give an amorphous foam, referred to as **T-gel a**.

Large scale synthesis of (c-$C_6H_{11})_6Si_6O_7(OH)_4$ (**2**).

To a suspension of **1** (80.0 g, 98 mmol) in THF (500 mL) was added a solution of tetraethylammonium hydroxide (35 wt% in water, 40 mL, 95 mmol). The mixture became clear within 7 minutes and was stirred for one hour. A solution of concentrated hydrochloric acid (37 wt%, 14 g) in 100 mL of water was added. The mixture was concentrated by evaporation to give solids and an aqueous phase. The water layer was removed, and the solids were washed three times with water. The solids were dissolved in diethyl ether (500 mL). After drying the ether solution on $MgSO_4$, the solution was evaporated until crystallization started. Crystallization at – 30°C afforded 27 g of **2**. A second crop of **2** (2.5 g) was obtained by adding acetone to the filtrate, making the total yield to 29.5 g (35 mmol, 39 %).

Synthesis of (i-$C_4H_9)_8Si_8O_{12}$ (**5**).

To a stirred solution of Isobutyltrimethoxysilane (446 g, 2.5 mole) in acetone (4300 mL) was added a solution of KOH (6.4 g, 0.11 mole) in water (200 mL). The mixture was stirred and heated to 30°C for 3 days. At the start of the reaction the reaction mixture was seeded with 10 g of the product. The resulting precipitate was filtered off, and dried at 70 °C in vacuo. Yield: 262 g (96%).

*Synthesis of (i-$C_4H_9)_7Si_7O_9(OH)_3$ (**4**) from (i-$C_4H_9)_8Si_8O_{12}$ (**5**)*

Octasilsesquioxane **5** (55.0 g, 63.0 mmol) was suspended in 84 / 16 acetone / methanol (500 ml) containing water (5.0 ml, 278 mmol) and LiOH (10.0 g, 437 mmol) at 55°C. The reaction mixture was stirred for 18h at 55°C, then was acidified by quenching it into 1N HCl(aq) (500 mL) and stirring for 5 min. The resulting solid was filtered off and washed with CH_3OH (100 mL) and air dried. The product (54.8 g) was isolated in 96 % yield with very high purity.

Solvent variation. Setup: Four double walled glass reactors (250 mL) with magnetic stirrers and reflux condensors; heating through a thermostat. Octasilsesquioxane **5** (25.0 g, 28.6 mmol) was suspended in 225 mL of either acetone, methanol, ethanol or isopropanol. Added to the suspention was $LiOH.H_2O$ (8.14 g, 199 mmol). The reaction mixture was stirred for 20h at 60°C, then quenched into 250 mL of 1N HCl and stirred for 5 minutes. The resulting solid was filtered off and washed with CH_3OH (50 mL) and dried in a vacuum-oven at 20°C for one week.

Synthesis of $(i\text{-}C_4H_9)_8Si_8O_{12}$ (**5**) *from Isobutyltrimethoxysilane.*

Isobutyltrimethoxysilane (653 g, 3.66 mole) was added over 45 minutes to $LiOH.H_2O$ (70.0 g, 1.66 mole) dissolved in water (56 ml, 3.1 mole) and MeOH (420 mL) and acetone (3080 mL) at 55 ^oC. The reaction mixture was heated at 50 ^oC for 18 h. The reaction mixture was cooled to 20^oC and 1N HCl(aq) (1.5 L) was added followed by stirring for 1h. The resulting solid was filtered off and washed with water and dried at 70^oC in vacuo. Yield 390 g (94 %).

Synthesis of $(c\text{-}C_6H_{11})_6Si_6O_7(OH)_3OSiPh_3$ (**6**).

To a solution of **2** (5.15 g, 6.0 mmol) and Ph_3SiCl (2.40 g, 8.0 mmol) in THF (50 mL) was added Et_3N (3.0 mL, 21 mmol). The mixture turned cloudy after one hour and was stirred for 5 days. After evaporation, the solid was extracted with hexane and the hexane extract was evaporated until it turned turbid, after which it was allowed to crystallize at - 30^oC. This gave slightly impure **6**, which was purified with benzene/acetonitrile diffusion to give **6**.0.5 C_6H_6 (yield 2.13 g, 1.86 mmol, 31%). ^{29}Si {^1H} NMR ($CDCl_3$) δ -21.3 (Ph_3SiO), -58.0, -58.5, -58.8 (1:1:1 Cy-Si-OH), -67.2, -67.8, -68.1 (1:1:1), ^1H NMR ($CDCl_3$) δ 7.68 (dm, 6 H, Ph), 7.43 (m, 9 H, Ph) 1.73, m 30 H, CH_2 *c*-C_6H_{11}), 1.26 (m, 30 H, CH_2 *c*-C_6H_{11}), 0.73 (m, 6 H, C*H* *c*-C_6H_{11}), ^{13}C {^1H} NMR ($CDCl_3$) δ 135.43, 134.97, 129.63, 127.59 (Ph), 27.669, 27.65, 27.62, 27.58, 26.96, 26.90, 26.84, 26.73, 26.72, 26.68, 26.65, 26.63 (*C*H_2 *c*-C_6H_{11}) 24.60, 23.69, 23.58, 23.53, 23.51, 23.41 (1:1:1:1:1:1 *C*H *c*-C_6H_{11}). IR (CCl_4) cm^{-1} 3281. Anal. calcd for $C_{54}H_{84}Si_7O_{11}$ (found) : C 58.65 (58.50), H 7.66 (7.62).

Preparation of $(c\text{-}C_6H_{11})_6Si_6O_7(OH)_2(OSiMePh_2)_2$ (**7a**).

To a cooled (- 80^oC) solution of **2** (4.2 g, 5.0 mmol) Et_3N (4.0 mL, 28 mmol) in THF (50 mL) was added $Ph_2MeSiCl$ (2.42g, 10 mmol). After stirring for two days, the white milky mixture was evaporated, dissolved in hexane and filtered to give **7a** as a sticky paste (5.4 g, 4.3 mmol 87 %, ca 75% pure, remainder mainly monosilylated product).

^{29}Si {^{1}H} NMR ($CDCl_3$) δ- 11.3 ($SiMePh_2$), - 59.4 (Cy-Si-OH), - 67.6, - 67.8, ^{1}H NMR ($CDCl_3$) δ 7.70, (dd, 8 H, Ph), 7.45 (m, 12 H, Ph) 1.80 (m, 30 H, C*H*$_2$ *c*-C_6H_{11}), 1.24 (30 H, C*H*$_2$ *c*-C_6H_{11}), 0.77 (m, 6 H, C*H* *c*-C_6H_{11} + CH_3) ^{13}C {^{1}H} NMR δ 137.83, 137.72, 134.04, 133.99, 129.50, 129.48, 127.72, 127.70 (Ph), 27.56, 27.52, 26.82, 26.77, 26.69, 26.65, 26.61, 26.56 (*C*H$_2$ *c*-C_6H_{11}), 24.34, 23.64, 23.38 (2:2:2, *C*H *c*-C_6H_{11}), - 0.94 IR (CCl_4) cm^{-1} 3590, 3445.

Preparation of (c-C_6H_{11})$_6$Si$_6$O$_7$(OH)$_2$(OSiC$_2$H$_3$Ph$_2$)$_2$ (**7b**).

Procedure as for **7a** Oil, yield: 1.84 g, 1.46 mmol, 73 % from **2** 1.70 g (2.0 mmol) and vinylPh_2SiCl (980 mg, 4.0 mmol).

^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 23.1 ($C_2H_3Ph_2SiO$), - 59.4 (Cy-Si-OH) , - 67.6, -68.0, ^{1}H NMR ($CDCl_3$) δ 7.64 (m, 8 H, Ph), 7.42 (m, 12 H, Ph), 6.57 (m, 1 H, -C*H*=), 6.23 (dd, 1H, =C*H*$_2$), 5.91 (dd, 1 H, =C*H*$_2$), 1.76 (m, 30 H, C*H*$_2$ *c*-C_6H_{11}), 1.20 (m, 30 H, C*H*$_2$ *c*-C_6H_{11}), 0.70 (m, 6 H, C*H* *c*-C_6H_{11}), ^{13}C {^{1}H} NMR δ 136.07, 135.67, 135.63, 135.14 (=*C*H$_2$), 134.75, 129.68 (-*C*H=) 127.77, 127.69, 27.58, 27.54, 27.51, 26.80, 26.76, 26.72, 26.69 (*C*H$_2$ *c*-C_6H_{11}), 24.39, 23.67, 23.41 (2:2:2, *C*H *c*-C_6H_{11}), IR (CCl_4) cm^{-1} 3590, 3453.MALDI-TOF: M + Na = 1286.5 (major peak is 1327.4).

Preparation of (c-C_6H_{11})$_6$Si$_6$O$_7$(OH)$_2$O$_2$SiPh$_2$ (**8a**).

To a cooled (- 80^{o}C) solution of **2** (0.85 g, 1.0 mmol) and Et_3N (1.0 mL, 7 mmol) in THF (20 mL) was added Ph_2SiCl_2 (0.26 g, 1.0 mmol). The mixture was warmed to room temperature and stirred for 2 days. The mixture was evaporated and the residue was extracted with hexane, which yielded **8a** (0.76 g, 0.74 mmol, 74%). Analytically pure material was obtained from benzene/acetonitrile (0.65 g, 0.63 mmol, 63%) ^{29}Si {^{1}H} NMR δ - 47.08 ($SiPh_2$), - 59.5 (Cy-Si-OH, 2 Si), - 67.5, - 68.0, - 68.1 (1:1:2).

^{1}H-NMR ($CDCl_3$) δ 7.83 (m, 2 H, *endo*-Ph), 7.65 (m, 2 H, *exo*-Ph), 7.46 (m, 6 H, Ph), 2.94 (br s, 2 H, OH), 1.76 (m, 30 H, C*H*$_2$ *c*-C_6H_{11}), 1.26 (m, 30 H, C*H*$_2$ *c*-C_6H_{11}), 0.79 (m, 6 H, C*H* *c*-C_6H_{11}), ^{13}C {^{1}H} NMR $CDCl_3$) δ 135.39, 135.33, 134.31, 133.82, 130.56, 130.11, 128.22, 127.74 (Ph), 27.46, 26.85, 26.78, 26.60, 26.55 (*C*H$_2$ *c*-C_6H_{11}) 23.62, 23.38, 23.14, 23.09 (2:2:1:1 *C*H *c*-C_6H_{11}) IR (CCl_4) cm^{-1} 3591 3458.

Preparation of (c-C_6H_{11})$_6$Si$_6$O$_7$(OH)$_2$O$_2$SiMe$_2$ (**8b**).

Same procedure as **8a**, but with Me_2SiCl_2 (130 mg, 1.0 mmol). Crude product is mixture of **8b**, unreacted **2** and fully silylated product (*c*-C_6H_{11})$_6$Si$_6$O$_7$(O_2SiPh_2)$_2$.

Pure **8b** was obtained by fractional crystallization from benzene/acetonitrile (yield: 530 mg, 0.59 mmol, 59%). ^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 17.9 ($SiMe_2$), - 59.2 (Cy-Si-OH, 2 Si), - 67.7,

69.98, - 68.03 (1:1:2), ^{1}H ($CDCl_3$) δ 4.61 (br s, 2 H, OH), 1.77 (m, 30 H, C*H*$_2$ *c*-C_6H_{11}), 1.27 (m, 30 H, C*H*$_2$ *c*-C_6H_{11}), 0.79 (m, 6 H, C*H* *c*-C_6H_{11}), 0.186 (s, 3 H, Me), 0.176 (s, 3 H, Me), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 27.54, 27.48, 26.87, 26.84, 26.80, 26.71, 26.67, 26.59, 26.56 (*C*H$_2$ *c*-C_6H_{11}), 23.79, 23.55, 23.20, 23.11 (2:2:1:1 *C*H *c*-C_6H_{11}), 0.85, 0.13 (1:1 Me) IR (CCl_4) cm^{-1} 3445, 3279.

Preparation of (c-C_6H_{11})$_6$Si$_6$O$_7$(O$_2$SiPh$_2$)$_2$ (**9**).

See procedure for **8a**, with two equivalents of Ph_2SiCl_2 (0.52 g, 2.0 mmol) Yield: 1.04 g, (0.86 mmol, 86%, 59 % after recrystallization).

^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 45.3 ($SiPh_2$), - 67.1, - 68.1 (2:4), ^{1}H ($CDCl_3$) δ 7.66 (m, 4 H, *exo*-Ph), 7.58 (m, 4 H, *endo*-Ph), 7.43 (m, 8 H), 7.16 (t, 4 H, Ph), 1.75 (m, 30 H, C*H*$_2$ *c*-C_6H_{11}), 1.29 (m, 30 H, C*H*$_2$ *c*-C_6H_{11}), 0.81 (m, 6 H, C*H* *c*-C_6H_{11}), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 135.83, 134.32, 134.21, 133.88, 129.84, 129.67, 127.58, 127.46 (Ph), 27.56, 27.54, 27.51, 26.86, 26.77, 26.69, 26.60 (*C*H$_2$ *c*-C_6H_{11}), 24.07, 23.16 (4:2, *C*H *c*-C_6H_{11}). Anal. calcd for $C_{60}H_{86}Si_8O_{11}$ (found) : C 59.66 (59.59), H 7.18 (7.25).

Preparation of (c-C_6H_{11})$_6$Si$_6$O$_7$(OSiPh$_3$)O$_3$P (**14**).

To a solution of **6** (0.58 g, 0.50 mmol) and PCl_3 (0.080 g, 0.58 mmol) in toluene (10 mL) was added Et_3N (0.3 mL, 2.2 mmol). The turbid mixture was stirred overnight and evaporated. The residue was extracted with hexane (20 mL), which was evaporated after filtration to give an amorphous solid, which could not be recrystallized. ^{29}Si {^{1}H} NMR ($CDCl_3$) δ (Ph_3SiO (1:1:1), ^{1}H NMR ($CDCl_3$) δ 7.66 (dm, 6 H, Ph), 7.41 (m, 9 H, Ph), 1.76 (m, 30 H C*H*$_2$ *c*-C_6H_{11}), 1.26 (m, 30 H C*H*$_2$ *c*-C_6H_{11}), 0.87 (m, 6 H, C*H* *c*-C_6H_{11}), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 135.57, 135.10, 129.69, 127.64 (Ph), 27.41, 27.38, 27.20, 27.16, 26.68, 26.55, 26.49, 26.42, 26.15, 25.78, 25.71, 25.65 (*C*H$_2$ *c*-C_6H_{11}), 24.37, 23.41, 23.19, 22.98, 22.60, 22.50 (1:1:1:1:1:1 *C*H *c*-C_6H_{11}), ^{31}P {^{1}H} NMR ($CDCl_3$) δ 104.31.

Preparation of (c-C_6H_{11})$_6$Si$_6$O$_7$(OSiPh$_3$)O$_3$GeMe (**15**).

To a solution of **6** (0.59 g, 0.50 mmol) and $MeGeCl_3$ (0.12 g, 0.58 mmol) in toluene (10 mL) was added Et_3N (0.80 mL, 5.8 mmol). A white precipitate formed immediately, and the mixture was stirred overnight. The mixture was filtered and the filtrate was evaporated to give an amorphous solid in quantitative yield. Crystallization attempts from pentane or benzene/acetonitrile lead to oiling out instead of crystal formation. ^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 21.93 (Ph_3SiO), - 55.27, - 57.29, - 66.98, - 67.34, - 68.44, - 69.49 (1:1:1:1:1:1), ^{1}H NMR ($CDCl_3$) δ 7.69 (dm, 6 H, Ph), 7.41 (m, 9 H, Ph), 1.76 (m, 30 H C*H*$_2$ *c*-C_6H_{11}), 1.27 (m, 30 H

C*H*$_2$ *c*-C_6H_{11}), 0.74 (m + s, 9 H, C*H* *c*-C_6H_{11}+ C*H*$_3$-Ge), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 136.92, 135.18, 129.54, 127.52 (Ph), 27.58, 27.49, 27.38, 26.83, 26.70, 26.61, 26.35 (*C*H$_2$ *c*-C_6H_{11}), 24.57, 23.99, 23.55, 23.19, 23.06 (1:1:1:2:1 *C*H *c*-C_6H_{11}), - 0.94 (*C*H$_3$-Ge). MALDI-TOF: M+Na=1213.81 (major peak, other important peaks at m/z 1127.9 and 1253.8 Anal. calcd for $C_{55}H_{84}Si_7O_{11}Ge$ (found) : C 55.49 (55.33), H 7.11 (7.09).

Preparation of (c-C_6H_{11})$_6$Si$_6$O$_7$(OSiPh$_3$)O$_3$TiC$_5$Me$_5$ (**16**).

To a solution of **6** (0.25 g, 0.22 mmol) in toluene (2.5 mL) was added $C_5Me_5TiMe_3$ (0.050 g, 0.22 mmol). Gas evolution took place, and the solution was stirred overnight. The reaction mixture was evaporated to give **16** (0.214 g, 0.16 mmol, 76 %) as an amorphous yellow solid, which is pure according to NMR. Further attempts to purify the solid by toluene/acetonitrile diffusion led to formation of an oil. Crystallization from other solvents also failed due to high solubility or oil formation. ^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 22.34 (Ph_3SiO), - 57.99, - 60.66, - 67.15, - 67.91, - 68.94, - 69.00 (1:1:1:1:1:1), ^{1}H NMR ($CDCl_3$) δ 7.67 (dm, 6 H, Ph), 7.40 (m, 9 H, Ph) , 1.97 (s, 15 H, C_5 (C*H*$_3$)$_5$), 1.90-0.70 (m, 66 H, *c*-C_6H_{11}), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 136.05, 135.08, 129.53, 127.61 (Ph), 125.83 (*C*$_5$(CH$_3$)$_5$), 27.96, 27.78, 27.58, 27.50, 27.34, 26.88, 26.82, 26.64 (*C*H$_2$ *c*-C_6H_{11}), 24.91, 24.75, 24.13, 23.74, 23.29, 23.04 (1:1:1:1:1:1 *C*H *c*-C_6H_{11}), 11.51 (C_5(*C*H$_3$)$_5$).

Preparation of [(c-C_6H_{11})$_6$Si$_6$O$_7$(OSiMePh$_2$)$_2$O$_2$GaMe)$_2$] (**17**).

7a (0.62 g, 0.50 mmol) was weighed out as a paste, which was dried by evacuation and crushing at 77 K.

Toluene (15 mL) was added, and when dissolved, trimethylgallium (2.50 g 0.39 mol/kg, 0.98 mmol) was added at - 50^{o}C. Gas formed slowly upon heating to reflux. A mixture of **17** and possibly (*c*-C_6H_{11})$_6$Si$_6$O$_7$(OSiMePh$_2$)$_2$(OGaMe$_2$)$_2$ was formed. The latter was the goal of the reaction, but the former crystallized out from a toluene/acetonitrile diffusion mixture. Crystals suitable for X-ray diffraction were obtained from hexane (140 mg, 0.044 mol, 23 %).

^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 10.63, - 12.08 (1:1, $SiMePh_2$), - 63.56, - 64.78, - 65.60, - 66.00, - 66.54, - 67.77 (1:1:1:1:1:1), ^{1}H NMR ($CDCl_3$) δ 7.6-7.2, (m, 20 H, Ph), 1.71- (m, 30 H, C*H*$_2$ *c*-C_6H_{11}), 1.34 (30 H, C*H*$_2$ *c*-C_6H_{11}), 0.77 (m, 6 H, C*H*$_2$ *c*-C_6H_{11}), 0.52 (s, 3 H, C*H*$_3$-Si), 0.49 (s, 3 H, C*H*$_3$-Si), - 0.15 (s, 3 H, *CH*$_3$-Ga), ^{13}C {^{1}H} NMR δ 137.57, 137.43, 137.41, 137.31, 134.30, 134.14, 129.42, 129.29, 127.51, 127.50, 127.47 (Ph), 28.07, 27.99, 27.89, 27.80, 27.65, 27.57, 27.43, 27.37, 27.13, 26.96, 26.84, 26.77, 26.63, 26.30 (*C*H$_2$ *c*-C_6H_{11}), 25.10, 24.87, 24.83, 24.72, 24.20 (2:1:1:1:1, *C*H *c*-C_6H_{11}), - 0.44, - 0.88 (1:1 *C*H$_3$-Si), - 7.28 (CH$_3$-Ga).

Anal. calcd for $C_{63}H_{95}Si_8O_{11}Ga$ (found) : C 57.20 (57.06), H 7.24 (7.17).

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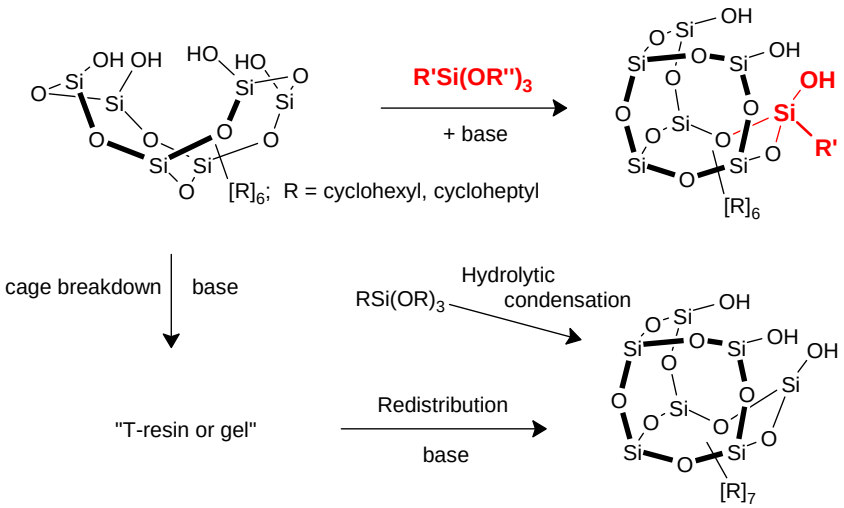
Chapter 3

Functionalized silsesquioxane triols for catalysis research

***Abstract**:Silsesquioxane tetrasilanols were reacted with a series of trialkoxysilanes to from organofunctionalized silsesquioxane trisilanols. Another means of introducing chemical functionality to silsesquioxane compounds is demonstrated to involve hydroformylation or Wacker oxidation of olefinic side chains to produce aldehydes and ketones respectively*

3.1 Introduction

Functionalization of silsesquioxanes offers great advantages to construct ancillary groups close to metal centers as well as possibilities for catalyst immobilization.[1] Silsesquioxane homologation or functionalization reaction is a kind of corner-capping reaction, forming trisilanols from tetrasilanols (Scheme. 3.1).[2]



***Scheme 3.1** Base-catalyzed homologation of silsesquixoanes.*

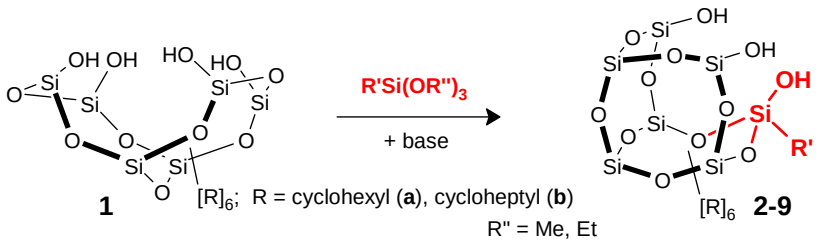
In this reaction, one equivalent of a quaternary ammonium hydroxide brings about the formation of a trisilanol, which at the time is very probably present as the monoanion, as the *p*Ka of trisilanols lie at around 9.5 in THF.[3] This reaction suffers from one problem, as the tetrasilanol itself is also prone to decomposition, normal trisilanol (*c*- $C_6H_{11})_7Si_7O_9(OH)_3$ can be formed.

In this chapter, the functionalization of silsesquioxane tetrasilanols to different monofunctionalized trisilanols is described, and its scope revealed. It is demonstrated that relatively small non-polar side chains give the highest yields, whereas amino groups and derivatives give gels, consisting of many different species. Furthermore, silsesquioxanes, containing unsaturated side chains are subjected to hydroformylation to produce aldehydes, and to a modified Wacker oxidation to create ketone functions.[4]

3.2 Results and Discussion

3.2.1 Scope of homologation reaction

The reaction of tetrasilanol (*c*-$C_6H_{11})_6Si_6O_7(OH)_4$ with different trialkoxysilanes in THF, using tetraethylammonium hydroxide to form functionalized trisilanol silesquioxanes, was investigated. The results are shown in Scheme 3.2 and Table 3.1. As decomposition of the tetrasilanol during the reaction may occur, an excess of trialkoxysilane was used. A selection of easily available trialkoxysilanes with R-groups varying in polarity, together with different Lewis and Brönsted properties as well as bulkiness, was made.



R' = $Cl(CH_2)_3$ (**2**), $ClCH_2$ (**3**), $NC\text{-}(CH_2)_3$ (**4**), $HS(CH_2)_3$ (**5**), $H_3CO(CH_2)_3$ (**6**), $H_3CS(CH_2)_3$ (**7**), $CH_2OCHCH_2O(CH_2)_3$ (**8**), $H_2C{=}CHCH_2S(CH_2)_3$ (**9**)

Scheme 3.2 *Reaction of tetrasilanol (c-*$C_6H_{11})_6Si_6O_7(OH)_4$ *with different trialkoxysilanes.*

From Table 3.1 it is clear that the reaction is very sensitive to the organic groups on the trialkoxysilane and to those of the tetrasilanol. Product yields vary from low (23%) to fair (75%) but in the experimental data set no clear structure / activity relations can be identified. As these base catalyzed reactions can also causo cleavage of siloxy ethers it is not surprising that truly excellent yields were not realized. Also incorporation of highly polar side chains, urea or amino groups of any kind did not work out. Precipitation gave oily residues only, consisting of silsesquioxane oligomers.

Table 3.1 Homologation of tetrasilanol $R_6Si_6O_7(OH)_4$ with trialkoxysilanes[a]

Entry	R	R'	Mol equiv. R'	R''	time (h)	Yield (%) (product)
1	c-C_6H_{11}	$Cl(CH_2)_3$	1.50	Et	5	23 (**2a**)
2	c-C_6H_{11}	$Cl(CH_2)_3$	1.43	Et	18	61 (**2a**)
3	c-C_7H_{13}	$Cl(CH_2)_3$	1.50	Et	2	76 (**2b**)
4	c-C_7H_{13}	$Cl(CH_2)_3$	1.67	Et	18	75 (**2b**)
5	c-C_6H_{11}	$ClCH_2$	1.50	Me	4	25 (**3a**)
6	c-C_6H_{11}	$NC(CH_2)_3$	1.22	Me	18	54 (**4a**)
7	c-C_7H_{13}	$NC(CH_2)_2$	1.42	Me	18	63 (**4b**)
8	c-C_6H_{11}	$HS(CH_2)_3$	1.12	Me	18	50 (**5a**)
9	c-C_6H_{11}	$H_3CO(CH_2)_3$	1.14	Me	18	31 (**6a**)
10	c-C_6H_{11}	$CH_2OCHCH_2O(CH_2)_3$	1.27	Me	18	46 (**8a**)
11	c-C_6H_{11}	$H_3CS(CH_2)_3$	1.20	Me	18	63 (**7a**)
12	c-C_6H_{11}	$H_2C=CHCH_2S(CH_2)_3$	1.60	Me	18	49 (**9a**)

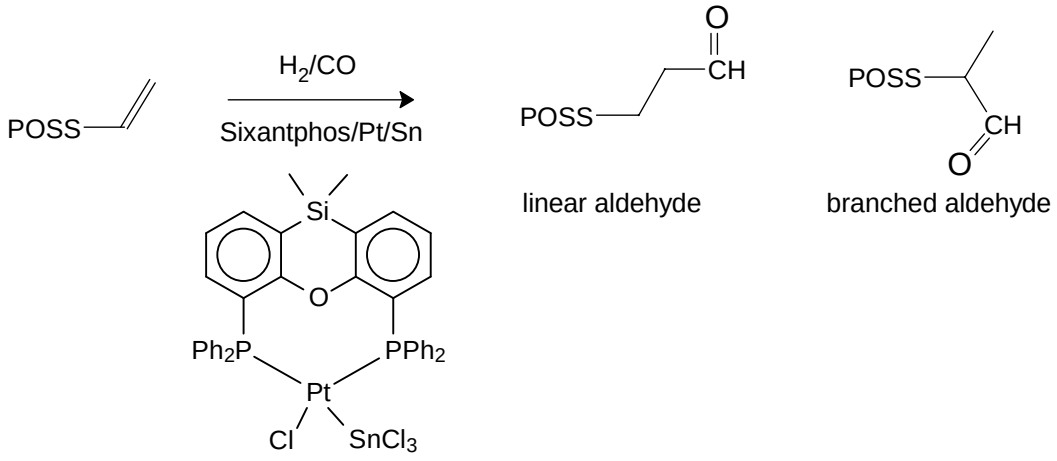
[a] Reaction conditions: Tetrasilanol used at 1.0 - 2.0 mmol scale, equimolar amount of $Et_4N^+OH^-$ (35 % aq.), THF (25 mL), 21 ^oC.

Protection of the amine group may be the solution to the problem, for example -NH_2 or -NHMe with a BOC (*t*-Butoxycarbonyl, $(CH_3)_3OC(=O)$- group, to form a non-basic amide. Methods for tertiary amines include oxidation to amine-*N*-oxide or complexation with BH_3, but due to loss of BH_3 or the high polarity of the amine-*N*-oxide, amides or urea functions, no product could be obtained but oligomeric silsesquioxane gels and silsesquioxane trisilanol. Amino-functionalized silsesquioxanes show limited stability: for example $(C_4H_9)_7Si_7O_{12}(CH_2)_3NH_2$ is stable up to 330^oC[5], but polyfunctionalized $(NH_2(CH_2)_3)_8Si_8O_{12}$ is stable in its octaprotonated form only[6], whereas disilanol silsesquioxane (*c*-$C_5H_9)_7Si_7O_9(OH)_2OSiMe_2CH_2NMe_2$[7] dehydrates slightly above room temperature,

and could be made from the trisilanol (c-$C_5H_9)_7Si_7O_9(OH)_3$ and $Me_2NSiMe_2CH_2NMe_2$ via direct deprotonation in anhydrous environment. The homologation reaction is quite critical, when trichlorosilanes were used with four equivalents of base, forming three equivalents of ammonium chloride, only T-gels were formed instead.

3.2.2 Hydroformylation of olefinic silsesquioxanes

Aldehyde groups pose great advantages for mild functionalizing reactions employed in organic synthesis, medicinal chemistry, material science and in the design of complex ligand systems[8]. As such, it would be advantageous to have access to silsesquioxane derivatives with aldehyde functions. Remarkably, prior to this work, unlike aromatic aldehydes[9], aliphatic silsesquioxane aldehydes were not known. Clearly, catalytic hydroformylation may be the method of choice to functionalize readily available olefinic silsesquioxanes (Scheme 3.3).



Scheme 3.3 *Targeted functionalization of olefinic silsesquioxane (POSS) derivatives.*

Catalytic hydroformylation can sometimes meet with complications. Besides hydroformylation, which leads to linear and branched aldehydes, hydrogenation to alkyl groups may occur. Also hydrogenation of carbonyl functions to alcohol groups may pose a complication especially in the context of undesirable consecutive reactions that may follow, for instance aldol condensation.

Hydroformylation of silyl-substituted olefins, especially when catalyzed by Rh, suffers from low selectivity towards the linear aldehyde.[10]

Consequently, we subjected a wide range of olefinic silsesquioxanes and metal complexes thereof to hydroformylation using a Pt/Sn-Sixantphos catalyst, which we had currently in study[11].

Selected silsesquioxanes are shown in Fig. 3.1 and involve completely condensed, T_8 compounds, silanols and titanium silanolate complexes. These titanium derivatives can be regarded as protected silanol compounds.

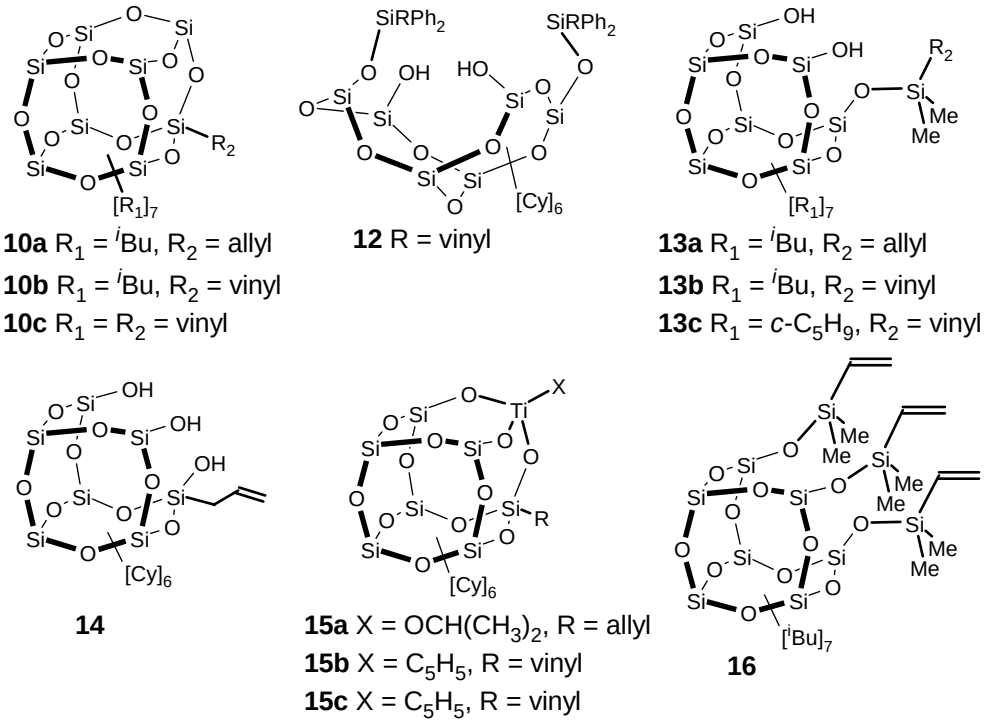


Fig. 3.1 *Selected olefinic silsesquioxanes for catalytic hydroformylation.*

From Table 3.2 it can be concluded that all closed-cage silsesquioxanes (entries 1-3, 10-11) as well as other non-hydroxylic compounds, like **16**[12] (entry 12) show the best hydroformylation behavior. Titanium silsesquioxanes **15b-c** (entries 9, 10), containing cyclopentadienyl work equally well, giving crystallizable materials; although titanium isopropoxy compound **15a** (entry 9) gave a less defined aldehyde system, hampering us to determine the l/b ratio. Moreover the Ti-isopropoxy moiety is lost, possibly due to reaction with trace water or internal attack of the aldehyde group.

The effect of OH-groups on the silsesquioxane (entries 4-6, 8) shows detrimental effects, giving lower selectivity to aldehydes, but we were not able to identify the side products clearly. Molecular masses corresponding to hydrogenated products were not

found in MALDI-TOF-MS analysis. Whereas in the case of silsesquioxanes no further reduction of the formed aldehyde was found, vinyltrimethoxysilane (entry 13) led to the linear alcohol $(MeO)_3Si(CH_2)_3OH$ in ca 50 %. The enol ether formed by 1,3 silicon shift from carbon to oxygen as found in homogeneous rhodium-catalyzed hydroformylation was not seen.[13]

Table 3.2 Hydroformylation of silsesquioxanes by SixantphosPt/Sn catalyst[a]

Entry	Compound (mmol)	Selectivity to aldehyde	Ratio l/b	Purity
1	**10a** (3.0)	100	15/1	pure
2	**10b** (3.0)	100	> 15/1	pure
3	**10c** (0.40)	100	> 15/1	Contains insoluble polymers
4	**12** (1.5)	> 50	n.d.	Well defined
5	**13a** (3.0)	20	n.d.	Ill-defined cage
6	**13b** (2.2)	30-40	n.d.	Ill-defined cage
7	**13c** (3.0)	50	Two linear aldehydes?	Well-defined cage
8	**14** (0.52)	60	10/1	Ill-defined cage
9	**15a** (0.46)	good	n.d.	Ti-O hydrolysis
10	**15b** (0.50)	100	9/1	Well-defined
11	**15c** (0.52)	100	> 15/1	Well-defined
12	**16** (3.4)	100	> 15/1	Well-defined
13	$C_2H_3Si(OMe)_3$ (37)	14	n.d.	> 50 % linear alcohol

[a] Reaction conditions: Sixantphos-$PtCl_2$/$SnCl_2$ 20 mg in 20 ml CH_2Cl_2 preformed with 40 bar H_2 / CO for 1 h / 60 °C. Silsesquioxane solution in CH_2Cl_2 (10 mL) added and stirred for 18 h / 60 °C / 40 bar.

In the hydroformylation of octavinyl silsesquioxane **10c**, besides the expected octa-aldehyde, insoluble polymer was also formed during workup. This solid could not be dissolved in any solvent and had a resinous character. Thorough extraction with THF gave slightly soluble material, which proved to be oligomers, as measured by MALDI-TOF. The fully extracted material appears as a hard off-white powder. Solid-state ^{13}C-NMR shows a carbonyl peak at 180 ppm, which may correspond to a carboxylic acid; the typical aldehyde peak at 201.5 ppm was not found. The peak at 3 ppm, corresponding to the CH_2 group near Si did not drastically change position, but the CH_2 near the aldehyde, went upfield from 37 ppm to 27 ppm. The peak at 70 ppm

could be a methoxy group. Investigation by ^{29}Si-NMR gave besides the silsesquioxane positions at – 67 ppm resonances at – 102 and – 113 ppm which were assigned to silicate silicons Q^3 and Q^4 respectively. Q^3 corresponds with cage $(SiO)_3SiOH$ or $(SiO)_3SiOR$ but the Q^4 linkage ($(SiO)_3SiOSi$) may be one of the clues of material polymerization.

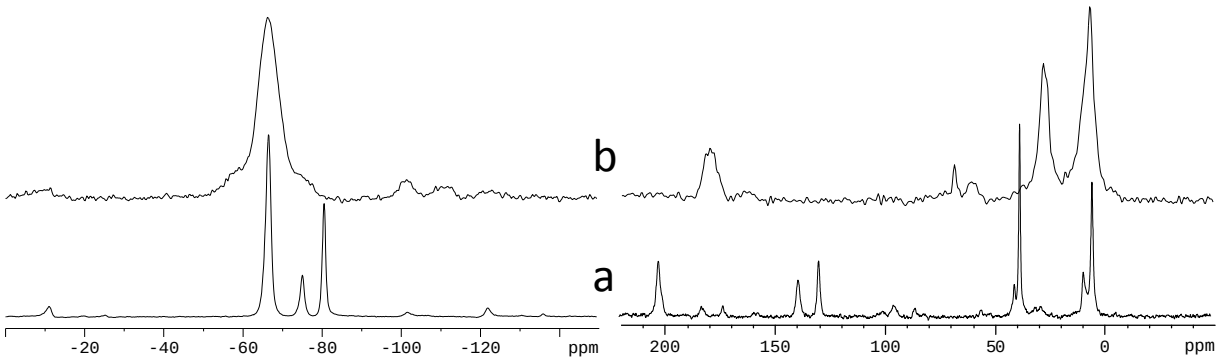
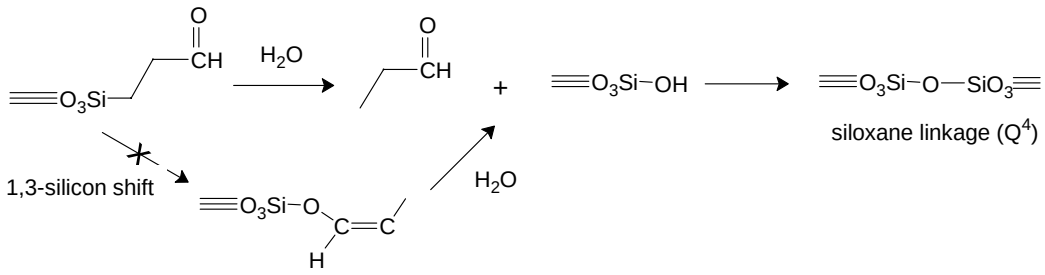


Fig. 3.2 *^{29}Si (left) and ^{13}C-MAS NMR of soluble (a) and insoluble material (b) obtained by hydroformylation of octavinyl POSS* ***1c***

A 1,3-silicon silicon-shift[14] is a well-known mechanism to account for decomposition of aldehyde-containing silanes, but this generally holds for branched aldehydes (Si-CH(CHO)Me).



Scheme 3.4 *Proposed decomposition of POSS aldehyde*

Although octa-aldehyde, which can be prepared without in-reactor polymerization, by performing the hydroformylation reaction of **10c** in a shorter time, the pure material is also not fully inert to degradation. The solid, which is well soluble in THF can get insoluble when allowed to stand at room temperature in air for a couple of days. As NMR shows conversion of Si-C into Si-O and the hydroformylated silsesquioxane

displays a smell of aldehyde, we think that the compound gradually loses the hydroformylated side group as aldehyde.

In order to prove this hypothesis, we heated solid octa-aldehyde to 200^{o}C under vacuum and collected the volatiles at – 196^{o}C. After heating, the solid became insoluble in THF.

The main product which distilled off was propanal, though propanoic acid was formed from samples which were stored at room temperature in air. This supports a hydrolysis reaction. Propanoic acid may have come from air oxidation of the aldehyde group prior to hydrolysis. We did not see intermediates in the hydrolysis, like enol ether resulting from 1,3-silicon shift, possibly by the fact that the intermediate is quickly hydrolyzed (Scheme 3.4).

3.2.3. Characterization of the insoluble material formed by octa-aldehyde decomposition.

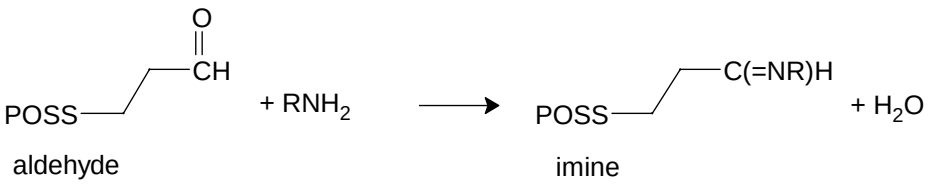
Similar results were obtained in more conventional rhodium-mediated hydroformylation. A batch of octa-aldehyde was made from octavinyl silsesquioxane, **10c**, catalyst Rh(acac)$(CO)_2$ and Xantphos at 50^{o}C and 5-9 bar CO/H_2 pressure[15]. The fully hydroformylated material, which showed a l/b ratio of 85/15 was measured by solid-state NMR. Another batch was heated to 200 ^{o}C under vacuum immediately after hydroformylation to form an insoluble powder. After measurement the samples were exposed to air for 10 days and measured again. The sample developed an acidic smell of propanoic acid and developed more Q sites. As we expect this material to be nanostructured, we did a nitrogen physisorption experiment, which whoever showed no defined micro or mesoporosity.

3.2.4. Coupling of amines to silsesquioxanes: imine formation.

A simple reaction of aldehydes[16] is the condensation with primary amines to form imines as shown in Scheme 3.5.

Aldehydes derived from closed-cage silsesquioxanes **10a-c** and **15b-c** show a clean reaction towards primary amines in chloroform in about 10 min., with aldehydes

derived from **10a-b** even giving off visible water in the reaction with α-phenylethylamine. Quantitative reaction was obtained by addition of 4 Å molecular sieves. Clear products were obtained with small primary amines like methylamine, isopropylamine and α-phenylethylamine. The disilanol-dialdehyde, formed from **2,** however, shows total loss of structure upon reaction with amines, possibly because of intramolecular attack of the imine group on the open cage.



Scheme 3.5 *Condensation of aldehydes with primary amines*

To test the feasibility of amine coupling we tested amines with a polar moiety, like 2–amino-1-propanol, semicarbazide (H_2N-$NHCONH_2$), or 2-amino-2-phenylethanol, reactions occurred, but clear products could not be obtained.

3.2.5. Reduction to alcohols by sodium borohydride.

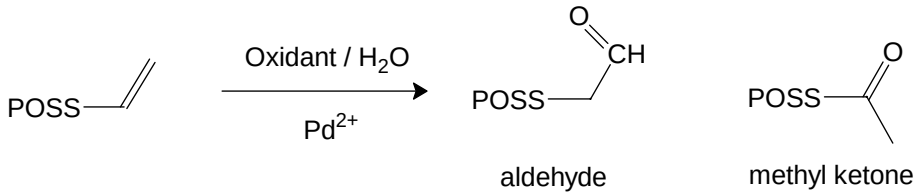
The reduction of aldehydes to alcohols by sodium borohydride was effective for simple aldehydes derived from silsesquioxanes **10a-c**, giving linear alcohols quantitatively. More complex aldehydes, including titanium silsesquioxanes already show decomposition or other kinds of interaction between the OH –group and the rest of the cage, hampering full characterization.

3.2.5. Scope of Wacker-type oxidation

Next to catalytic hydrofomylation of olefinic silsesquioxanes the Wacker oxidation thereof was investigated. Wacker-type oxidation of terminal olefins is a Pd^{2+}-mediated reaction, normally performed with oxygen assisted by the Cu^{2+}/Cu^{+} couple (Scheme 3.6).[17] In such cases non-flammable or low-vapor pressure solvents are

required. Commonly polar solvents like *N,N*-dimethylacetamide are used, but this is a poor solvent for silsesquioxanes that are typically apolar compounds. Alternatively oxidants like p-benzoquinone are used, but this produces hydroquinone or quinhydrone as reduction products.[18] The choice for THF was made as it dissolves both the silsesquioxane substrate and aq. H_2O_2 as oxidant. Generally $PdCl_2$ is used, which only slowly dissolves in THF.

An alternative method[19] involves the use of a small amount of saturated palladium nitrate solution in conc. HNO_3 (prepared from Pd foil in 60 % HNO_3 and evaporating the contents until crystallization occurs). The resulting palladium salts dissolve freely in THF under reaction conditions, and possess no inhibiting halide ions,[20] while maintaining a slightly acidic environment.[21], which should be a powerful method to oxidize even internal an cyclic olefins. Following previously mentioned conditions, we got a procedure in which the oxidation reaction immediately started with the evolution of heat observable within 5 min. We have not had problems due to THF peroxides, although some THF was indeed oxidized to 4-hydroxybutanal.



Scheme 3.6 *Wacker oxidation of POSS alkenes*

Aldehydes normally only form when the organic chain contains only two carbon atoms (vinyl), otherwise the formation of methyl ketones is highly favored due to Markovnikov effects.[22]

The reaction of olefinic silsesquioxane (see Fig. 3.1) was performed in THF solution using three methods, i.e. classical Wacker oxidation using copper(I) chloride / O_2, p-benzoquinone as well as hydrogen-peroxide as oxidant, mediated by $PdCl_2$ or $Pd(NO_3)_2$ conc. solution in HNO_3.

Although a considerable number of experiments were conducted, a convenient laboratory scale experiment to oxo functionalized silsesquioxanes could not be developed; see experimental section and Table 3.3. therein.

Experiments conducted at small scale revealed that simple closed-cage silsesquioxanes**, 10a-c** give full conversion with the highest yields of methyl ketones.

From Table 3.3 (experimental section), it is clear that simple closed-cage silsesquioxanes give full conversion with the highest yields of methyl ketones. Vinyl groups directly attached to the cage (T-Si) are quickly oxidized to aldehydes, but open cage silsesquioxanes are susceptible to further oxidation resulting in acids. Unfortunately the cage structures of trisilanol silsesquioxanes ($c\text{-}C_6H_{11})_6R'Si_7O_9(OH)_3$ (**14**, R' = allyl (**a**). vinyl (**b**), 3-butenyl (**c**)), (entries 7-9) were featureless in ^{13}C-NMR.

Surprisingly, vinyl groups attached to M-type silicon present in **12** and **13b** are fully inert in Wacker oxidation, which is also the case for the internal isomers present in 5-hexenyl in $(i\text{-}C_4H_9)_7Si_8O_{12}(CH_2)_4CHCH_2$ (**10e**) and 3-butenyl analogues of **14c**.

3.3 Conclusions

Aiming at future applications of silsesquioxanes in catalysts and catalytic material science, routes to organofunctionalized silsesquioxanes were explored. Emphasis was on achieving access to functionalized silsesquioxane trisilanols.

With excellent access to T_6-type silsesquixoanes of formula $R_6Si_6O_7(OH)_4$, established in the previous chapter, its homologation to functionalized trisilanols of type $R_6R'Si_7O_9(OH)_3$ [R'= functional group containing alkyl] has now been realized. The scope of functionalization includes, next to olefinic groups, relatively short alkyl chains bearing halide, ether, thiol, epoxy or nitrile groups.

Besides homologation reactions, the post synthesis modification of olefinic silsesquioxanes through catalytic hydroformylation was shown to work well for a variety of silsesquioxanes but found to be of limited use for silanol containing derivatives. Similar reactivity patterns were observed in Wacker oxidation of olefinic silsesquioxanes

3.4 Experimental Section

General considerations. All reactions with air- or moisture-sensitive materials were carried out under argon using standard Schlenk techniques[23]. Freshly distilled, dry and oxygen-free solvents were used throughout. The silsesquioxanes $(c\text{-}C_6H_{11})_6Si_6O_7(OH)_4$ and $(c\text{-}C_7H_{13})_6Si_6O_7(OH)_4$ were obtained by synthesis methods described in literature and through improved methods reported in chapter 2 of this thesis. ^1H (400 MHz) and ^{13}C (100.6 MHz)-NMR were recorded on a Varian Mercury 400 spectrometer, ^{29}Si-NMR (99.3 MHz) was recorded on a Varian Inova 500 spectrometer, MALDI-TOF-MS analysis was performed on a Voyager-DE™ STR Biospectrometry™ Workstation with *trans*-2-[3-(4-Butylphenyl)-2-methyl-2-propenylidene]malononitrile as matrix and sodium trifluoroacetate as Na^+ source.

Preparation of $Cl(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3$ (**2a**).

To a solution of **1** (1.70g, 2.0 mmol) and 3-chloropropyltriethoxysilane (0.69 g, 2.86 mmol) in THF (20 mL) was added tetraethylammonium hydroxide (35% aq soln, 0.84 g, 2.0 mmol) The mixture was stirred overnight, after which hydrochloric acid (1 mL 37%) was added and the mixture was extracted with H_2O (30 mL) and Et_2O (30 mL). The organic layer was dried over magnesium sulfate and concentrated to about 5 mL. The product was precipitated by addition of acetonitrile to give a white powder (1.19g, 1.23 mmol, 61%). Further purification was achieved by recrystallization from benzene/acetonitrile diffusion (0.86g, 0.88 mmol, 44%).

^{29}Si {^1H} NMR ($CDCl_3$) δ - 59.31, -60.35 (1:2 Cy-Si-OH), -68.09, -69.54 (1:2:1), ^1H NMR ($CDCl_3$) δ 6.90 (br s, 3 H, OH), 3.57 (t, 2 H, ^3J = 7.2 Hz, CH_2Cl), 1.95 (m, 2 H, CH_2), 1.77 (m, 30 H, CH_2 *c*-C_6H_{11}), 1.27 (m, 30 H, CH_2 *c*-C_6H_{11}), 0.76 (m, 8 H, C*H c*-C_6H_{11}+ CH_2-Si), ^{13}C {^1H} NMR ($CDCl_3$) δ 47.31 (CH_2Cl), 27.53, 27.48, 26.85, 26.73, 26.64, 26.55 (*C*H_2 *c*-C_6H_{11}), 23.88 (*C*H), 23.53 (*C*H_2), 23.52, 23.42, 23.08 (1:2:1, *C*H C_6H_{11}), 10.46 (*C*H_2). MALDI-TOF-MS: M+Na=989.

Preparation of $Cl(CH_2)_3(c\text{-}C_7H_{13})_6Si_7O_9(OH)_3$ (**2b**).

To a solution of **1b** (0.97 g, 1.0 mmol) and 3-chloropropyltriethoxysilane (0.40 g, 1.67 mmol) was added tetraethylammonium hydroxide (35% aq soln, 0.42 g, 1.0 mmol). The mixture was stirred overnight, after which hydrochloric acid (1 mL 37%) was added and the mixture was extracted with H_2O (30 mL) and Et_2O (30 mL). The organic layer was dried over magnesium sulfate and concentrated to about 5 mL. The product was precipitated by addition of

acetonitrile to give a white powder (0.791 g, 0.75 mmol, 75%). Further purification was achieved by recrystallization from benzene/acetonitrile diffusion (0.67 g, 0.64 mmol, 64%). ^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 59.35, - 59.56 (1:2 Ch-Si-OH), - 66.92, - 68.58, - 68.85 (1:2:1), ^{1}H NMR ($CDCl_3$) δ 7.18 (br s, 3 H, OH), 3.56 (t, 2 H, ^{3}J = 7.0 Hz, CH_2Cl), 1.95-1.18 (m, 74 H, CH_2 + CH_2 *c*-C_7H_{13}), 0.92 (m, 8 H, C*H* *c*-C_7H_{13} + CH_2-Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 47.22 (CH_2Cl), 29.53, 29.47, 29.24, 28.60, 28.54, 28.47, 28.42, 28.02, 27.97, 27.87, 26.79 (*C*H_2 *c*-C_7H_{13}), 24.57, 24.19, 24.11, 23.72 (*C*H *c*-C_7H_{13}), 10.58 (CH_2). MALDI-TOF-MS: M+Na=1073.8.

Preparation of $ClCH_2(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3$ (**3a**).

A solution of **1** (1.71 g, 2.0 mmol), $ClCH_2Si(OC_2H_5)_3$ (0.650 g, 3.0 mmol) and Et_4NOH (35% aq soln, 0.84 g, 2.0 mmol) in THF (30 mL) was stirred for 4 h. After acidification and aqueous workup, the sticky solid was crystallized by benzene/acetonitrile diffusion to yield 445 mg (0.50 mmol, 25 %) of pure crystals. ^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 60.2, - (2 Cy-Si-OH), - 68.2 , - 69.0 , - 69.9 (1:2:1), - 70.0 (1 $ClCH_2SiOH$). ^{1}H NMR ($CDCl_3$) δ 6.83 (br s, 3 H, OH), 2.78 (s, 2 H, CH_2Cl), 1.76 (m, 30 H, CH_2 *c*-C_6H_{11}), 1.27 (m, 30 H CH_2 *c*-C_6H_{11}), 0.77 (m, 6 H, C*H* *c*-C_6H_{11}), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 27.51, 27.45, 26.90, 26.83, 26.81, 26.64, 26.61, 26.51, 26.49 (*C*H_2 *c*-C_6H_{11}) 25.24 (*C*H_2Cl), 23.85, 23.49, 23.25, 23.03 (*C*H *c*-C_6H_{11}).

Preparation of $NC(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3$ (**4a**).

From **1** (0.85 g, 1.0 mmol) and 3-cyanopropyltrimethoxysilane (0.215 g, 1.22 mmol) and half the amounts of other reagents. Yield: 0.51 g, (0.54 mmol, 54 %). Recrystallization from benzene/acetonitrile gave 251 mg (0.25 mmol, 25%). ^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 60.25, - 60.31 (1:2 Cy-Si-OH), - 68.07, - 69.59, - 69.80(1:2:1), ^{1}H NMR ($CDCl_3$) δ 6.85 (br s, 3 H, OH), 2.42 (t, 2 H, ^{3}J = 6.8 Hz, CH_2CN), 1.76 (m, 32 H, CH_2 + CH_2 *c*-C_6H_{11}), 1.27 (m, 30 H CH_2 *c*-C_6H_{11}), 0.79 (m, 8 H, CH_2 + C*H* *c*-C_6H_{11}), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 27.42, 26.82, 26.64, 26.52 (*C*H_2 *c*-C_6H_{11}), 23.86, 23.49, 23.40, 23.03 (2:1:2:1, *C*H_2 *c*-C_6H_{11}), 19.99, 19.85, 12.31. MALDI-TOF-MS: M+Na=980.

Preparation of $NC(CH_2)_2(c\text{-}C_7H_{13})_6Si_7O_9(OH)_3$ (**4b**).

From **1b** (0.99 g, 1.0 mmol) and 2-cyanoethyltrimethoxysilane (0.250 g, 1.42 mmol), Et_4NOH (35 % aq. soln, 420 mg, 1.0 mmol) in THF (15 mL) was obtained 0.650 g (0.63 mmol, 63 %). Recrystallization from benzene/acetonitrile gave fine crystals (0.35 g, 0.34 mmol, 34 %) of the mono-benzene solvate. ^{1}H NMR ($CDCl_3$) δ 7.15 (br s, 3 H, OH), 2.39 (m, 2 H, CH_2CN), 1.95-1.26 (m, 72 H, CH_2 *c*-C_7H_{13}), 1.07 (m, 2 H CH_2Si), 0.86 (m, 6 H C*H* *c*-C_7H_{13}), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 29.49, 29.44, 29.40, 29.22, 28.56, 28.44, 28.39, 27.99, 27.95, 27.85 (*C*H_2 *c*-

C_7H_{13}), 24.51, 24.12, 24.00, 23.64 (2:1:2:1, *C*H *c*-C_7H_{13}), 11.27, 9.76,. Anal. calcd for $C_{40}H_{75}Si_7O_{12}N$ (found) : C 50.12 (50.16), H 7.89 (7.98), N 1.46 (1.02).

Preparation of $HS(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3$ (**5a**).

From **1** (1.70 g, 2.0 mmol) and 3-mercaptopropyltrimethoxysilane (0.44 g, 2.24 mmol). Synthesis under argon. Yield: 0.97 g (1.0 mmol, 50 %). Pure product obtained from benzene/acetonitrile diffusion (0.57 g, 0.59 mmol, 30 %).^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 59.00, - 60.34 (1:2, Cy-Si-OH), - 68.11, - 69.58, - 69.85 (1:2;1), ^{1}H NMR ($CDCl_3$) δ 6.71 (br s, 3 H, OH), 2.59 (q, 2 H, $^3J_{HH}$ =7.2 Hz, HSCH_2), 1.77 (m, 32 H, CH_2 *c*-C_6H_{11} + CH_2), 1.35 (m, 30 H, CH_2 *c*-C_6H_{11}), 0.77 (m, 8 H, C*H* *c*-C_6H_{11}+ CH_2Si) , ^{13}C {^{1}H} NMR ($CDCl_3$) δ 27.93, 27.53, 27.49, 26.86, 26.64, 26.55 (*C*H *c*-C_6H_{11}+ SH-*C*H_2-*C*H_2), 23.89, 23.54, 23.45, 23.08 (2:1:2:1, *C*H *c*-C_6H_{11}), 11.89 (*C*H_2-Si), MALDI-TOF-MS: M+Na=988 Anal. calcd for $C_{40}H_{75}Si_7O_{12}N$ (found) : C 48.51 (48.61), H 7.93 (7.87).

Preparation of $H_3CO(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3$ (**6a**).

From **1** (1.70 g, 2.0 mmol) and 3-methoxypropyltrimethoxysilane (0.44 g, 2.27 mmol). Yield: 0.95 g, (0.99 mmol, 49 %). Recrystallization from benzene/acetonitrile gave 0.60 g, (0.62 mmol, 31 %) as a ca 50 % pure crystalline product with low incorporation of methoxypropyltrimethoxysilane.

^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 59.43, - 60.37 (1:2, Cy-Si-OH), - 68.83, - 69.49, - 69.61 (1:2:1), unknown peaks at 57.82, 60.09, 68.10, 68.24, 69.76 (1:2:1:1:2) ^{1}H NMR ($CDCl_3$) δ 6.71 (br s, 3 H, OH), 3.41 (t, 2 H, $^3J_{HH}$ =6.6 Hz, CH_2O), 3.37 (s, 3 H, CH_3O), 1.76 (m, 32 H, CH_2 *c*-C_6H_{11} + CH_2), 1.27 (m, 30 H, CH_2 *c*-C_6H_{11}), 0.77 (m, 6 H, C*H* *c*-C_6H_{11}), 0.67 (m, 2 H, CH_2Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 74.96 (*C*H_2O), 58.25 (*C*H_3O), 27.55, 27.51, 26.92, 26.86, 26.64, 26.63, 26.56 (*C*H_2 *c*-C_6H_{11}), 23.88, 23.55, 23.46, 23.11 (2:1:2:1, *C*H *c*-C_6H_{11}), 22.87, 9.00 (*C*H_2-Si).

Preparation of $CH_2(O)CHCH_2O(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3$ (**8a**).

From **1** (0.85 g, 1.0 mmol) and 3-glycidoxypropyltrimethoxysilane (0.30 g, 1.27 mmol). Yield: 0.47 g, (0.46 mmol, 46 %). Recrystallization from benzene/acetonitrile gave 0.17 g (0.17 mmol, 17 %) ^{1}H NMR ($CDCl_3$) δ 6.59 (br s, 3 H, OH), 3.74 (dd, 1 H), 3.50 (m, 3 H,), 3.20 (m, 1 H), 2.84 (t, 2 H), 2.67 (m, 2 H), 1.76 (m, 32 H, CH_2 *c*-C_6H_{11} + CH_2), 1.27 (m, 30 H, CH_2 *c*-C_6H_{11}), 0.78 (m, 6 H, C*H* *c*-C_6H_{11}), 0.68 (m, 2 H, CH_2Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 76.69, 73.72, 71.04, 50.91, 44.39, 27.55, 27.51, 26.86, 26.64, 26.57 (*C*H_2 *c*-C_6H_{11}), 23.81, 23.51, 23.45, 23.12 (2:1:1:2, *C*H *c*-C_6H_{11}), 9.14 (*C*H_2-Si).

Preparation of $H_3CS(CH_2)_3Si(OCH_3)_3$

Sodium (0.48 g, 20 mmol) was reacted with methanol (10 mL) under argon with cooling to give a clear sodium methoxide solution. To this was added 3-mercaptopropyltrimethoxysilane (2.64 g, 13.4 mmol) at – 80°C. Iodomethane (4.45 g, 31 mmol) was added, and a precipitate of sodium iodide was formed upon warming. After stirring overnight, the mixture was evaporated under vacuum and the residue was washed with hexane. The hexane filtrate was distilled under vacuum (1.0 mbar, 50°C) to give 3-methylthiopropyltrimethoxysilane as a colorless liquid (1.60 g, 7.6 mmol, 57 %) . ^{1}H NMR ($CDCl_3$) δ 3.60 (s, 9 H, CH_3O), 2.54 (t, 2 H, $^3J_{HH}$ =7.2 Hz, CH_2S), 2.11 (s, 3 H, CH_3S), 1.74 (m, 2 H, CH_2), 0.78 (m, 2 H, CH_2Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 50.48 (*C*H_3O), 37.09, 22.33, 15.25, 8.39.

Preparation of $H_3CS(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3$ (**7a**).

Preparation as for **2a**, using **1** (1.70 g, 2.0 mmol) with 3-methylthiopropyltrimethoxysilane (0.50 g, 2.4 mmol). Yield: 1.23 g, 1.25 mmol, 63 %). Recrystallized yield: 0.88 g (0.90 mmol, 45 %) ^{29}Si {^{1}H} NMR ($CDCl_3$) δ -58.86, - 60.34 (1:2, Cy-Si-OH), - 68.12, - 69.59, - 69.86 (1:2:1).

^{1}H NMR ($CDCl_3$) δ 6.94 (br s, 3 H, OH), 2.56 (t, 2 H, $^3J_{HH}$ =7.3 Hz, CH_2S), 2.12 (s, 3 H, CH_3S), 1.77 (m, 32 H, CH_2 *c*-C_6H_{11} + CH_2), 1.27 (m, 30 H, CH_2 *c*-C_6H_{11}), 0.77 (m, 8 H, C*H* *c*-C_6H_{11} + CH_2Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 37.19, 27.98, 27.58, 27.54, 26.89, 26.68, 26.59 (*C*H_2 *c*-C_6H_{11}), 23.94, 23.58, 23.51, 23.13 (2:1:2:1, *C*H *c*-C_6H_{11}), 22.81, 15.16, 12.25.,MALDI-TOF-MS: M+Na=1001.

Preparation of $H_2C=CHCH_2S(CH_2)_3Si(OCH_3)_3$.

Preparation as for 3-methylthio-propyltrimethoxysilane, with allyl bromide (3.50 g, 28 mmol) and 3-mercapto-propyltrimethoxysilane (2.57 g, 13.1 mmol). Vacuum distillation gave 2.58 g (10.9 mmol, 83 %).

^{1}H NMR ($CDCl_3$) δ 5.80 (m, 1 H, CH_2=C*H*), 5.11 (m, 2 H, CH_2=CH), 3.59 (s, 9 H, CH_3O), 3.14 (d, $^3J_{HH}$ =7.0 Hz, =CH-CH_2S), 2.50 (t, 2 H, $^3J_{HH}$ =7.7 Hz, CH_2S), 1.70 (m, 2 H, CH_2), 0.77 (m, 2 H, CH_2Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 134.50, 116.67, 50.48 (*C*H_3O), 34.49, 33.54, 22.46, 8.48.

Preparation of $H_2C=CHCH_2S(CH_2)_3(C_6H_{11})_6Si_7O_9(OH)_3$ (**9a**).

Preparation as for **2a** from **1** (1.70 g, 2.0 mmol) with 3-(allylthio)propyltrimethoxysilane (0.75 g, 3.2 mmol). Yield: 0.98 g, (0.97 mmol, 49 %). Recrystallized yield: 0.60 g (0.60 mmol, 30 %).

^{1}H NMR ($CDCl_3$) δ 6.74 (br s, 3 H, OH), 5.84 (m, 1 H, CH_2=C*H*), 5.12 (m, 2 H, CH_2=CH), 3.15 (d, 2 H $^{3}J_{HH}$ =7.0 Hz, =CH-CH_2S), 2.52 (t, 2 H, $^{3}J_{HH}$ =7.3 Hz, CH_2S), 1.76 (m, 32 H, CH_2 *c*-C_6H_{11} + CH_2), 1.27 (m, 30 H, CH_2 *c*-C_6H_{11}), 0.75 (m, 8 H, C*H* *c*-C_6H_{11}+ CH_2Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 134.51, 116.62, 34.38, 33.62, 27.54, 27.50, 27.54, 26.85, 26.64, 26.56 (*C*H_2 *c*-C_6H_{11}), 23.88, 23.54, 23.46, 23.09 (2:1:2:1, *C*H *c*-C_6H_{11}), 22.99, 12.30, MALDI-TOF-MS: M+Na= 1028.

Hydroformylation: general considerations;

Synthesis of *cis*- Sixantphos-$PtCl_2$ and its $SnCl_2$ complex, including preformation and hydroformylation protocol have been described by R. van Duren[11]

In a 75 mL autoclave equipped with addition funnel, suitable to withstand 100 bar, Sixantphos-$PtCl_2$-$SnCl_2$ (20 mg, 19.0 mmol) was dissolved in CH_2Cl_2 (20 mL). The solution was stirred at 60^{o}C under synthesis gas (CO/H_2 1:1, 40 bar).

The substrate was dissolved in CH_2Cl_2 (10 mL), and added to the dropping funnel, while keeping the reactor under pressure. After filling pressurizing the dropping funnel with synthesis gas to equal pressure, its contents were added to the reactor. Stirring was continued for 18 h. The autoclave was cooled to room temperature and slowly vented. The contents were evaporated to dryness. The mixture was then filtered over silica to remove the catalyst, and evaporated to dryness.

Hydroformylation of *(i-C_4H_9)$_7$$Si_8O_{12}CH_2CH=CH_2$* (**10a**).

10a gave 2.24g (2.50 mmol, 84 % calculated as (*i*-C_4H_9)$_7$$Si_8O_{12}$($CH_2CH_2$ CH_2)$_3$CHO). NMR and MALDI-TOF showed full conversion to aldehydes. Recrystallization gave cubic crystals with identical composition. ^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 67.60, - 67.84, - 68.20 (3:3:1), ^{1}H NMR ($CDCl_3$) δ 9.78 (t, 1 H, $^{3}J_{HH}$ =1.6 Hz, linear *H*C=O), 9.64 (d, intensity ca 7 % from linear $^{3}J_{HH}$ =1.2 Hz, branched *H*C=O), 2.50 (dt, 2 H $^{3}J_{COHH}$ =1.6 Hz, $^{3}J_{CH2H}$ =7.2 Hz), 1.89 (m, 7 H, C*H* isobutyl), 1.80 (m, 2 H, CH_2), 1.00 (m, 42 H, CH_3 isobutyl), 0.69 (m, 2 H, CH_2Si), 0.64 (m, 14 H, CH_2 isobutyl), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 202.47 (linear H*C*=O, branched not found), 46.40 (*C*H_2C(=O)H), 25.70, 25.67 (*C*H_3 isobutyl) , 23.90, 23.86 (*C*H isobutyl), 22.50, 22.46 (4:3, *C*H_2 isobutyl), 15..76 (*C*H_2), 11.70 (*C*H_2Si). MALDI-TOF-MS: M+Na = 909.3,

IR(CCl_4): ν C=O = 1731 cm^{-1}. Anal. calcd for $C_{32}H_{70}Si_8O_{13}$ (found) : C 43.30 (43.37), H 7.95 (7.90).

Hydroformylation of (i-C_4H_9)$_7Si_8O_{12}CH=CH_2$ (**10b**).

10b (2.54 g, 3.0 mmol) gave 2.44g (93 % calculated as (*i*-C_4H_9)$_7Si_8O_{12}(CH_2CH_2\ CH_2)_2CHO$). NMR and MALDI-TOF showed > 95 % conversion to linear aldehyde. Recrystallization gave cubic crystals with identical composition. ^{1}H NMR ($CDCl_3$) δ 9.80 (t, 1 H, $^3J_{HH}$ =1.5 Hz, linear *H*C=O), 9.75 (d, intensity <5%, from linear $^3J_{HH}$ =2.4 Hz, branched *H*C=O), 2.52 (dt, 2 H $^3J_{COHH}$ =1.5 Hz, $^3J_{CH2H}$ =8.0 Hz), 1.89 (m, 7 H, C*H* isobutyl), 1.00 (m, 42 H, C*H*$_3$ isobutyl), 0.94 (m, 2 H, C*H*$_2$Si), 0.63 (m, 14 H, C*H*$_2$ isobutyl), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 202.38 (linear H*C*=O, branched not found), 37.33 (*C*H_2C(=O)H), 25.69, 25.66 (*C*H_3 isobutyl) , 23.89, 23.85 (*C*H isobutyl), 22.48, 22.46, 22.39 (1:3:3, *C*H_2 isobutyl), 4.09 (*C*H_2Si). MALDI-TOF-MS: M+Na = 895.4, IR(CCl_4): ν C=O = 1729 cm^{-1}.

Hydroformylation of ($H_2C=CH)_8Si_8O_{12}$ (**10c**).

10c (0.255 g, 0.40 mmol) was subjected to hydroformylation for 20 h, to give complete reaction to linear octaaldehyde $Si_8O_{12}(CH_2)_2CHO)_8$. The reaction mixture was evaporated, and 20 mL of CH_2Cl_2 was added. Some white insoluble material (85 mg, insoluble in $CDCl_3$) was filtered off. The slightly yellow filtrate was concentrated to ca 5 mL, and pentane was allowed to diffuse in overnight. Yellow material (37 mg, not completely soluble in $CDCl_3$) came out containing some product. To the remaining colorless solution, pentane (20 mL) was added to precipitate 108 mg (0.12 mmol, 31 %) of pure (HC(=O)-H_2C-CH_2)$_8Si_8O_{12}$, ^{13}C-NMR showed silsesquioxane cage only. ^{29}Si {^{1}H} NMR ($CDCl_3$) δ -66.90, ^{1}H NMR ($CDCl_3$) δ 9.79, (t, 8, $^3J_{HH}$ =1.2 Hz, linear *H*C=O), 2.56 (dt, 16 H, H $^3J_{COHH}$ =1.5 Hz, $^3J_{CH2H}$ =8.4 Hz, C*H*$_2$COH), 0.94 (t, 16 H, , $^3J_{CH2H}$ =7.7 Hz C*H*$_2$Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 201.34 (H*C*=O), 37.06 (*C*H_2C(=O)H), 3.45 (*C*H_2Si),. MALDI-TOF-MS: M+Na = 895.3 (minor peak, but no lower masses of hydrogenated products).

Hydroformylation of Trans-($H_2C=CH(C_6H_5)_2SiO)_2(c\text{-}C_6H_{11})_6Si_6O_7(OH)_2$ (**12**).

Trans-($H_2C=CH(C_6H_5)_2SiO)_2(c\text{-}C_6H_{11})_6Si_6O_7(OH)_2$ **12** (1.90 g, 1.5 mmol) gave 1.78 g (1.34 mmol, 90 %) as a slightly yellow amorphous solid which could not be recrystallized from benzene/acetonitrile or pentane. NMR showed full conversion although the aldehyde integral is ca 40 % of theory Trans-($OHC(CH_2)_2(C_6H_5)_2SiO)_2(c\text{-}C_6H_{11})_6Si_6O_7(OH)_2$. ^{1}H NMR ($CDCl_3$) δ 9.73 (t, 0.7 H (2 H expected), $^3J_{HH}$ =1.6 Hz, linear *H*C=O, ca 5 % of branched aldehyde), 7.7-7.2 (m, 20 H, C_6H_5) 2.46 (m, 2 H) 1.76-0.70 (m, 70 H, C_6H_{11} + CH_2Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 204.49 (linear H*C*=O), 134.27, 129.91, 129.85, 127.86, 127.81 (Ph) 37.41

($CH_2C(=O)H$), 27.53, 27.49, 26.73, 26.68 (CH_2 *c*-C_6H_{11}) , 24.40, 23.70, 23.44 (1:1:1, *C*H *c*-C_6H_{11}), 7.37 (CH_2Si), MALDI-TOF: M+Na = 1346.7, IR(CCl_4): ν C=O = 1723, 3409 (OH) cm^{-1}.

Hydroformylation of *(i-C_4H_9)$_7Si_7O_9(OH)_2OSiMe_2CH_2CH=CH_2$* (**13a**).

(*i*-C_4H_9)$_7Si_7O_9(OH)_2OSiMe_2CH_2CH=CH_2$ **13a** (2.68 g, 3.0 mmol) gave oily material. Aldehyde formation ca. 15 % (^{1}H-NMR) of theory ((*i*-C_4H_9)$_7Si_7O_9$ $(OH)_2OSiMe_2(CH_2)_3CHO$), ^{13}C-NMR showed silsesquioxane cage only. MALDI-TOF-MS gave small abundance for aldehyde (M + Na = 941.5). No hydrogenation product was found.

Hydroformylation of (i-C_4H_9)$_7Si_7O_9$ $(OH)_2OSiMe_2CH=CH_2$ (**13b**).

(*i*-C_4H_9)$_7Si_7O_9$ $(OH)_2OSiMe_2CH=CH_2$ **13b** (1.94 g, 2.2 mmol) gave oily material (1.80 g), which after recrystallization from pentane gave a mixture of oil and low-melting semi-crystalline material. ^{1}H-NMR gave 20-40 % conversion to aldehyde. ^{13}C-NMR gave no signals for *C*HO and *C*H_2CHO. IR gave a low absorption at 1727 cm^{-1}. No hydrogenation product was found.

Hydroformylation of (c-C_5H_9)$_7Si_7O_9(OH)_2OSiMe_2CH=CH_2$ (**13c**).

(*c*-C_5H_9)$_7Si_7O_9(OH)_2OSiMe_2CH=CH_2$ **13c** (2.88 g, 3.0 mmol) gave a sticky paste (2.23 g). ^{1}H-NMR showed 50 % selectivity to aldehydes. ^{29}Si {^{1}H} NMR ($CDCl_3$) δ 9.28 ($SiMe_2$), - 57.43, - 65.50 - 65.73, - 66.86, - 67.80 (2:1:1:1:2, foreign peaks of ca 1/3 intensity near expected peaks, 9.60, - 57.79, - 60.4, - 65.59, - 67.00, - 67.98), ^{1}H NMR ($CDCl_3$) δ 9.79, 9.77 (2 triplets, 1:3, 0.5 H (1 H expected), linear *H*C=O), 5.17 (s, OH) 2.54 (2 m 3:1, 2 H, C*H*$_2$CHO), 1.70 (m, 56 H, C*H*$_2$ *c*-C_5H_9), 1.00 (m, 9 H, C*H* *c*-C_5H_9 + C*H*$_2$-Si), 0.20 (several peaks, CH_2Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 206.28 (H*C*=O), 37.63 ($CH_2C(=O)H$), 27.56, 27.49, 27.44, 27.42, 27.36, 27.29, 27.27, 27.04, 27.01, 26.96 (CH_2 *c*-C_5H_9) , 23.83, 33.70, 23.02, 22.69, 22.28 (1:2:2:2, *C*H *c*-C_5H_9), 9.63 (CH_2Si), - 0.04 (H_3CSi). MALDI-TOF-MS: M+Na = 1011.5 (major peak, no lower masses of hydrogenated products).

Hydroformylation of *$H_2C=CHCH_2$(c-C_6H_{11})$_6Si_7O_9(OH)_3$* (**14**).

$H_2C=CHCH_2$(*c*-C_6H_{11})$_6Si_7O_9(OH)_3$ **14** (0.48 g, 0.52 mmol) gave 0.47 g (0.49 mmol, 95 %) of product. NMR showed full conversion to 10:1 mixture of linear and branched aldehydes, with a somewhat low integral for aldehyde H and undefined silsesquioxane cage structure. Crystallization was not possible, due to its complexity. ^{1}H NMR ($CDCl_3$) δ 9.79 (t, 0.4 H (1 H expected), linear *H*C=O, ca 5 % of branched aldehyde), 7.2 (s, OH) 2.54 (m, 2 H), 1.76 (m,

30 H, CH_2 C_6H_{11}), 1.27 (m, 30 H, CH_2 C_6H_{11}), 0.82 (m, 8 H, CH_2-Si + CH C_6H_{11}), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 45.98 (CH_2C(=O)H), 27.5-22.3 (C_6H_{11}), 15.53, 11.45 (CH_2Si).

Hydroformylation of H_2C=CHCH_2(c-C_6H_{11})$_6Si_7O_{12}TiO(^iC_3H_7)$ (**15a**)

H_2C=CHCH_2(c-C_6H_{11})$_6Si_7O_{12}TiO(^iC_3H_7)$ **15a** (0.475 g, 0.46 mmol), prepared from **14** and one equivalent of $Ti(O^iC_3H_7)_4$ (175 mg, 0.61 mmol) gave foamy material on hydroformylation. (0.40 g, 3.77 mmol, 82 % calculated as aldehyde). ^{1}H- NMR-features broad, possibly due to partial hydrolysis of Ti-O bond, ^{13}C-NMR not informative. ^{1}H NMR ($CDCl_3$) δ 9.79 (br s, 1 H, HC=O), 7.25 (br s, unknown), 3.85 (br s, 1 H, OCH), 2.54 br s, 2 H), 1.76 (m, 30 H, CH_2 *c*-C_6H_{11}), 1.27 (m, 30 H, CH_2 *c*-C_6H_{11}), 0.82 (m, 8 H, CH_2-Si + CH *c*-C_6H_{11}).

Hydroformylation of H_2C=CHCH_2(c-C_6H_{11})$_6Si_7O_{12}TiCp$ (**15b**).

H_2C=CHCH_2(*c*-C_6H_{11})$_6Si_7O_{12}$TiCp **15b** (0.52 g, 0.50 mmol, prepared from **14** and $CpTiCl_3$) gave 540 mg (0.50 mmol, 100 % calculated as OCH$(CH_2)_3$(*c*-C_6H_{11})$_6Si_7O_{12}$TiCp). NMR gave a 80:10:9 mixture of linear and branched aldehydes and an unknown product. ^{1}H-NMR ($CDCl_3$) δ 9.84 (t, 1 H $^3J_{HH}$ =1.8 Hz, linear HC=O), 9.79 (t, 10 % from linear, unknown), 9.70 (d, $^3J_{HH}$ =1.2 Hz, 9 % from linear), 6.52 (s, 5 H, C_5H_5), 2.55 (dt, 2 H $^3J_{COHH}$ =1.8 Hz, $^3J_{CH2H}$ =7.3 Hz), 1.76 (m, 30 H, CH_2 *c*-C_6H_{11}), 1.25 (m, 30 H, CH_2 *c*-C_6H_{11}), 0.75 (m, 6 H, CH *c*-C_6H_{11}), 0.62 (m, 2 H, CH_2-Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 202.89 (linear HC=O, branched not found), 116.18 (C_5H_5), 46.53 (CH_2C(=O)H), 27.64, 27.56, 27.52, 27.11, 27.00, 26.89, 26.82, 26.64 (CH_2 *c*-C_6H_{11}), 23.40, 23.18 (1:2, CH *c*-C_6H_{11}), 16.31, 11.66. IR(CCl_4): ν C=O = 1730 cm^{-1}.

Hydroformylation of H_2C=CH(c-C_6H_{11})$_6Si_7O_{12}TiCp$ (**15c**).

H_2C=CH(*c*-C_6H_{11})$_6Si_7O_{12}$TiCp **15c** (543 mg, 0.52 mmol) gave 520 mg (0.49 mmol, 94 %, calculated as OCH$(CH_2)_2$(*c*-C_6H_{11})$_6Si_7O_{12}$TiCp) of product. NMR showed full conversion to linear aldehyde. ^{1}H NMR ($CDCl_3$) δ 9.85 (t, 1 H $^3J_{HH}$ =1.5 Hz, linear HC=O), 9.75 (d, intensity <5%, from linear $^3J_{HH}$ =2.4 Hz, branched HC=O), 6.52 (s, 5 H, C_5H_5), 2.53 (dt, 2 H $^3J_{COHH}$ =1.5 Hz, $^3J_{CH2H}$ =8.0 Hz, CH_2COH), 1.76 (m, 30 H, CH_2 C_6H_{11}), 1.26 (m, 30 H, CH_2 C_6H_{11}), 0.87 (m, 2 H, CH_2-Si), 0.84 (m, 6 H, CH C_6H_{11}), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 203.02 (linear HC=O, branched not found), 116.32 (C_5H_5), 37.90 (CH_2C(=O)H), 27.63, 27.55, 27.51, 27.11, 26.99, 26.91, 26.86, 26.82 26.64 (CH_2 C_6H_{11}), 23.39, 23.20, 23.17, 23.13 (2:1:1:2, CH C_6H_{11}), 4.13, MALDI-TOF-MS: M+Na = 1079.6 (major + matrix reaction) IR(CCl_4): ν C=O = 1728 cm^1.

Hydroformylation of (i-C_4H_9)$_7$$Si_7O_9$(OSi$Me_2$CH=$CH_2$)$_3$ (**16**).

(*i*-C_4H_9)$_7$$Si_7O_9$(OSi$Me_2$CH=$CH_2$)$_3$ **16** (3.55 g, 3.4 mmol) gave 3.69 g (3.26 mmol, 96 %), of trialdehyde (*i*-C_4H_9)$_7$$Si_7O_9$(OSi$Me_2$($CH_2$)$_2$CHO)$_3$. NMR showed full conversion to aldehydes. The product is an amorphous solid, which could not be crystallized from either pentane or benzene/acetonitrile. ^{1}H NMR ($CDCl_3$) δ 9.78 (t, 3 H, $^3J_{HH}$ =1.6 Hz, linear *H*C=O, no sign of branched aldehyde), 2.46 (dt, 2 H $^3J_{COHH}$ =1.6 Hz, $^3J_{CH2H}$ =8.4 Hz), 1.86 (m, 7 H, C*H* isobutyl), 0.98 (m, 42 H, CH_3 isobutyl), 0.84 (m, 2 H, CH_2Si), 0.59 (m, 14 H, CH_2 isobutyl), 0.18 (s, 18 H, H_3CSi) ^{13}C {^{1}H} NMR ($CDCl_3$) δ 202.75 (linear H*C*=O), 37.71 (*C*H_2C(=O)H), 25.97, 25.79, 25.57 (*C*H_3 isobutyl) , 24.91, 24.06, 23.97, 23.86, 23.80, 23.67, 22.34 (*C*H + *C*H_2 isobutyl), 9.54 (*C*H_2Si), 0.15 (H_3*C*Si). MALDI-TOF: M+Na = 1156.9 (many other peaks, which however do not correspond to hydrogenation), IR(CCl_4): ν C=O = 1727 cm^{-1}.

Wacker oxidation reactions involving olefinic silsesquioxanes

The reaction of olefinic silsesquioxane (see Fig. 3.1) was performed in THF solution using three methods, i.e. classical Wacker oxidation using copper(I) chloride / O_2, p-benzoquinone as well as hydrogen-peroxide as oxidant, mediated by $PdCl_2$ or $Pd(NO_3)_2$ conc. solution in HNO_3, made by dissolving Pd foil (0.15 g) in HNO_3 (1 mL) and concentrating under reduced pressure until crystals appear (ca 0.25 mL).

Table 3.3 Wacker oxidation of silsesquioxanes

Entry	Cmpnd	$PdCl_2$/$C_6H_4O_2$/65 °C[a]	O_2/$Cu(OAc)_2$/PdX_2[b]	H_2O_2/PdX_2[c]
1	**10a**	n.r.	n.r. X = Cl	100 (X = NO_3)
2	**10b**	75%conv / 3days, 20% ald	X = Cl, 35 %, X = NO_2, n.r.	Full conv (X = Cl, NO_3) 50 % ald, remainder acid?
3	**10d**	85 %	X = Cl, full conv.	Full conv (X = Cl, NO_3)
4	**10e**	n.d.	n.d.	50 % methyl ketone, remainder unreacted int. olefin
5	**12**	n.d.	n.d.	n.r. (X = Cl, NO_3)
6	**13b**	n.d.	n.d.	n.r.(X = Cl, NO_3)
7	**14a**	n.d.	n.d.	90%/ 1 day (X = Cl), 70 % / 3 h (X = NO_3), sel ald 15-20%
8	**14b**	n.d.	n.d.	Full conv/3d, sel ket 5 %
9	**14c**	n.d.	n.d.	n.r. (int olefin)

[a] Reaction conditions: Benzoquinone, 120 mg (1.2 mmol), silsesquioxane (0.5 mmol) in THF (2-5 mL), $PdCl_2$ (25 mg), H_2O, 0.1 mL, T = 65°C/1 day. [b] silsesquioxane (0.5 mmol), THF (5 mL), $PdCl_2$ (25 mg), or conc. $Pd(NO_3)_2$ (0.025 mL), in 100 mL Schlenk with O_2 gas at r.t. overnight. [c] THF (25 mL, silsesquioxane (1 mmol), aq. H_2O_2 35 wt% (0.5 mL, 5 mmol), $PdCl_2$ (25 mg), or conc. $Pd(NO_3)_2$ (0.025 mL)

Further manipulation of the oxidation products with respect to addition of receptor groups was harder, due to the lower electrophilicity of methyl ketones compared to aldehydes. No imine formation was observed when reacted with simple primary amines. As is the case for silsesquioxane aldehydes, reaction with semicarbazide did not give the semicarbazone, although the reaction was performed in THF with extracted semicarbazide base.

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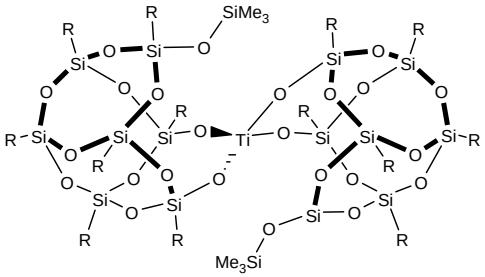
Chapter 4

Synthesis and characterization of Titanium silsesquioxanes with organofunctionalized ancillaries

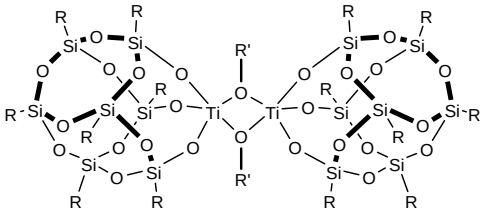
***Abstract**: Macrocyclic silsesquioxane silanolate titanium complexes were made from a partly silylated tetrasilanol ligand. X-ray structure analysis reveals that the macrocycles contain an almost perfect tetrahedrally coordinated titanium site. The stability of the complexes to hydrolysis can be improved by chemical linking of two silsesquioxane ligands thus forming a macrocycle. Organofunctionalized silsesquioxane trisilanols are converted to their titanium counterparts.*

4.1 Introduction

An inherent characteristic of heterogeneous catalytic systems is the difficulty to study their true active sites. As such we and others have studied soluble model catalysts containing silsesquioxanes as support mimic.[1] For titanium silsesquioxanes, the titanium site is incorporated via spatially oriented siloxy bonds (Ti-O-Si), which structurally resemble surface sites that have been purportedly identified on silica surfaces.[10] Silsesquioxanes also resemble silica surfaces in their electronic features. Unlike alkoxy and siloxy ligands, silsesquioxanes are electron withdrawing, as is the case with silica.[2] These structural and electronic resemblances to silica make silsesquioxanes excellent candidates for modeling silica surfaces.[1] Previously, several groups have reported titanium silsesquioxanes,[3] modeling monodentately, but also bidentately and terdentately bonded titanium on silica through siloxy chelation. (Fig. 4.1).

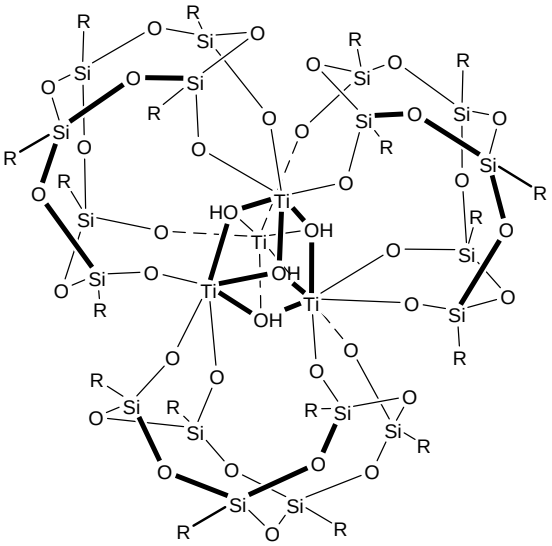


R = *c*-C_5H_9, *c*-C_6H_{11}, *c*-C_7H_{13}, i-C_4H_9

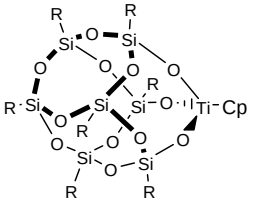


R = *c*-C_5H_9, *c*-C_6H_{11}, *c*-C_7H_{13} , i-C_4H_9

R'= H, Me, Et, O^{i}Pr



R = *c*-C_6H_{11}, *c*-C_7H_{13}



R = *c*-C_5H_9, *c*-C_6H_{11}, *c*-C_7H_{13}, i-C_4H_9

Cp = C_5H_5, C_5H_4-$SiMe_3$, $C_5H_3[(SiMe_3)_2$-1,3], C_5Me_5

Fig. 4.1 *Examples of titanium silsesquioxane silanolate complexes.*

Using state of the art silsesquioxane chemistry developed in chapters 2 and 3, silsesquioxane silanolate chemistry of titanium is further explored in this chapter.

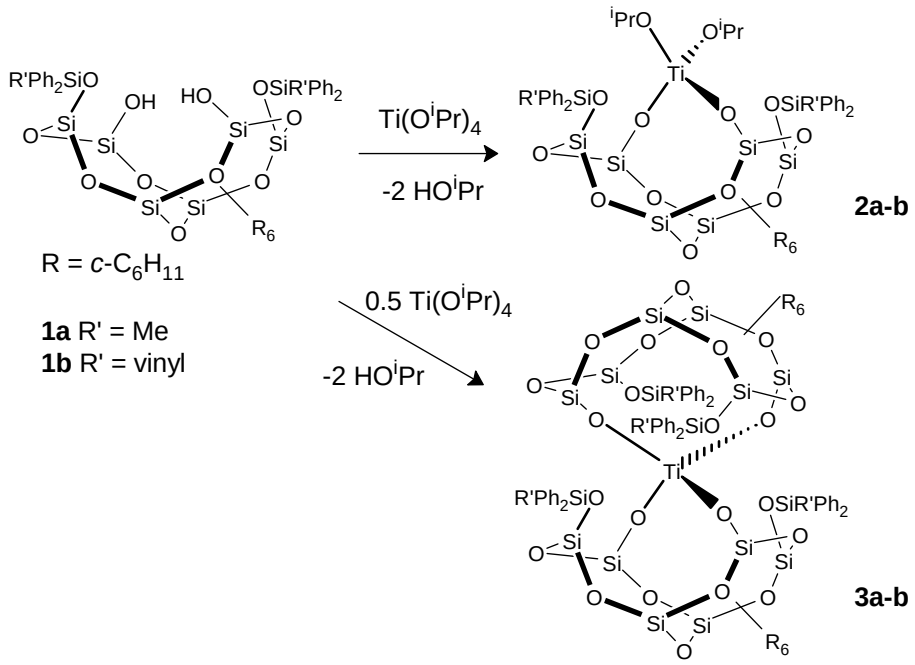
As a result, new titanium complexes are reported here. These are derived from either silsesquioxane tetrasilanols, especially partially silylated tetrasilanols, as well as trisilanols and organofunctionalized trisilanols. Particular novel are the titanium complexes (**3a-b**) derived from a selectively disilylated tetrasilanol. In these complexes an ideally tetrahedrally surrounded titanium atom will be shown to be coordinated to two highy distorted silsesquioxane bissilanolate ligands. These new complexes will utilized in the synthesis of titanium macrocycles, containing 3D-netted silsesquioxane ligands. Complexes described here will be screened in catalytic epoxidation in chapter 5 of this thesis. The functionalized trisilanols described in chapter 3 were transformed into trisilanolate titanium cyclopentadienide complexes and their hydrolytic stability was studied. Finally, complex interactions with the

strongly bis-chelating ligand TMEDA were investigated and shown to lead to some interesting adducts.

4.2 Results and Discussion

*4.2.1 Synthesis of [((R'Ph$_2$SiO)$_2$(c-C$_6$H$_{11}$)$_6$Si$_6$O$_7$O$_2$)$_2$Ti] (**3a-b**)*

The reaction of Ti(O^{i}Pr)$_4$ with 2 equivalents of *trans*-disilylated silsesquioxane disilanol, (R'Ph$_2$SiO)$_2$(*c*-C$_6$H$_{11}$)$_6$Si$_6$O$_7$(OH)$_2$ **1a-b**, yields the corresponding complexes **3** with 2 cages per titanium atom. When a 1:1 ratio of both reagents was used, a clean reaction occurred which afforded complexes **2** (Scheme 4.1). Complexes **2** relate to titanium silanolate complexes derived from the vicinal disilanol Me$_3$SiO(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_9$(OH)$_2$.[4]



Scheme 4.1 *Synthesis of difunctional titanium disilanolates (trans-(R'Ph$_2$SiO)$_2$(R$_6$Si$_6$O$_7$)O$_2$)$_2$Ti, R = c-C$_6$H$_{11}$, R' = Me (**3a**), vinyl (**3b**)*

Compounds **2**, like the starting materials, are oils, which could not be crystallized. Lack of intermolecular interactions as well as the symmetry may cause this effect. The bis-silsesquioxane compounds **3a-b** have a strong tendency to give oversaturated solutions, producing crystals after a prolonged period.

*4.2.2 Characterization of [((C$_2$H$_3$Ph$_2$SiO)$_2$(c-C$_6$H$_{11}$)$_6$Si$_6$O$_7$O$_2$)$_2$Ti] (**3b**)*

X-ray structure analysis (Fig. 4.2 and Table 4.1) reveals that the titanium complex **3b** like the earlier prepared methylgallium complex (see chapter 2) contains conformationally flexible ligands surrounding an undistorted tetrahedral titanium atom with O-Ti-O angles varying from 107.32(11) to 111.86(11) Å.

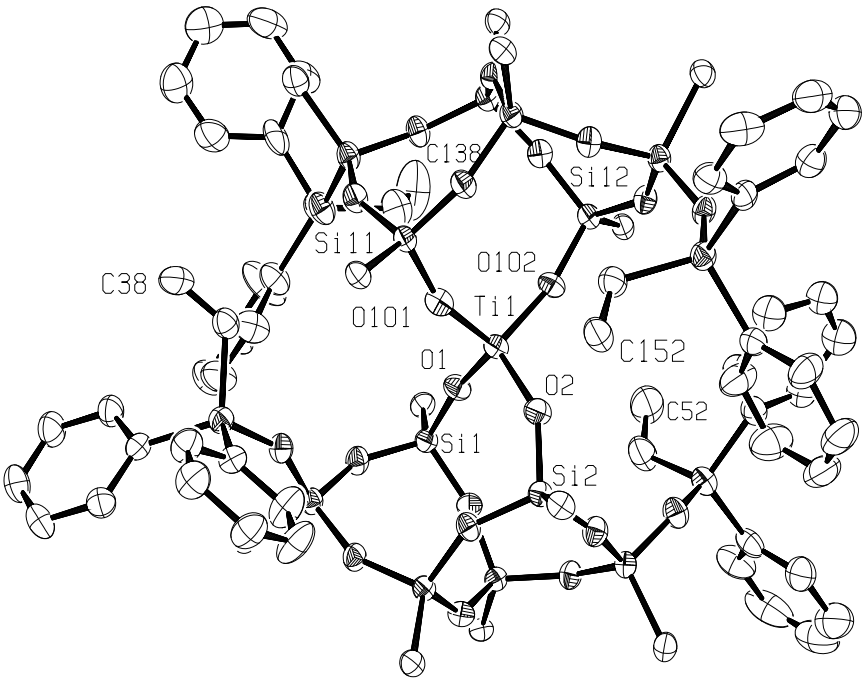


Fig. 4.2 *Molecular structure and labeling scheme of [((c-C$_6$H$_{11}$)$_6$Si$_6$O$_7$(OSi(Vinyl)Ph$_2$)$_2$O$_2$)$_2$Ti] (**3b**): displacement ellipsoid drawing (50 % probability). Cyclohexyl groups apart from ipso carbon atoms have been omitted for clarity.*

In **3b**, all silanolate oxygen atoms are bonded towards the titanium with similar Ti-O distances (1.787(2)-1.796(2) Å) which are comparable to those earlier reported for bis-disilanolate Ti(O$_2$(OSiMe$_3$)Si$_7$O$_9$(*c*-C$_6$H$_{11}$)$_7$)$_2$,[4] (Fig. 4.1 upper left) which displays Ti-O distances of 1.786(6) and 1.828(11). The titanium bound oxygen atoms O1 and O2 are 2.897 Å apart whereas the distance of the silyl protected O- atoms O9-O10 is

8.525 Å. In this molecule, the skeletal titanoxy silicons Si1 and Si2 are 4.598 Å apart and the siloxy-substituted atoms Si3-Si4 are bent away to a distance of 6.703 Å. These findings indicate a high flexibility of the ligand system.

Table 4.1 Selected Atomic Distances (Å) and Angles (deg) for [$((C_2H_3(C_6H_5)_2SiO)_2(c\text{-}C_6H_{11})_6Si_6O_7O_2)_2Ti$] (**3b**)

Atomic Distances			
Ti-O1	1.792(2)	Si-C(cyclohexyl)	1.840(2)-1.860(4)
Ti-O2	1.791(2)	Si-C(phenyl)	1.799(4)-1.871(4)
Ti-O101	1.781(2)	Si-C(vinyl)	1.843(4)-1.856(5)
Ti-O102	1.796(2)	C-C (vinyl)	1.267(7)-1.305(7)
Si1-O1	1.636(2)	Spatial distances	
Si2-O2	1.633(2)	C138-C152 (vinyls in same ligand)	11.2 (shortest distance)
Si11-O101	1.629(2)	C52-C138 (vinyls across ligands)	7.0 (shortest distance)
Si12-O102	1.629(2)		
Bond Angles			
O1-Ti-O2	107.91(11)	O101-Ti-O102	107.32(11)
O1-Ti-O101	111.86(11)	Ti-O1-Si1	164.67(16)
O1-Ti-O102	110.34(11)	Ti-O2-Si2	147.30(15)
O2-Ti-O101	108.69(11)	Ti-O101-Si11	160.24(15)
O2-Ti-O102	110.74(11)	Ti-O102-Si12	165.12(16)

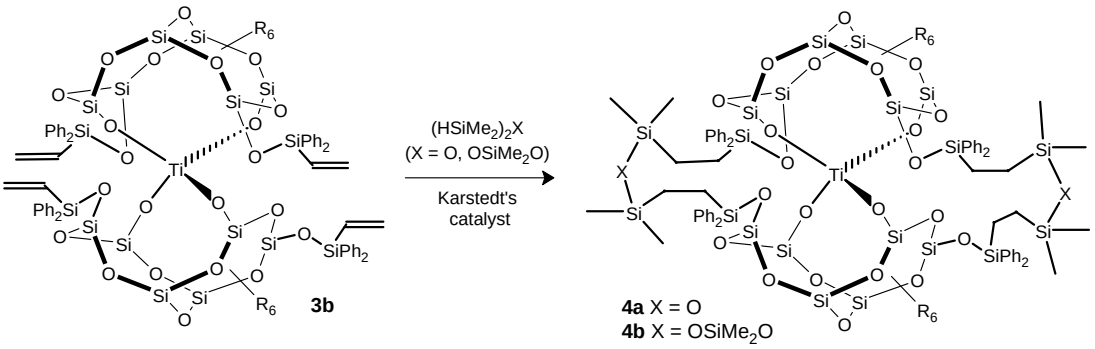
Compound **3b** contains four vinyl groups, to which in principle linkers can be attached or which can be bound together to form a robust single ligand system. The shortest distance of the vinyl groups was calculated with ORTEP for the CH_2 groups to be 7.010 and 9.073 Å in the two ligands. The largest distance is found for the vinyl groups within the same ligand, and is about 11-12 Å. In solution, all structural NMR (^{13}C and ^{29}Si-NMR) features of the parent disilanol and complexes **3a-b** are similar showing three equal signals for the cyclohexyl *ipso*-carbon and cage silicon atoms respectively. These data, support its D_2-symmetry. In contrast to the parent disilanols **1a-b,** the ^1H-NMR resonances of the phenyl ortho H-atoms in **3a-b**, are doubled with a difference of 0.06 ppm, showing the restricted motion of the phenyl groups in the titanium complex.

4.2.1.3 Cross-linking of [((C$_2$H$_3$Ph$_2$SiO)$_2$(c-C$_6$H$_{11}$)$_6$Si$_6$O$_7$O$_2$)$_2$Ti] ***(3b)***

In the structure of **3b**, titanium acts to spatially align the two silsesquioxane ligands in such a fashion that their vinyl groups are in close interligand proximity. This situation is ideal for attempting to chemically link the two ligands. As a result of linkage, the two ligands would unify to one macrocycle. In this context, several types of chemistry were explored.

All experiments to link the ligands together by metathesis using Grubbs' catalysts met with complications. Using either first or second generation catalyst, the desired ring closing metathesis reaction did not occur. Seemingly, this is a known complication for Si-containing alkenes.[5]

Fortunately, hydrosilylation with difunctional silane reagents provided relatively smooth linking (Scheme 4.2). Reaction of **3b** with two equivalents of 1,1,3,3-tetramethyldisiloxane (X = O) in C_6D_6, catalyzed by platinum(0) divinyltetramethyldisiloxane (Karstedt's catalyst) gave ca. 80% conversion to **4a** after heating to 60^{o}C overnight. No viscosity increase or gel formation was seen in the formation of **4a**. Using the longer chain silane, 1,1,3,3,5,5-hexamethyltrisiloxane (X = $OSiMe_2O$), in the synthesis of **4b**, a less selective reaction occurred that next to **4b**, produced polymers. In this case, gel formation provided a first indication that intermolecular reactions occurred.



Scheme 4.2 *Crosslinking of* ***3b*** by *hydrosilylation with a bifunctional silylating agent, giving titanium macrocycles a$_2$b$_2$* ***4a-b****. Possible silylation isomers are not drawn.*

After linking the cages present in **3b**, to form complexes **4a-b**, ^{1}H NMR shows broad peaks of Si-Ph due to α and β hydrosilylation, also possibly reflecting intermolecular ways of linking next to the desired intramolecular linking. Unfortunately, the linking reaction proceeds with incomplete conversion, consuming 70-80 % of the Si-H crosslinking groups. ^{13}C and ^{29}Si-NMR are non-informative, possibly due to differences in strain around the Ti-center.

4.2.3. Hydrolytic stability of POSS-macrocycle-titanium complexes.

In order to obtain additional information about the fate of the crosslinking reactions that form the presumed macrocycles **4a-b**, their hydrolytic stability was investigated in detail. Assuming that a complete hydrolysis or alcoholysis liberates the silsesquioxane ligands as silanols from titanate complexes, characterization of silanols liberated will provide information on the titanium complexes themselves.

When a drop of water is added to clear THF solutions of the bis-cage compounds **3a-b** or the crosslinked, presumably macrocyclic, compounds **4a-b**, a white precipitate is formed in time, indicating hydrolysis to titanium dioxide. Addition of an excess of aqueous hydrogen peroxide leads to a gradual yellowing of the aqueous layer. The change to yellow occurs in the course of 30 minutes, with the aqueous layer of **3b** being more intensely colored than that of the cross-linked species **4a-b**. These findings are indicative for titanium leaching and upon complete reaction, the organic phase will contain free silanol ligands. In these experiments, non crosslinked complexes **3**, hydrolyzed faster (~ca. 10 minutes) than their crosslinked counterparts **4a-b**. Compound **4a** seemed to be the most resistant to hydrolysis. Unfortunately, all compounds of types **3-4** are hydrolytically unstable which will render them largely unsuitable for catalytic application using aqueous hydrogen peroxide.

Silsesquioxanes thus obtained were further analyzed with MALDI-TOF-MS. This analysis (Fig. 4.3) shows that cross-linking with $(HSiMe_2)_2O$ and $(HSiMe_2O)_2SiMe_2$ gives mainly intramolecular reactions forming structures containing 2 silsesquioxanes a and 2 linker residues b (a_2b_2). As such, the assumption that complexes **4a-b** are essentially macrocyclic compounds is correct.

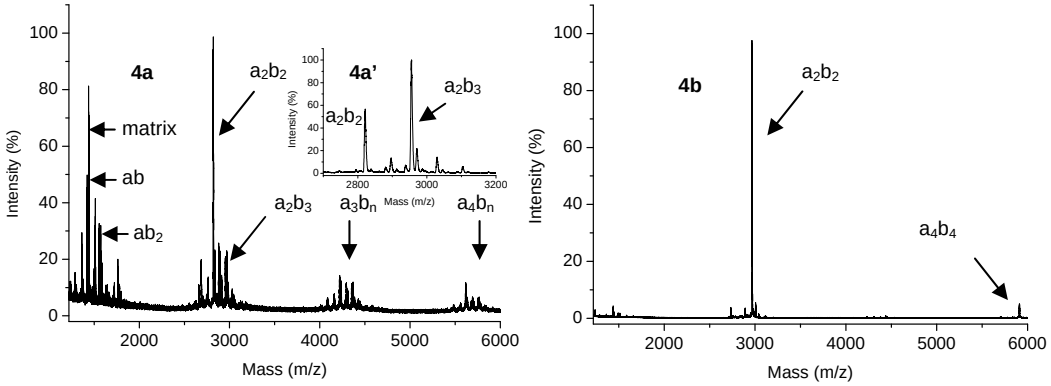
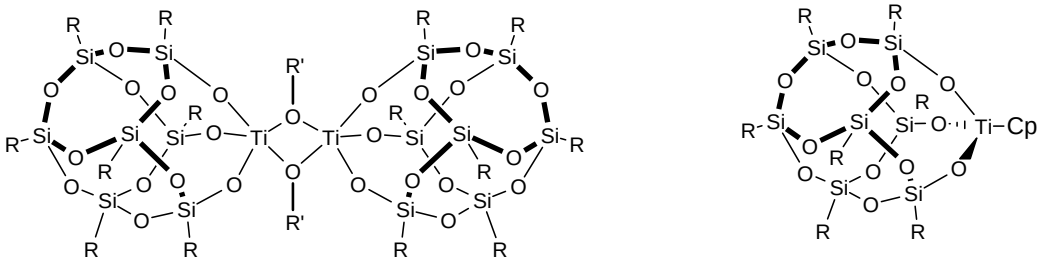


Fig. 4.3 *MALDI-TO-MS analysis of Ti-macrocycles* ***4a-b*** *after epoxidation of cyclooctene with 35 % aq.* H_2O_2.

MALDI-TOF-MS analysis was inconclusive for the titanium complexes due to matrix effects, but the ligands recovered after reaction with H_2O_2 during an epoxidation experiment (see chapter 5), giving full leaching of Ti[6], shows the ligand fragments. From Fig. 4.3, we conclude that macrocycle formation is most selective for **4b** as the MALDI-TOF-MS analysis shows a high preference for the a_2b_2-fragment. In the case of **4a**, this analysis shows both fragments relating to incomplete crosslinking (ab, ab_2) together with fragments relating to intermolecular cross coupling (a_2b_n, a_4b_n).

4.2.4 Synthesis of organofunctionalized R'(c-C_6H_{11})$_6Si_7O_{12}$TiCp complexes

Tripodally chelated silsesquioxanes are well known (Fig. 4.4) and relate to titanium cyclopentadienides, titanols and titanium alkoxides. Their synthesis departs from silsesquioxane trisilanols that only contain inert alkyl or cycloalkyl groups. Conversion to the corresponding titanium complexes is straightforward employing either Cl_3TiCp or titanium tetraalkoxides; hydrolysis of silsesquioxane titanium alkoxides affords the corresponding titanols in high yield.

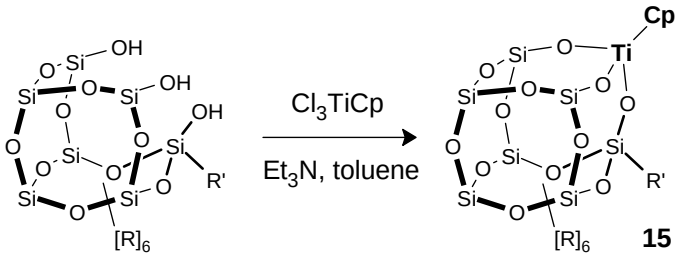


5 R = i-C_4H_9, R' = H
6 R = *c*-C_5H_9, R' = H
7 R = *c*-C_6H_{11}, R' = H
8 R = *c*-C_7H_{13}, R' = H

9 R = i-C_4H_9, Cp = C_5H_5
10 R = *c*-C_5H_9, Cp = C_5H_5
11 R = *c*-C_6H_{11}, Cp = C_5H_5
12 R = *c*-C_7H_{13}, Cp = C_5H_5
13 R = *c*-C_6H_{11}, Cp = $C_5H_3[(SiMe_3)_2$-1,3]
14 R = *c*-C_6H_{11}, Cp = C_5Me_5

Fig. 4.4 *Known tripodal silsesquioxane titanium complexes.*

Using the organofunctionalized trisilanols described in chapter 3, the synthesis of the corresponding cyclopentadienyl titanium complexes **15** was done, in analogy to known procedures.[7] This involved reacting organofunctionalized trisilanols with $CpTiCl_3$ in toluene. Addition of Et_3N gave quick precipitation of $Et_3NH^+Cl^-$. These relatively water and acid stable compounds were obtained after aqueous extraction with dilute hydrochloric acid to remove the salts and excess base, after which the complex was precipitated from the organic phase using acetonitrile. Further purification could be accomplished by vapor diffusion of acetonitrile into a benzene solution of the complexes (Scheme 4.3).



15a R = *c*-C_6H_{11}, R' = *c*-C_6H_{11}
15b R = *c*-C_6H_{11}, R' = C_2H_3
15c R = *c*-C_6H_{11}, R' = C_3H_5
15d R = *c*-C_6H_{11}, R' = $Cl(CH_2)_3$
15e R = *c*-C_6H_{11}, R' = $NC(CH_2)_3$
15f R = *c*-C_6H_{11}, R' = $H_3CO(CH_2)_3$
15g R = *c*-C_6H_{11}, R' = $HS(CH_2)_3$
15h R = *c*-C_6H_{11}, R' = $H_3CS(CH_2)_3$
15i R = *c*-C_6H_{11}, R' = $H_2C{=}CHCH_2S(CH_2)_3$
15j R = *c*-C_7H_{13}, R' = $H_3CO(CH_2)_3$

Scheme 4.3 *Synthesis routes to various synthesized cyclopentadienyl ligated titanium silsesquioxane complexes.*

Compounds with small relatively non-polar R' groups give higher yields (typically 70-90 % for **15 a-e**), whereas larger side chains (**15f**, **h**, **i, j**) give about 20-40 % yield. Mercaptopropyl complex **15g** could not be made, possibly because of the acidic nature of SH. Unlike the Ti-OH complexes **5-8** shown above, all TiCp compounds **9-15** easily form cubic crystals, which in the cases of side arm compounds **15b-j** are not suitable for structure analysis due to disordering. For all new complexes of type **15**, the ^{13}C or ^{29}Si-NMR for the methine carbon or cage silicon atoms reveal their C_S symmetry in the form of a characteristic 2:2:1:1 pattern. This pattern is also observed for the starting trisilanol materials. MALDI-TOF-MS of these complexes give the expected molecular masses as minor peaks only, accompanied by unexplainable side peaks, due to reaction with matrix materials.

4.2.5. Post synthesis modification of organofunctionalized R'(c-$C_6H_{11})_6Si_7O_{12}$TiCp

When synthesis of functionalized trisilanols or synthesis of their titanium complexes fail, functionalization could also be done after first inserting Ti into the trisilanol. A powerful starting material is found in the form of Ti-Cp complexes with an unsaturated side chain. For example, allyl complex **15c** could be ozonolyzed, to give a mixture of aldehydes and acids, but with complete retention of the Ti-Cp group, or hydroformylated, which is described in chapter 3, giving ($CHO(CH_2)_3$(*c*-$C_6H_{11})_6Si_7O_{12}$TiCp **15k**. Another means to introduce the COOH-group is hydrolysis of the CN group, but that required concentrated acid solutions, and in our case led to leaching of TiCp. Urea-functionalized silsesquioxanes using coupling to aldehydes, hydrosilylation or metathesis of allylurea by Grubbs' catalysts to an olefin **15c** could not be made.

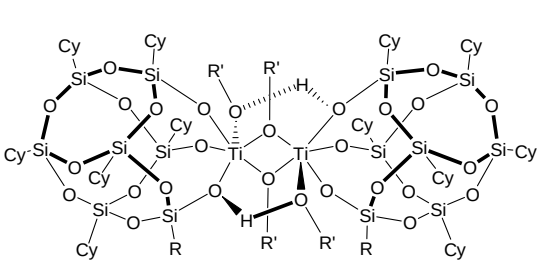
4.2.6. Stability of Ti-Cp complexes: reaction with protic reagents.

As we ultimately aim at performing epoxidation catalysis employing organic peroxides and aqueous hydrogen peroxide, complex resistance to hydrolysis and alcoholysis presents a topic that should be investigated.

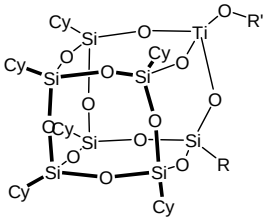
The commonly employed organic peroxide, TBHP is a relatively unreactive compound, resembling small alcohols in acidity[8]. Consequently, we investigated the reaction of silsesquioxane titanates with alcohols, phenols and water.

Tests were performed in the homogeneous phase, as bilayer phase mixtures could hamper the reaction, resulting in complete retention. For example a solution of **15a** in $CDCl_3$ treated with a droplet of water or hydrochloric acid did not give loss of the cyclopentadienyl moiety[9].

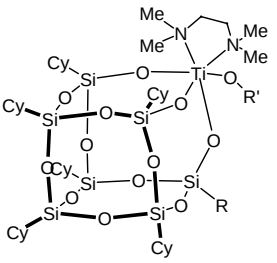
Table 4.2 and corresponding Figure 4.5 show the reactivity and reaction products of various TiCp silsesquioxanes with protic reagents. Under neutral conditions the relatively small alcohols (entries 4 and 5) and water (entry 19) react smoothly with Ti-Cp complexes to give dimeric alkoxide-alcohol adducts **16**[10], whereas *t*-butanol $(CH_3)_3COH$ (entry 1) does not react, mainly due to its bulkiness. Bulkiness is not the only factor as the 'acidic' hydroxy compounds phenol and 2,2,2-trifluorothanol (entries 2 and 3) do not react as well.



16a R = Cy, R' = Me
16b R = Cy, R' = Et
16c R = $(CH_2)_3C(O)H$, R' = Me
16d R = $(CH_2)_3CN$, R' = Me



17a R = Cy, R' = CMe_3
17b R = Cy, R' = Ph



18a R = Cy, R' = CH_2CF_3
18b R = Cy, R' = Ph
18c R = $(CH_2)_3Cl$, R' = Ph
18d R = $(CH_2)_3C(O)H$, R' = Ph
18e R = Cy, R' = *o*-NH_2Ph

Fig. 4.5 *Reaction products from alcoholysis of Ti-Cp silsesquioxanes.*

Addition of amines greatly enhances the hydrolysis of Ti-Cp, supporting a base-catalyzed reaction, which is known for triethylamine-catalyzed alcoholysis of Cp_2TiCl_2, yielding $CpTiCl_2OR$[11].

Table 4.2 Homogeneous protolysis of Ti-Cp complexes with R'OH and amines[a] or aqueous (H_2O)[d] systems

Entry	TiCp	Solvent	R'OH/base	Conversion/Time	Yield/Product
1	**15a**	C_6H_6	$(CH_3)_3COH$	n.r.	
2	**15a**	C_6H_6	PhOH	n.r.	
3	**15a**	THF	CF_3CH_2OH	n.r.	
4	**15a**	C_6H_6	MeOH	Full/1 day	80 %/**16a**
5	**15a**	C_6H_6	EtOH	Full/1 day	**16b**
6	**15a**	C_6H_6	$(CH_3)_3COH$/TMEDA	80 %/3 days	**17a**[b]
7	**15a**	C_6H_6	MeOH/TMEDA	Full/2-12 h	**16a**
8	**15a**	C_6H_6	EtOH/TMEDA	Full/12 h	**16b**
9	**15a**	C_6H_6	CF_3CH_2OH/TMEDA	Full/1 day	85 %/**18a**
10	**15a**	C_6H_6/CH_3CN	PhOH/TMEDA	Full/1 day	85 %/**18b**
11	**15k**	C_6H_6	MeOH	Full/1 day	10 %/**16c**
12	**15e**	C_6H_6	MeOH	Full/1day	70 %/**16d**
13	**15d**	C_6H_6/CH_3CN	PhOH/TMEDA	Full/1 day	85 %/**18c**
14	**15k**	C_6H_6/CH_3CN	PhOH/TMEDA	Full/1 day	10 %/**18d**
15	**15a**	C_6H_6/CH_3CN	*o*-$NH_2C_6H_4OH$/TMEDA	Full/1 day	**18e**
16	**15a**	C_6H_6/CH_3CN	PhOH/Et_3N	Full/1 day	**17b**[b]
17	**13**	C_6H_6	MeOH	Crystals after 4 days	**16a**
18	**14**	C_6H_6	MeOH	n.r.	

Other protic conditions

Entry	TiCp	Solvent	Reagent	Conversion/Time	Yield/Product
19[c]	**15a**	THF	HOH	80 %/1 day	Trisilanol[d]
20	**15a**	C_6H_6	TBHP	Full/1 day	**17a**
21[c]	**15a**	THF	HOOH(35% aq)	Full/1 day	**7**
22[c]	**15a**	THF	HCl (1 M aq)	Full/ 1 day	Trisilanol[d] +**15a** 1:1 ratio

[a] Reaction conditions: TiCp (50 mg, ca 0.050 mmol), solvent (0.50 mL), R'OH (50 equivalents), T = 50°C, [b] Contains loosely coordinated amine [c] TiCp (50 mg), THF (1 mL), aqueous solution (0.2 mL), T = 50°C; [d] Trisilanol refers to the free silsesquioxane, $Cy_7Si_7O_9(OH)_3$.

Bulkier cyclopentadienyl groups are more reluctant to their removal, as proven by a slow reaction of Ti-(1,3-bisTMSCp), (**13**) with MeOH, while Ti-$CpMe_5$-complex **14** is unreactive (entries 17 and 18), which is also reflected in catalysis for **13**, but unlike **14**, which seems to show intrinsic catalytic activity without an induction period (Chapter 5), though the latter is not fully stable when stirred with TBHP. We did not observe reactions of the side groups in complexes **15d-e** and the aldehyde **15k**,

indicating their low reactivity when bound to the silsesquioxane cage. The influence of the side group on the rate of alcoholysis or hydrolysis cannot be fully supported form these data.

Depending on the coordinative ability of the amine, the bulkiness and electronic properties of the hydroxy compound, different protolysis compounds are being formed: MeOH and EtOH still give amine-free dimeric alkoxide/alcohol adducts (entries 7 and 8), whereas *t*-butanol gave the *t*-butoxy complex, which due to the bulkiness of their groups gave an amorphous monomer/dimer mixture, loosely coordinating *N,N,N',N'*-tetramethylethylenediamine, TMEDA (entry 6). Interestingly the more electron-withdrawing trifluoroethanol (entry 9) and phenols (entries 10 and 15) cleanly gave monomeric TMEDA adducts **18** in high yields, which shows the critical effect of the electronic properties of the alkoxide group on the Lewis acidity of the titanium silsesquioxane complex. Triethylamine also catalyzed the reaction with phenol, but the colorless product could not be crystallized and contained loosely coordinating triethylamine.

More detail on the coordination of amines will be will be highlighted in a UV-Vis study described below. It is noteworthy to find that in all cases excess of protic reagent does not lead to formation of the trisilanol by full leaching, though acidic conditions in water (entry 22) will give some detitanation rendering trisilanol $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$. In the case of hydrogen peroxide (entry 21), however, this trisilanol is the only product. This is also confirmed with TiOH complex **7** or its TiO^iPr analogue, which did in our case not leach by water in THF for periods up to 1 week at room temperature, but addition of aqueous H_2O_2 or even anhydrous H_2O_2, ($MgSO_4$ dried H_2O_2 extract in methyl-*tert*-butyl ether) immediately gave a yellow solution, which gave precipitation of inorganic titanium peroxide within five minutes, leaving a colorless solution of free trisilanol.

*4.2.7. Characterization and chemistry of (c-$C_6H_{11})_7Si_7O_{12}TiOC_6H_5$ (**17b**) and (c-$C_6H_{11})_7Si_7O_{12}TiOC_6H_5$-TMEDA (**18b**)*

We were prompted to further go into the chemistry of tripodal titanium phenoxide as this intriguing compound allows us to use UV-Vis, infrared and NMR techniques for characterization and determination of the Lewis acidity of the free **(***c*-$C_6H_{11})_7Si_7O_{12}TiOPh$ (**17b**) earlier reported by Crocker et al[4]. Infrared spectroscopy (KBr) of **17b** and its bright yellow TMEDA adduct **18b** shows a shift in the Ti-O-Si stretching band going from 937 cm^{-1} to 953 cm^{-1}, which together with the UV absorption of the phenolate part, showing $\lambda_{max}(CH_2Cl_2)$ = 271 to 325 nm with a higher intensity, clearly states the electron donating properties of the amine to the titanium complex. In contrast to that of the free titanium phenoxide, the ^{1}H-NMR of **21b** (Fig. 4.6) shows a well resolved aromatic pattern of the phenolate moiety, which is due to the fact that the Ti atom is no longer accepting extra electron density from the phenolate oxygen or phenyl ring, to fulfill its coordination sphere, which is also indicative for its axial position, *cis* to both N-atoms.

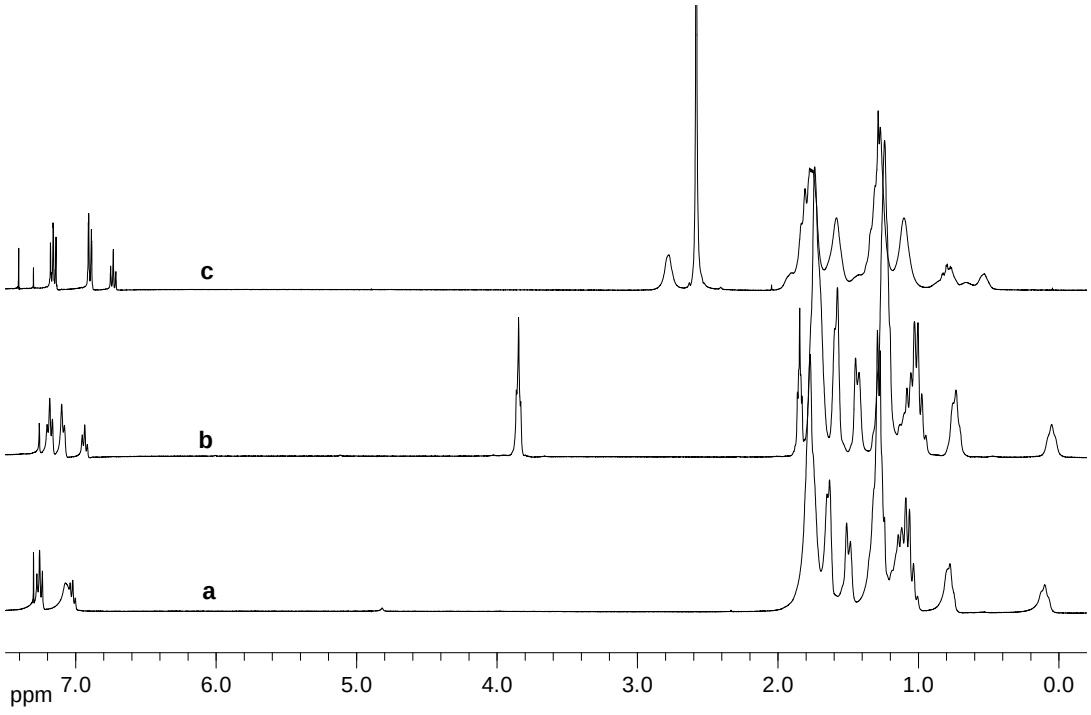


***Fig 4.6** ^{1}H-NMR spectra (400 mHz, $CDCl_3$, 25^{o}C) of **a)** (c-$C_6H_{11})_7Si_7O_{12}TiOPh$(**17b**); **b)** (c-$C_6H_{11})_7Si_7O_{12}TiOPh.THF$; **c)** (c-$C_6H_{11})_7Si_7O_{12}TiOPhTMEDA$ (**18b**)*

The TMEDA ^{1}H-resonances of the CH_3 and CH_2 show a downfield shift of 0.29 and 0.35 ppm. When extra TMEDA was added, the free and coordinated ligands could be identified separately, indicating a slow exchange on NMR time scale. At 80^{o}C, the peaks of coordinated TMEDA peaks get sharper, without changing position, indicating more rotational freedom.

Addition of TMEDA to free **17b** immediately gave a yellow coloration and the same characteristic NMR and UV-Vis spectra as pure **18b**. This prompted us to test other Lewis bases as well to get more insight about the Lewis acidity and steric constraints. Besides TMEDA, we added the following compounds to the phenoxytitanium complex: ethylenediamine $(CH_2NH_2)_2$, *N,N,N'*-trimethylethylenediamine ($Me_2NCH_2CH_2NMeH$), *N,N,N',N'*-tetramethylmethylenediamine ($Me_2NCH_2NMe_2$), triethylamine (Et_3N) and TMEDA-*N,N'*-dioxide $(Me_2N(O)CH_2)_2$, a possible oxidation product of TMEDA. The spectra are presented in Fig. 4.7, showing that only TMEDA (**e**) gives the absorption peak at higher wavelength

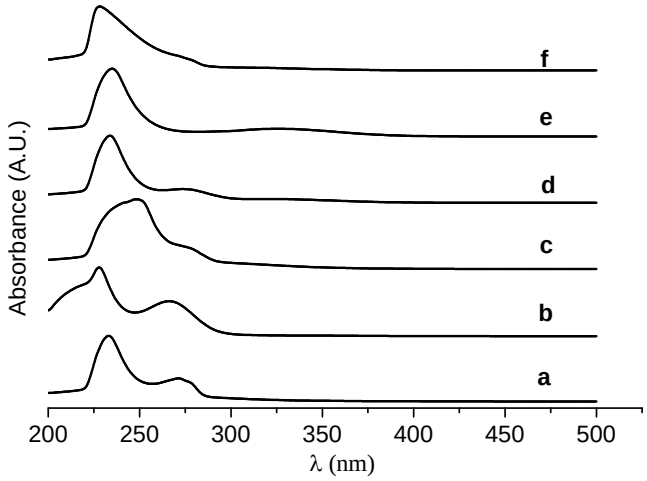


Fig. 4.7 *UV-Vis spectra of **17b** in CH_2Cl_2: **a**) no additive; **b**) ethylenediamine; **c**) Et_3N; **d**)N,N,N' trimethylethylenediamine; **e**) TMEDA; **f**) TMEDA-N,N'-dioxide*

Except for TMEDA, all of these abovementioned Lewis bases did not result in the formation of a well-defined crystalline compound. THF does so, forming a crystalline colorless 1:1 adduct $(c\text{-}C_6H_{11})_7Si_7O_{12}TiOPh.THF$, which, like **17b** are mixtures of monomers and dimers in C_6D_6 solution. Although there is some coordination, this is definitely weaker than in the TMEDA adduct, as all former products are almost colorless, as is reflected in their UV-Vis spectra and in poorly defined NMR spectra.

Besides the phenoxy complex **18b** and **(***c*-$C_6H_{11})_7Si_7O_{12}TiOCH_2CF_3$.TMEDA adduct **18a**, though with a slightly smaller downfield shift (0.275 and 0.230 ppm for CH_2 and CH_3 respectively), all other tripodal titanium alkoxides **(***c*-$C_6H_{11})_7Si_7O_{12}TiOR'$ (R' = H, Me, Et, ^{i}Pr) do not form well resolved TMEDA adducts, however, still give some line broadening of the TMEDA resonances in ^{1}H-NMR. This is also reflected by titanium alkoxides. When TMEDA is added to a $Ti(OR')_4$, in $CDCl_3$, no interaction was found in the case of R' = Et, ^{i}Pr, however $Ti(OPh)_4$, which is known to give a stable bis-DMF[12] adduct, also gives very stable THF and TMEDA adducts, giving a downfield shift for the ^{1}H-resonances of the TMEDA CH_3 and CH_2 groups of 0.489 and 0.556 ppm respectively, compared to free TMEDA.

4.2.8. Structural characterization of ($C_6H_{11})_7Si_7O_{12}$*TiOPh.TMEDA (**18b**)*

Crystals suitable for X-ray diffraction were obtained in a small NMR tube under abovementioned conditions and gradually formed as small monoclinic crystals in space group Pc with two independent molecules in the unit cell, which differ slightly in the conformation of the ethylene bridge of the TMEDA ligand (Fig. 4.8).

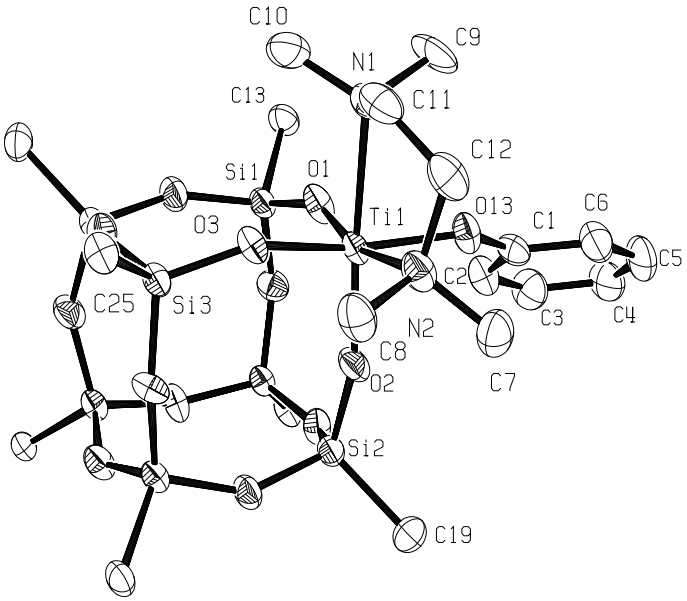


Fig. 4.8 *Molecular structure and labeling scheme of [(c-*$C_6H_{11})_7Si_7O_{12}$*TiOPh.TMEDA]**18b** displacement ellipsoid drawing (50 % probability) The cyclohexyl C-atoms except for the ipso carbons have been omitted for clarity*

Table 4.3 Selected Atomic Distancs (Å) and Angles (°) for (c-$C_6H_{11})_7Si_7O_9O_3TiOPhTMEDA$] **18b**, residue 1

Atomic Distances			
Ti-N1	2.323(4)	C1-O13	1.339(7)
Ti-N2	2.339(4)	C1-C2	1.380(7)
Ti-O1	1.821(4)	C2-C3	1.385(10)
Ti-O2	1.817(4)	C3-C4	1.382(9)
Ti-O3	1.893(4)	C4-C5	1.372
Ti-O13	1.897(4)	C5-C6	1.386(10)
Si1-O1	1.606(3)	C1-C6	1.391(8)
Si2-O2	1.612(4)	N1-C9	1.479(10)
Si3-O3	1.604(4)	N1-C10	1.485(7)
Other Si-O	1.608(3)-1.636(4)	N2-C7	1.473(7)
Si1-C13	1.852(2(7)	N2-C8	1.491(8)
Si2-C19	1.853(5)	N1-C11	1.479(7)
Si3-C25	1.866(6)	N2-C12	1.479(7)
Bond Angles			
O1-Ti-O2	102.75(17)	Ti-O3-Si3	150.6(2)
O1-Ti-O3	97.46.(18)	Ti-O13-C1	139.6(3)
O1-Ti-O13	94.81(19)	Ti-N1-C9	112.8(3)
O2-Ti-O3	96.03(18)	Ti-N1-C10	112.2(3)
O2-Ti-O13	95.15(17)	Ti-N1-C11	105.5(3)
O3-Ti-O13	161.14(15)	Ti-N2-C7	111.0(3)
O1-Ti-N1	87.39(16)	Ti-N2-C8	112.7(3)
O1-Ti-N2	165.19(16)	Ti-N2-C12	106.2(3)
O2-Ti-N1	169.86(17)	C9-N1-C10	107.4(5)
O2-Ti-N2	91.62(16)	C9-N1-C11	110.7(4)
O3-Ti-N1	82.46(16)	C10-N1-C11	108.2(4)
O3-Ti-N2	84.41(16)	C7-N2-C8	106.7(4)
O13-Ti-N1	83.86(15)	C7-N2-C12	109.5
O13-Ti-N2	80.14(17)	C8-N2-C12	110.9(4)
N1-Ti-N2	78.26(15)	N1-C11-C12	112.3(5)
Ti-O1-Si1	152.8(3)	N2-C12-C11	111.9(4)
Ti-O2-Si2	158.8(2)		

The molecular structure of **18b** is depicted in Fig 4.6. The titanium atom is octahedrally coordinated with the two equatorial nitrogen atoms *cis* positioned with a

bite angle of 78.3 °, whereas the Ti-N bond lengths are normal[13]. The *trans* positions are maximally distorted by 19° (O3-Ti-O13) from ideal geometry. The two equatorial Ti-OSi (Ti-O1 and Ti-O2) bond distances and angles fall well in range of other tripodal Ti-silsesquioxanes **13**[9] and **15a**[10]. The axial oxygens O3 and phenolate O13 are elongated by ca 0.07 Å. These Ti-O bonds may be more ionic, which supports the shift in λ_{max} of the phenolate group in the UV-VIS spectrum of **18b**.

*4.2.9. Stability of the TMEDA adduct **18b**.*

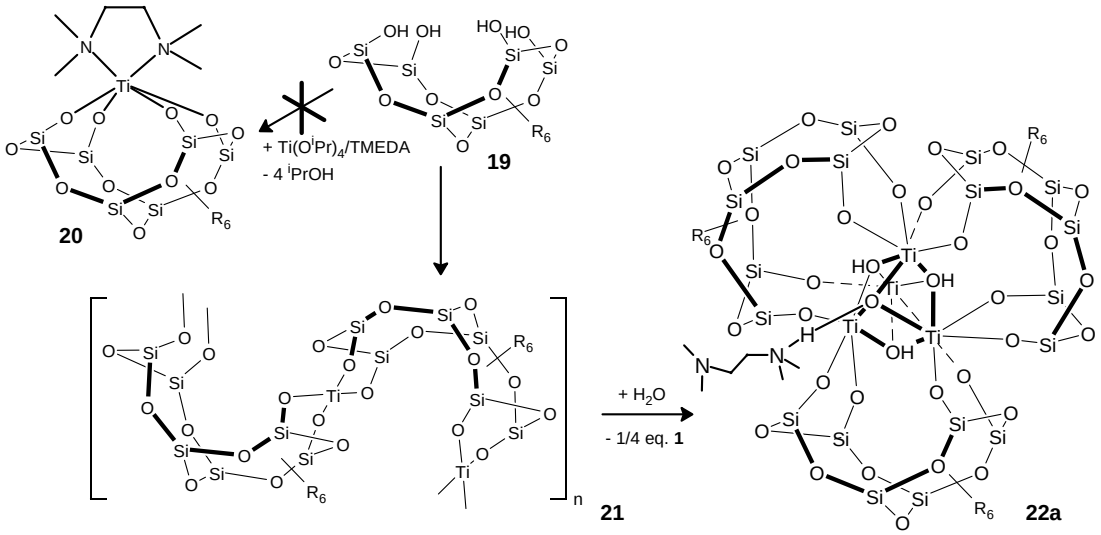
The thermal stability of TMEDA adduct **18b** is surprisingly high, showing less than 1 % weight loss at 175°C, when heated with 10°C per minute, after which unknown decomposition occurs. It seems to be even more stable than parent compound **17b**, which starts to lose weight below 100°C. This could be possible by a small amount of water present in the sample, facilitating loss of part of the phenoxy ligand as phenol. In aqueous THF, **18b** is stable for hours, showing 50 % decomposition to trisilanol and free phenol at 50°C overnight. Under the same circumstances, parent compound **17b** also loses phenol (ca 25 %), but the remainder was not identifiable: no trisilanol system was found. These reactions are however (partially) reversible: reacting titanol **7** with excess phenol and TMEDA, gave **18b** cleanly.

4.2.10. Interactions of TMEDA with other silsesquioxane Ti-complexes.

As TMEDA is now found to show interactions with, or even binding to, tripodal titanium silsesquioxanes, the question arises whether other titanium silsesquioxanes will show similar features. Double dipodal complex $((R'Ph_2SiO)_2(c\text{-}C_6H_{11})_6Si_6O_7O_2)_2Ti$ **3a-b** and $(Me_3SiO(c\text{-}C_5H_9)_7Si_7O_9O_2)_2Ti$ (see Fig. 4.1, upper left) showed no interaction at all, which may be due to the symmetric tetrahedral surrounding of Ti atom. The low Lewis acidity may also account for the low epoxidation activity of non-tripodal titanium silsesquioxanes.

Even when other factors, like entropy may favor TMEDA complexation. This, however, could not be demonstrated. For example, when $Ti(O^iPr)_4$ is reacted with

tetrasilanol (c-$C_6H_{11})_6Si_6O_7(OH)_4$ **19**, even in the presence of TMEDA the product is not a monomeric TMEDA adduct **20** but remains a polymeric substance **21** (Scheme 4.7). The Lewis acidity of the bis-dipodal titanium atoms is too low to combine with TMEDA, and an entropically favored breakdown into a monomeric complex, depicted as **20** in Scheme 4.7 did not occur.



Scheme 4.7 *Synthesis of the polyoxotitanate* $[R_6Si_6O_{11}]_3(TiOH)_4$ (***22a*** *R =* c-C_6H_{11}*, TMEDA adduct,* ***22b*** *R =* c-C_7H_{13}*, no TMEDA).*

The amine had no influence on the tetratitanium cluster formation of **22a** itself. As with the earlier reported titanium cluster **22b**[9] addition of water immediately gave dissolution of the polymeric complex to afford cluster **22a** as a mono-hydrogen bonded TMEDA adduct.

*4.2.11 Structural characterization of the hydrogen-bonded cluster **22a***

To get a full picture of the titanium silsesquioxane-TMEDA complex, crystals were grown by addition of a small amount of water to the reaction mixture of $Ti(O^iPr)_4$, tetrasilanol **29**, and TMEDA in chloroform, with subsequent addition of acetonitrile for precipitation. The unit cell contains a single molecule of $[(c\text{-}C_6H_{11})_6Si_6O_{11})]_3$ $[Ti_4(\mu^3\text{-}OH)_4]$-TMEDA, **22a**, together with disordered solvent molecules, presumably acetonitrile and chloroform, which were interpreted as partially occupied solvent positions. The molecular structure of **22a** along with the adopted numbering scheme is shown in Fig. 4.9; selected bond distances and angles were given in table 4.4.

Table 4.4 Selected Atomic Distancs (Å) and Angles (°) for $[(c\text{-}C_6H_{11})_6Si_6O_{11})]_3$ $[Ti(\mu^3\text{-}OH))_4]$TMEDA (**22a**)

Atomic Distances			
Ti-OH	2.084(3)-2.202(3)	N1-C3	1.504(6)
Ti-O4(HTMEDA)	2.052(3)-2.077(3)	N2-C4	1.449(8)
Ti-OSi	1.810(3)-1.860(3)	N2-C5	1.427(8)
Si-OTi	1.613(3)-1.628(3)	N2-C6	1.463(11)
Si-OSi	1.600(3)-1.653(3)	C1-C2	1.527(7)
N1-C1	1.478(7)	O4-N1	2.683(5)
N1-C2	1.492(6)	O4H-N1	1.68
Bond Angles			
Ti-O-Ti	100.50(12)-108.21(12)	C1-N1-C2	110.7(4)
Si-O-Ti	148.3(2)-170.8(2)	C1-N1-C3	114.7(4)
Si-O-Si	127.5(2)-165.1(2)	C2-N1-C3	112.5(3)
O-Si-O	105.41(17)-111.94(16)	C4-N2-C5	111.4(5)
O(H)-Ti-O(H)	71.42(10)-74.56(11)	C4-N2-C6	110.1(6)
Cis-SiO-Ti-O	82.80(12)-108.06(12)	C5-N2-C6	110.2(6)
TransO-Ti-O	152.94(12)-167.64(12)	N1-H-O1	177
O-Si-C	103.0(3)-116.24(19)		

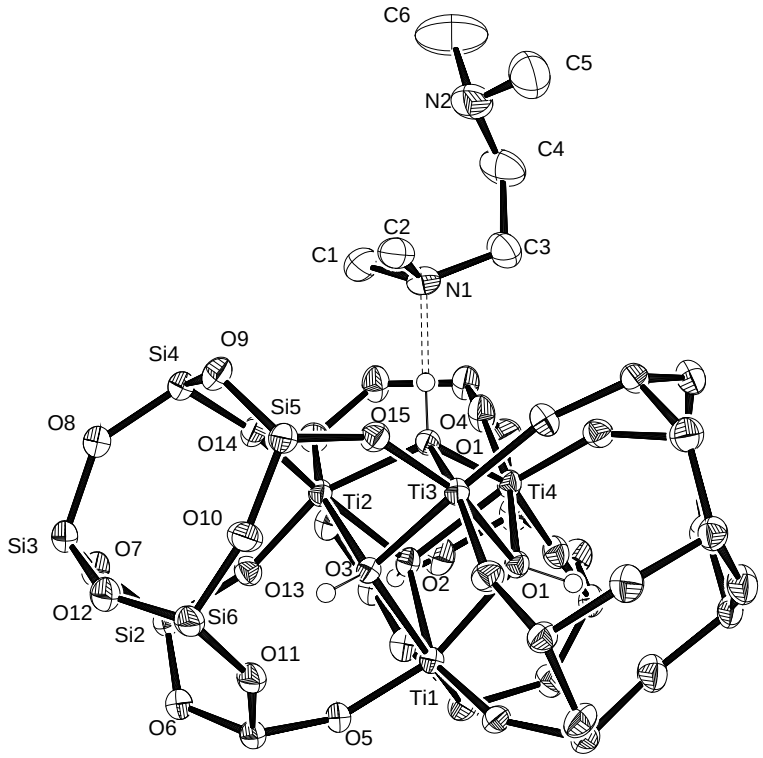


Fig. 4.9 *Molecular structure and labeling scheme of* ***22a*** *(side view); displacement ellipsoid drawing (50 % probability) The cyclohexyl groups and the solvent molecules have been omitted for clarity.*

The crystal structure determination shows **22a** to be a tetranuclear six-coordinated titanium complex with a distorted octahedral geometry of the titanium centers, very similar to the TMEDA-free cluster $[(c\text{-}C_7H_{13})_6Si_6O_{11})]_3\,[Ti_4(\mu^3\text{-}OH)_4]$, **22b**[9]. The core cuboid is surrounded by three silsesquioxane tetrasilanolate ligands, resulting in an overall structure that resembles a three-bladed propeller for which both enantiomers occur in crystals of **22a-b**. The structure of the central cuboid, is related to $[(CpTi)_3(\mu^2\text{-}OH)_3(\mu^3\text{-}O)]^+$ core of a formate complex[14] and has a high resemblance with a series of heterometallic carboxylates of general formula $[Ti_4(\mu^3\text{-}O)_4(OR)_4\{\mu\text{-}CO)_9CO_3(\mu^3\text{-}CCO_2)\}_4]$[15]. The structure of the core cuboid is distorted, which leads to small HO-Ti-OH angles involving the bridging hydroxides [HO-Ti-OH: 71.42(10)-74.56(11)^o, TiOH = 2.084(3)-2.202(3) Å], larger angles for the siloxy O-Ti-O units [SiO-Ti-OSi]: 97.31(13)-99.33(14)^o, Ti-OSi = 1.810(3)-1.860(3) Å) arise. As a result of different modes of silsesquioxane siloxy coordination, the coordination sphere of one of the titanium atoms [Ti(1)] is completed by a threefold η^1 coordination

involving one siloxy unit of all three silsesquioxanes [O5 and two similar]. The other titanium centers reach saturated coordination by a combination of η^1- and additional η^2-coordination involving three siloxy units of two different silsesquioxane ligands. As a result, the structure contains one titanium center that is bonded to all three silsesquioxane ligands while the other three titanium centers are each bonded to two out of three silsesquixanes. As observed by IR, the bridging hydroxy units that are attached to Ti(1)via O1-O3 are likely to engage in hydrogen bonding in bifurcating mode with non-coordinating silsesquioxane oxygen atoms. The fourth one is hydrogen bonded with a single nitrogen atom of the TMEDA molecule, with a N-O distance of 2.683(5) Å, which is a quite short hydrogen bond for TMEDA complexes. A stable triphenylsilanol-TMEDA 2:1 adduct has an N-O distance of 2.73 Å.[16] The IR(ATR) of **22a** shows a broad absorption at 3459 cm^{-1} with no sharp peaks, indicating that all OH groups are hydrogen bonded. However, the TMEDA is easily removed by TBHP, which results in the parent cluster, showing a sharp peak of the isolated OH group at 3619 cm^{-1}, with the other three OH groups forming a broad absorption at 3364 cm^{-1}.

4.3 Conclusions

Novel, bis-dipodal titanium complexes have been made and chemically converted to marcocylic compounds. With respect to hydrolytic stability, crosslinking slightly stabilizes the titanium silsesquioxane. Hydrolytic stability of tripodal silsesquioxane complexes is superior and a new series of such compounds featuring organofunctionalized ligands resulted from this work.

Titanium complexes with a single tripodal ligand and a non-bulky alkoxy group hardly leach the Ti-atom through hydrolysis or alcoholysis. The loss of the Ti-Cp group occurs by protolysis with non-bulky alcohols and is accelerated in the presence of amines. Tripodal Ti-alkoxides show the highest Lewis acidity and even affinity to the TMEDA ligand. For electron-withdrawing alkoxides, remarkably stable adducts can be isolated.

4.5 Experimental Section

Solvents were dried using an argon flushed column with γ-alumina pellets. Triethylamine was distilled from sodium benzophenone ketyl. All air and moisture sensitive reactions were performed using Schlenk techniques. ^{1}H (400 MHz),^{13}C (100.6 MHz) and ^{19}F (376.3 MHz) NMR spectra were recorded on on a Varian Mercury 400 spectrometer, ^{29}Si NMR (99.3 MHz) was recorded on a Varian Inova 500 spectrometer. Elemental analyses were performed by Selact BV, Groningen.
MALDI-TOF-MS analysis was performed on a Voyager-DE™ STR BioSpectrometry™ Workstation with *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (MM) as matrix and sodium trifluoroacetate as Na^{+} source.

Preparation of [((MePh$_2$SiO)$_2$(c-C$_6$H$_{11}$)$_6$Si$_6$O$_7$O$_2$)$_2$Ti] (**3a**).
(MePh$_2$SiO)$_2$(*c*-C$_6$H$_{11}$)$_6$Si$_6$O$_7$(OH)$_2$ **1a** (0.77 g, 0.62 mmol) was dissolved in THF (3 mL) after freeze drying. Titanium tetraisopropoxide (145 mg, 0.50 mmol) was added, after which the mixture was stirred at 50 ^{o}C for three hours. The mixture was evaporated to give a solid residue which consists of **3a** and some unknown by-product. Crystallization from hexane gave needle-shaped crystals (160 mg) of pure **3a.**
^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 10.58 ($SiMePh_2$), - 66.46, - 66.50, - 70.82 (1:1:1), ^{1}H NMR ($CDCl_3$) δ 7.65 (dd, 4 H, Ph), 7.52 (dd, 4 H, Ph), -7.35, (m, 12 H, Ph), 1.71 (m, 30 H, C*H*$_2$ C$_6$H$_{11}$), 1.25 (m, 30 H, C*H*$_2$ *c*-C$_6$H$_{11}$), 0.73 (s, 6 H, C*H*$_3$-Si), 0.57 (m, 6 H, C*H* *c*-C$_6$H$_{11}$), ^{13}*C* {^{1}H} NMR δ 137.75, 137.70, 134.18, 129.32, 127.57, 127.56 (Ph), 27.80, 27.64, 27.59, 27.41, 27.04, 26.90, 26.87, 26.78, 26.73, 26.68, 26.54 (*C*H$_2$ *c*-C$_6$H$_{11}$), 24.93, 24.34, 23.69 (2:2:2, *C*H *c*-C$_6$H$_{11}$).- 0.29 (*C*H$_3$-Si). Anal. calcd for $C_{124}H_{184}Si_{16}O_{24}Ti$ (found) : C 59.01 (57.94), H 7.35 (7.52), Ti 1.90 (1.71).

Preparation of [((C$_2$H$_3$Ph$_2$SiO)$_2$(c-C$_6$H$_{11}$)$_6$Si$_6$O$_7$O$_2$)$_2$Ti] (**3b**).
(C$_2$H$_3$Ph$_2$SiO)$_2$(*c*-C$_6$H$_{11}$)$_6$Si$_6$O$_7$(OH)$_2$ **1b** (0.64 g, 0.51 mmol) was dissolved in THF (3 mL) after freeze drying. Titanium tetraisopropoxide (0.093 g, 0.55 mmol) was added, after which the mixture was stirred at 65 ^{o}C overnight. The mixture was evaporated and the residue was crystallized form hexane to give pure **3b** as needle shaped crystals (180 mg). Crystals suitable for X-ray structure determination were obtained by slowly cooling down a cyclohexane/acetone solution.
^{1}H NMR ($CDCl_3$) δ 7.69 (dd, 4 H, Ph), 7.63 (dd, 4 H, Ph), -7.37, (m, 12 H, Ph), 6.46 (m, 1 H, -CH=), 6.29 (dd, 1H, =CH_2), 6.03 (dd, 1 H, =CH_2), 1.60 (m, 30 H, C*H*$_2$ *c*-C$_6$H$_{11}$), 1.20 (m, 30 H, C*H*$_2$ *c*-C$_6$H$_{11}$), 0.70 (m, 6 H, C*H* C$_6$H$_{11}$), ^{13}C {^{1}H} NMR δ 136.97, 135.07, 134.94, 134.24

(=CH_2), 129.56 (-CH=) 127.58, 27.84, 27.58, 27.36, 27.26, 26.88, 26.76, 26.59 (*C*H_2 *c*-C_6H_{11}), 24.97, 24.44, 23.49 (2:2:2, *C*H *c*-C_6H_{11}).

*Crosslinking of **3b** with $(HSiMe_2)_2O$: preparation of $[(O(SiMe_2C_2H_4Ph_2SiO)_2(c\text{-}C_6H_{11})_6Si_6O_7O_2)_2Ti]$ (**4a**).*

To a solution of Ti-disilanolate $[((C_2H_3Ph_2SiO)_2(c\text{-}C_6H_{11})_6Si_6O_7O_2)_2Ti]$ **3b** (128 mg, 0.0094 mmol) and $(HSiMe_2)_2O$ (7.6 mg, 0.0094 mmol) in benzene-d^6 (0.8 mL) was added platinum-divinyltetramethyldisiloxane (8 % in xylene, 1.5 mg). After mixing of the solution, the mixture was heated to 60^{o}C over three days. All vinyl groups disappeared, but around 30 % of Si-H remained. The reaction mixture, which did not increase in viscosity, was evaporated to give a non-crystallizable off-white solid. ^{1}H NMR (C_6D_6) δ 8.0-7.8 (8H, Ph), 7.6-6.8, 12, Ph), 5.0 (m, remaining 30 %, Si-H), 2.2-0.9 (132 H, *c*-C_6H_{11}), 0.2 (18 H, Si-*Me*), ^{13}C-NMR was not informative.

Empty macrocycle: MALDI-TOF-MS, m/z = 2819 (2cage-.2silane macrocycle + Na^+). ^{1}H NMR ($CDCl_3$) δ 7.60 (m, 8H, Ph), 7.35 (m, 12, Ph), 4.65 (m, remaining 30 %, Si-H), 3.10 (s, 2 H, OH), 1.8, (m, 30 H, C*H*$_2$ *c*-C_6H_{11}), 1.2, (m, 30 H, C*H*$_2$ *c*-C_6H_{11}), 0.6, (m, 6 H, C*H* *c*-C_6H_{11}) 0.2-0.0 (three peaks, intensity 1:2:1, 18 H, Si-*Me*).

*Crosslinking of **3b** with $(HSiMe_2O)_2SiMe_2$: preparation of $[(Me_2Si(OSiMe_2C_2H_4Ph_2SiO)_2(c\text{-}C_6H_{11})_6Si_6O_7O_2)_2Ti]$ (**4b**).*

Ti-disilanolate $[((C_2H_3Ph_2SiO)_2(c\text{-}C_6H_{11})_6Si_6O_7O_2)_2Ti]$ **3b** (128 mg, 0.0094 mmol) was dissolved in benzene-d^6 (0.8 mL) $(HSiMe_2O)_2SiMe_2$ (9.8 mg, 0.0094 mmol). Platinum-divinyltetramethyldisiloxane (8 % in xylene, 1.5 mg) was added, and the solution was mixed. The reaction mixture was kept at 60^{o}C, and formed a gel after two hours. NMR showed full conversion of the vinyl and H-Si groups. The mixture was kept overnight to ensure full conversion, before measurement. The volatiles were later removed by evaporation. ^{1}H NMR (C_6D_6) δ 8.4-8.0 (8H, Ph), 7.9-7.0 12, Ph), 2.6-0.8 (132 H, *c*-C_6H_{11}), 0.4-0.0 (18 H, Si-*Me*) ^{13}C-NMR was not informative.

Empty macrocycle: MALDI-TOF-MS (MM, NaTFA), m/z 2967 (2cage-.2silane macrocycle + Na^+), ca 5 % intensity of m/z = 5909 (4 cage-4 silane + Na^+).

Allyl(c-$C_6H_{11})_6Si_7O_{12}$TiCp, **15c** were prepared according to the literature[17]

*Preparation of $Cl(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_{12}$TiCp **(15d)***

To a solution of $Cl(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3$ (470 mg, 0.50 mmol) and $CpTiCl_3$ (150 mg, 0.68 mmol) in toluene (10 mL) was added Et_3N (0.4 mL 2.6 mmol) to give a precipitate

immediately. The mixture was stirred overnight, filtered, after which acetonitrile was added to give an off-white powder (426 mg, 0.39 mmol, 79 %) Recrystallization from benzene-acetonitrile diffusion gave 367 mg (0.34 mmol, 68 %), which was ca 90 % pure.

^{29}Si {^{1}H} NMR ($CDCl_3$) δ -64.96, -66.13, - 68.68, - 69.52 (1:2:1:3), ^{1}H NMR ($CDCl_3$) δ 6.52 (s, 5 H, C_5H_5), 3.62 (t, 2 H, ^{3}J = 7.0 Hz, CH_2Cl), 1.91 (m, 2 H, CH_2), 1.75 (m, 30 H, CH_2 C_6H_{11}), 1.26 (m, 30 H, CH_2 C_6H_{11}), 0.71 (m, 8 H, CH C_6H_{11} + CH_2-Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 116.22 (C_5H_5), 47.50 (CH_2Cl), 27.56, 27.53, 27.11, 27.00, 26.93, 26.88, 26.79, 26.64 (CH_2 C_6H_{11}), 23.40, 23.18, 23.16 (2:1:1, CH C_6H_{11}), 9.6 (CH_2Si). MALDI-TOF: M+Na= reaction with matrix. Anal. calcd for $C_{44}H_{77}ClTiSi_7O_{12}$ (found): C 49.02 (49.08), H 7.20 (7.29).

*Preparation of $NC(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_{12}TiCp$,(**15e**)*

Procedure as for **15d**, using $NC(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3$ (490 mg, 0.51 mmol), $CpTiCl_3$ (125 mg, 0.56 mmol), CH_2Cl_2 (10 mL) and Et_3N (0.7 mL, 5.0 mmol). Yield: 420 mg (0.39 mmol, 77 %). Recrystallization gave 351 mg, ca 90 % pure (0.33 mmol, 64 %). ^{29}Si {^{1}H} NMR ($CDCl_3$) δ -.66.09, - 69.48. ^{1}H NMR ($CDCl_3$) δ 6.53, (s, 5 H, C_5H_5), 2.46 (t, 2 H, ^{3}J = 7.0 Hz, CH_2CN), 1.76 (m, 32 H, CH_2 + CH_2 C_6H_{11}), 1.28 (m, 30 H CH_2 C_6H_{11}), 0.76 (m, 8 H, CH_2 + CH C_6H_{11}), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 116.30 (C_5H_5), 27.61, 27.57, 27.54, 27.49, 27.13, 27.09, 26.98, 26.92, 26.92, 26.63 (CH_2), 23.46, 23.37, 23.24, 23.15 (1:2:1:2, CH), 20.15, 19.89, 11.53 MALDI-TOF: M+Na= reaction with matrix.

*Preparation of $H_3CS(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_{12}TiCp$,(**15h**)*

Procedure as for **15d**, using $H_3CS(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3$ (490 mg, 0.50 mmol), $CpTiCl_3$ (127 mg, 0.57 mmol), CH_2Cl_2 (10 mL) and Et_3N (0.8 mL, 5.0 mmol). Yield: 450 mg (0.41 mmol, 82 %).

^{1}H NMR ($CDCl_3$) δ 6.52 (s, 5 H, C_5H_5), 2.58 (t, 2 H, $^{3}J_{HH}$ =7.3 Hz, CH_2S), 2.09 (s, 3 H, CH_3S), 1.78 (m, 32 H, CH_2 c-C_6H_{11} + CH_2), 1.24 (m, 30 H, CH_2 c-C_6H_{11}), 0.75 (m, 8 H, CH c-C_6H_{11} + CH_2Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 116.13 (C_5H_5), 37.13, 27.64, 27.54, 27.11, 27.00, 26.88, 26.81, 26.64 (CH_2 c-C_6H_{11}), 23.41, 23.20, 23.00 (3:1:2 CH c-C_6H_{11}), 15.16, 11.31.

*Preparation of $H_2C{=}CHCH_2S(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_{12}TiCp$, (**15i**)*

From $H_2C{=}CHCH_2S(CH_2)_3(C_6H_{11})_6Si_7O_9(OH)_3$ (512 mg, 0.50 mmol), $CpTiCl_3$ (150 mg, 0.68 mmol), toluene (10 mL) and Et_3N (0.5 mL, 3.6 mmol). Yield: 233 mg (0.21 mmol, 42 %). Recrystallization gave 138 mg (0.12 mmol, 25 %). ^{29}Si {^{1}H} NMR ($CDCl_3$) δ - 64.70, - 66.15, - 68.70, - 69.54, - 69.59 (1:2:1:1:2, foreign peak at – 66.24 ppm) ^{1}H NMR ($CDCl_3$) δ 6.52 (s,

5 H, C_5H_5), 5.84 (m, 1 H, CH_2=C*H*), 5.15 (m, 2 H, CH_2=CH), 3.19 (d, $^3J_{HH}$ =7.0 Hz, =CH-CH_2S), 2.56 (t, 2 H, $^3J_{HH}$ =7.0 Hz, CH_2S), 1.75 (m, 32 H, CH_2 C_6H_{11} + CH_2), 1.27 (m, 30 H, CH_2 C_6H_{11}), 0.67 (m, 8 H, C*H* C_6H_{11} + CH_2Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 134.55, 116.72, 116.12 (C_5H_5), 34.43, 33.50, 27.64, 27.54, 27.11, 27.00, 26.92, 26.89, 26.82, 26.65 (CH_2 *c*-C_6H_{11}), 23.42, 23.31, 23.20, 23.09 (2:1:2:1, *C*H *c*-C_6H_{11}), 11.50.

Preparation of $H_3CO(CH_2)_3(c\text{-}C_7H_{13})_6Si_7O_{12}TiCp$ (***15j***).

From $H_3CO(CH_2)_3(c\text{-}C_7H_{13})_6Si_7O_9(OH)_3$ (0.467 g, 0.44 mmol) and $CpTiCl_3$ (120 mg, 0.55 mmol), toluene (10 mL), and Et_3N (0.6 mL). Yield: 0.34 g (0.34 mmol, 34 %). Recrystallization gave pure $H_3CO(CH_2)_3(c\text{-}C_7H_{13})_6Si_7O_{12}TiCp$ as fine crystals (0.26 g, 0.22 mmol). ^{1}H NMR ($CDCl_3$) δ 6.50 (s, 5 H, C_5H_5), 3.42 (t, 2 H, $^3J_{HH}$ =7.0 Hz, CH_2O), 3.37 (s, 3 H, CH_3O), 1.92-1.34 (m, 74 H, CH_2 *c*-C_7H_{13} + CH_2), 0.82 (m, 6 H, C*H* *c*-C_7H_{13}), 0.58 (m, 2 H, CH_2Si), ^{13}C {^{1}H} NMR ($CDCl_3$) δ 116.05 (C_5H_5), 75.10 (CH_2O), 58.37 (CH_3O), 29.52, 29.41, 29.39, 29.33, 28.61, 28.59, 28.57, 27.93, (CH_2 *c*-C_7H_{13}), 24.09, 23.86, 24.84, 23.82 (1:2:2:1, *C*H *c*-C_7H_{13}), 23.25, 8.06 (CH_2-Si).

Synthesis of $(OCH(CH_2)_3(c\text{-}C_6H_{11})_6Si_7O_{12}TiCp$ **(*15k*)**.

See Ch 3, p 55: hydroformylaton of *H_2C=$CHCH_2(c\text{-}C_6H_{11})_6Si_7O_{12}TiCp$* (**15b**, Ch 3)**.**

Compound (c-$C_6H_{11})_7Si_7O_{12}TiOPh$ (**17**) was prepared from (c-$C_6H_{11})_7Si_7O_{12}TiO^iPr$ with phenol according to literature[4].

Synthesis of $(c\text{-}C_6H_{11})_7Si_7O_{12}TiOCH_2CF_3$(TMEDA) (***18a***) *from $(c\text{-}C_6H_{11})_7Si_7O_{12}TiCp$* (***11***).

To a solution of (c-$C_6H_{11})_7Si_7O_{12}TiCp$ (50 mg, 0.045 mmol) in benzene (0.5 mL) was added trifluoroethanol (50 mg, 0.55 mmol) and TMEDA (50 μL, 0.40 mmol). Acetonitrile was added until the starting material just stayed dissolved (100 μL). The solution was heated to 50 ^{o}C overnight and evaporated to give (c-$C_6H_{11})_7Si_7O_{12}TiOCH_2CF_3$(TMEDA) (44 mg, 0.035 mmol, 85 %), which is recrystalized from $CDCl_3$/acetonitrile, ^{1}H NMR ($CDCl_3$) δ 4.60 (q, 2 H, $^3J_{HF}$ = 9.9 Hz, C$H_2$$CF_3$), 2.66 (br s, 4 H, C$H_2$ TMEDA), 2.55 (s, 12 H, CH_3 TMEDA), 1.76 (m, 35 H, CH_2 *c*-C_6H_{11}), 1.27 (m, 35 H, CH_2 *c*-C_6H_{11}), 0.84-0.60 (m, 7 H, C*H* *c*-C_6H_{11}), ^{13}C {^{1}H} NMR δ 70.42 (q, CF_3), 57.35 (CH_2 TMEDA), 49.46 (CH_3 TMEDA), 27.79, 27.63, 27.31, 27.04, 27.01, 26.81, 26.77 (CH_2 *c*-C_6H_{11}), 24.05, 23.40 (1:6, *C*H *c*-C_6H_{11}), ^{19}F {1H} NMR δ – 76.50 (t, $^3J_{HF}$ = 9.9 Hz).

Synthesis of (c-$C_6H_{11})_7Si_7O_{12}TiOPh(TMEDA)$ (***18b***) *from (c-$C_6H_{11})_7Si_7O_{12}TiCp$* (***11***)

To a solution of (c-$C_6H_{11})_7Si_7O_{12}TiCp$ (50 mg, 0.045 mmol) in benzene (0.5 mL) was added phenol (50 mg, 0.55 mmol) and TMEDA (50 μL, 0.40 mmol). Acetonitrile was added until the starting material just stayed dissolved (100 μL). The solution was heated to 50 ^oC overnight to give yellow crystals of **18b** (44 mg, 0.035 mmol, 85 %). UV-Vis: λ_{max} (CH_2Cl_2) = 325 nm (phenolate).

^{29}Si {^1H} NMR ($CDCl_3$) δ -68.40 (broad), - 68.68 (sharp), - 69.51, - 69.77 (broad), ^1H NMR ($CDCl_3$) δ 7.16 (t, 2 H, $^3J_{HH}$ = 8 Hz m H Ph), 6.89 (d, 2 H, $^3J_{HH}$ = 8 Hz o H Ph), -6.73, (t, 1 H, $^3J_{HH}$ = 7.6 Hz, p H Ph), 2.78 (br s, 4 H, CH_2 TMEDA), 2.58 (s, 12 H, CH_3 TMEDA), 1.76 (m, 26 H, CH_2 c-C_6H_{11}), 1.59 (m, 9 H CH_2 c-C_6H_{11}), 1.27 (m, 26 H, CH_2 c-C_6H_{11}), 1.11 (m, 9 H, CH_2 c-C_6H_{11}), 0.90-0.50 (m, 7 H, CH c-C_6H_{11}), ^{13}C {^1H} NMR δ 166.05, 128.67, 119.20, 117.63 (Ph),57.51 (CH$_2$ TMEDA), 49.69 (CH$_3$ TMEDA), 27.77, 27.63, 27.06, 27.00, 26.85, 26.77 (CH$_2$ c-C_6H_{11}), 23.77, 23.43, 23.40,(1:4:2, CH c-C_6H_{11}). Anal. calcd for $C_{54}H_{98}Si_7O_{13}TiN_2$ (found) : C 52.82 (52.33), H 8.05 (8.10), N 2.28 (2.06) Ti 3.90 (8.11).

Synthesis of Cl($CH_2)_3$(c-$C_6H_{11})_6Si_7O_{12}TiOPh(TMEDA)$ (***18c***) *from Cl($CH_2)_3$(c-$C_6H_{11})_6Si_7O_{12}TiCp$* (***15d***).

To a solution of Cl($CH_2)_3$(c-$C_6H_{11})_6Si_7O_{12}TiCp$ (57 mg, 0.053 mmol) in benzene (0.5 mL) was added phenol (17 mg, 0.18 mmol) and TMEDA (25 μL, 0.20 mmol). Acetonitrile was added until the starting material just stayed dissolved (150 μL). The solution was heated to 50 ^oC overnight to give yellow crystals of **18c** (41 mg, 0.035 mmol, 85 %).

^1H NMR ($CDCl_3$) δ 7.18 (m, 2 H, $^3J_{HH}$ = 8 Hz m H Ph), 6.90 (d, 2 H, $^3J_{HH}$ = 8 Hz o H Ph), -6.74, (dt, 1 H, $^3J_{HH}$ = 7.6 Hz, p H Ph), 3.61 (br s, 1 H, CH_2Cl), 3.37 (br s, 1 H, CH_2Cl), (2.79 (br s, 4 H, CH_2 TMEDA), 2.58 (s, 12 H, CH_3 TMEDA), 1.76 (m, 25 H, CH_2 c-C_6H_{11}), 1.59 (m, 5 H CH_2 c-C_6H_{11}), 1.27 (m, 25 H, CH_2 c-C_6H_{11}), 1.11 (m, 5 H, CH_2 c-C_6H_{11}), 0.90-0.50 (m, 8 H, CH c-C_6H_{11} + Si-CH_2).

Preparation of [(c-$C_6H_{11})_6Si_6O_{11}]_3[Ti(\mu^3$ -OH)$_4$.(TMEDA) (***22a***).

To a solution of (c-$C_6H_{11})_6Si_6O_7(OH)_4$ (220 mg, 0.025 mmol) and TMEDA (0.050 mL,) in $CDCl_3$ (1.0 mL) was added Ti(O^{i}Pr)$_4$ (80 mg, 0.025 mmol). The mixture was heated to 60 ^oC to give a turbid mixture, containing polymeric Ti-silsesquioxane.

H_2O (10 μL, 0.5 mmol) was added to give a solution, from which the cluster [(c-$C_6H_{11})_6Si_6O_{11}]_3[Ti(\mu^3$ -OH)$_4$.(TMEDA) (100 mg, 60 %) was obtained by adding acetonitrile. ^1H NMR ($CDCl_3$) δ 7.59 (s, 3 H, OH), 3.90 (s, 1 H, OH), 2.58 (br s, 4 H, CH_2 TMEDA), 2.37 (br. s, 12 H, CH_3 TMEDA), 1.78 (m, 30 H, CH_2 c-C_6H_{11}), 1.26, (m, 30 H, 1.27 (m, 35 H, CH_2 c-C_6H_{11}), 0.84 (m, 7 H, CH c-C_6H_{11}), ^{13}C {^1H} NMR δ 27.92, 27.61, 27.37, 27.15,

27.00, 26.88, 26.77, 26.69, 26.30 (CH_2 C_6H_{11}), 24.12, 23.52, 23.20, 23.09 24.05, 23.40 (1:1:1:1:1:1, CH C_6H_{11}), ^{29}Si {1H} NMR δ – 62.31 (broad), - 63.15, - 64.03, - 66.01, - 66.63, - 69.91

IR (KBr, CCl_4): 3619, 3417 cm^{-1} (OH-N), 2923, 2849, 1549, 1460, 1447, 1384, 1355, 1268, 1194, 1070, 1040, 998, 935, 894, 848, 649, 506.

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Chapter 5

Titanium silsesquioxanes screened in catalytic epoxidation

***Abstract**: Novel silsesquioxane titanates are evaluated as catalysts for epoxidation of simple alkenes. Oxidants of choice are TBHP and aqueous hydrogen peroxide. Epoxidation activity is correlated to the mode of silsesquioxane or macrocycle chelation and encapsulation. The extent to which organofunctionalized silsesquioxane ligands acts as molecular substrate receptors seems to be limited.*

5.1 Introduction.

Metal-containing silsesquioxane derivatives provide new catalysts with both homogeneous and heterogeneous applicability. The steric and electronic properties of silsesquioxane silanolate ligands render metal centers more Lewis acidic than conventional alkoxide or siloxide ligands do. This concept has been exploited in newly developed catalysts for alkene metathesis, polymerization, epoxidation, and Diels-Alder reactions of enones[1]

There has been considerable research recently on heterogenization of homogeneous catalysts due to the ease of separation and purification of the products and the recovery of the catalysts.[2] Thus, development of active heterogeneous catalysts with predefined active sites by immobilizing silsesquioxane metal compounds on insoluble supports appears promising (Fig. 5.1).[3]

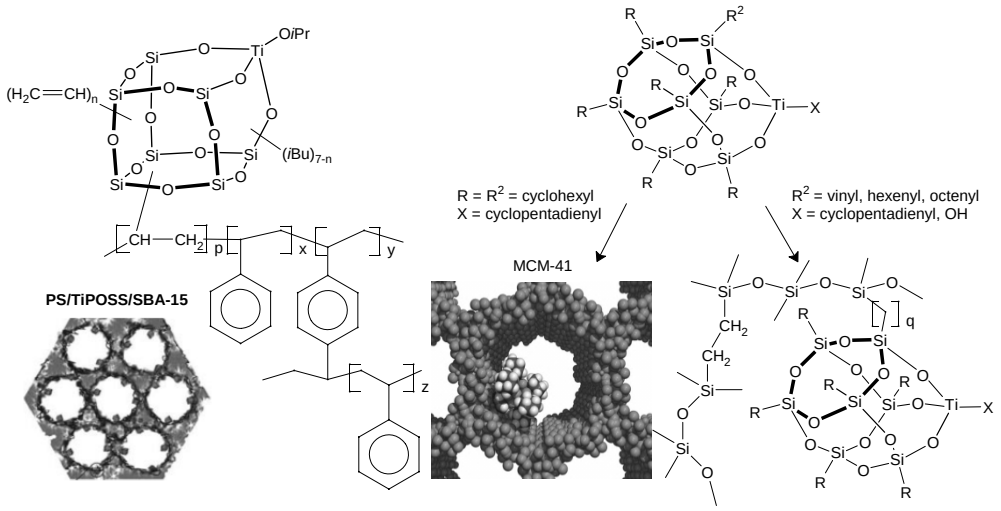


Fig. 5.1 *Approaches to catalytic materials for epoxydation: functionalized styryl POSS immobilized on SBA-15 (left); physisorbed POSS in all-silica MCM-41 (middle); 3D-netted silicone-grafted POSS (right) which presents the first silsesquioxane-based catalyst that works with aqueous hydrogen peroxide.*

Further aiming at catalytic epoxidation employing aqueous hydrogen peroxide, silsesquioxane ligand functionalization to include functional groups that may act as a receptor for peroxide molecules was addressed in the previous chapter. Inspired by the working of natural enzymes, the ultimate goal is to tailor catalytic ensembles with regard to actve site, cavity size and precise, substrate recognition.

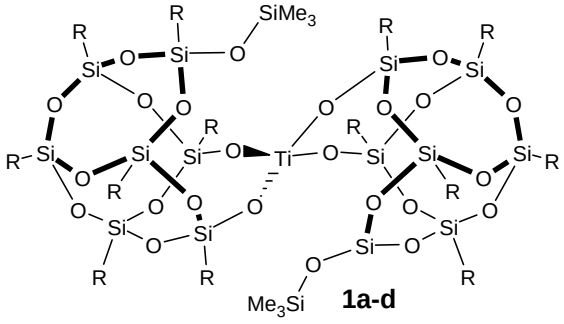
This chapter describes the epoxidation of olefins with TBHP and aqueous hydrogen peroxide, catalyzed by new silsesquioxane metal complexes. The extent of having realized a substrate receptor function to hydrogen peroxide will be discussed.

5.2 Results and Discussion

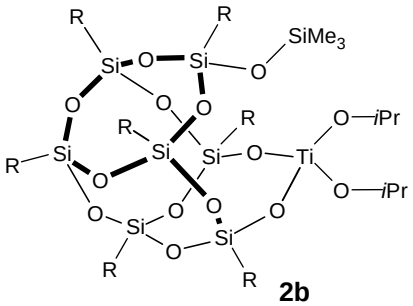
5.2.1. Catalytic epoxidation with POSS-macrocycle-titanium complexes.

Fig. 5.2 shows known (**1-2**) and new (**3-4**) titanates with bidentate coordinating silsesquioxane ligands. Previously, we demonstrated that non crosslinked complexes **3**, hydrolyze faster than their crosslinked, macrocyclic, counterparts **4** (chapter 4).

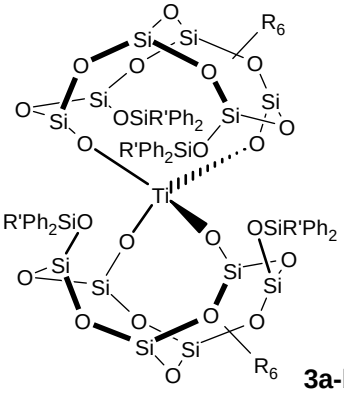
Macrocycle **4a** seemed to be the most resistant to hydrolysis (Fig. 5.2). Clearly, limited hydrolytic stability will be detrimental in catalytic epoxidation. However, driven by curiosity to see if macrocycles **4** behaved different in catalysis than bis-chelated **3**, we departed on an epoxidation study.



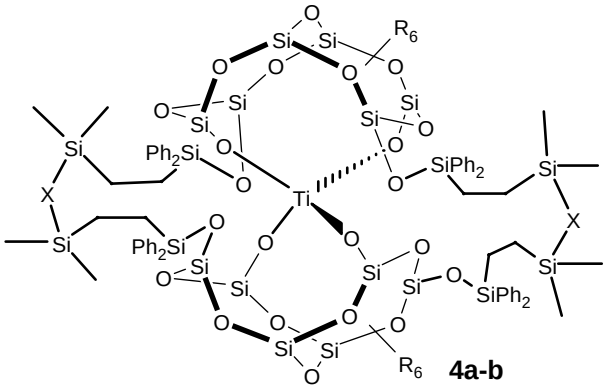
1a-d



2b



3a-b



4a-b

1a R = *c*-C_5H_9
1b R = *c*-C_6H_{11}
1c R = *c*-C_7H_{13}
1d R = i-C_4H_9

2b R = *c*-C_6H_{11}
3a R = *c*-C_6H_{11}, R' = Me
3b R = *c*-C_6H_{11}, R' = vinyl

4a R = *c*-C_6H_{11}, X = O
4b R = *c*-C_6H_{11}, X = $OSiMe_2O$

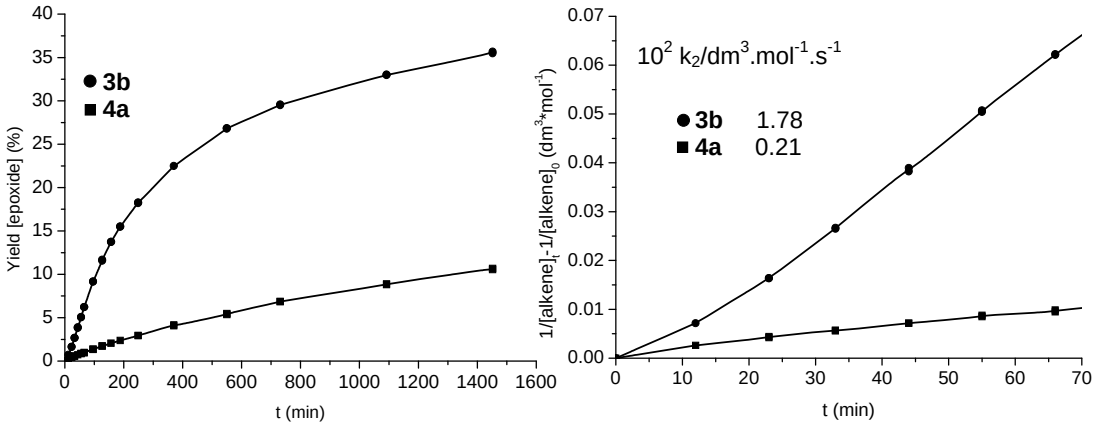


Fig. 5.2 *Bidentately chelated silsesquioxane compounds **1-4** and epoxidation of cyclooctene with TBHP by Ti disilanolate **3b** and Ti-macrocycle **4a** [conditions: [Ti] = 0.001 M, [TBHP] = [alkene] =1.0 M, T = 58 ^oC].*

The complexes **3** and **4** were first submitted to homogeneous epoxidation of cyclooctene with TBHP [conditions**:** [Ti] = 0.001 M, [TBHP] = [alkene] =1.0 M, T = 57 ^{o}C]. Generally, catalytic activity was low and comparable to that of known bidentately chelated silsesquioxane ligands (reference compounds **1**). Epoxidation activity of macrocycle **4a** was lower than that of non-crosslinked **3b.** Using **3b**, the reaction mixture got turbid in the first 10 minutes of reaction, indicating decomposition. Seemingly, this decomposition liberates catalytically active species as is evident from the second order kinetics plot (Fig. 5.2) of **3b** that shows an induction period.

From the linear part of the kinetic plot the k_2 value can be obtained which is about 20 times lower than that of typical tripodal Ti-catalysts (vide infra).
Macrocycle **4a** seems to be stable during the course of the reaction, showing no formation of insolubles, however its inherent k_2 value is even 10 times lower than that of non-crosslinked **3b**. These findings indicate that the dipodal titanium complexes are poor catalysts, that are already unstable with organic oxidants. Catalyst decomposition occurs probably through alcoholysis and generates Ti-species with higher, albeit still low, catalytic activity.[3]

Epoxidation of cyclooctene with aqueous hydrogen peroxide with abovementioned complexes was also performed, the results and conditions are given in Fig. 5.3.

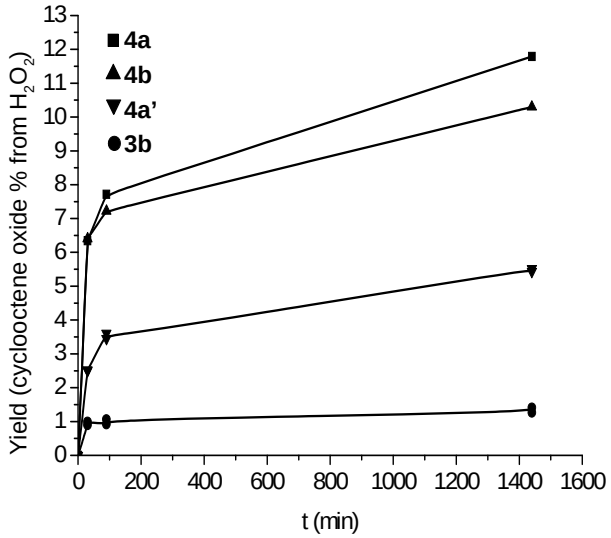


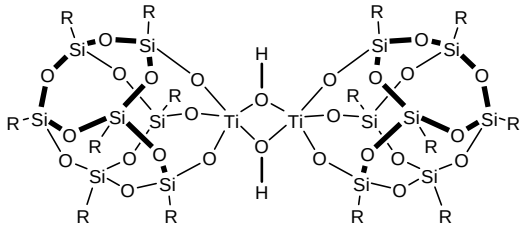
Fig. 5.3 *Epoxidation of cyclooctene with 35 % aq. H_2O_2 by Ti disilanolate **3b** and Ti-macrocycles **4a-b**. [conditions**:** [Ti] = 0.001 M, [alkene] ~ 1.0 M, [alkene] / [H_2O_2] = 4; T = 57 ^{o}C].*

In all cases of epoxidation by aqueous hydrogen peroxide epoxidations we observed a yellow coloration of titanium peroxide in the aqueous phase after 30 minutes. The aqueous layer of **3b** being more intensely colored than that of the cross-linked species, indicating Ti-leaching during the course of the reaction. The organic phase contains only free ligands after full reaction, which we further analyzed by MALDI-TOF-MS. This shows that cross-linking with $(HSiMe_2)_2O$ and $(HSiMe_2O)_2SiMe_2$ give mainly intramolecular reactions forming macrocyclic structures containing 2 silsesquioxanes a and 2 linker residues b (a_2b_2) (see chapter 4 for MALDI-TOF-MS). Though also intermolecular reactions in which more than two silsesquioxane ligands are bound together with both types of linker occur. In the case of $(HSiMe_2O)_2SiMe_2$ this may account for resinous Ti-complex **4b**. Unlike the TBHP-mediated epoxidations, the experiments with H_2O_2 gave the opposite order of activity, indicating that now the bound catalysts have higher activity than the leached titanium.

The two different activities of **4a (**Fig. 5.3, indicated as **4a** and **4a'**) result from the fact that as the crosslinking experiment is not fully reproducible: **4a'** had slightly less crosslinking, ca 30 %, compared to **4a**, with about 20 % of the unsaturated side groups and Si-H groups are still present, as indicated by NMR.

5.2.2 Tripodal titanates: benchmarking epoxidation kinetics.

Before investigating new organofunctionalized titanium silsesquioxanes, robust titanol complexes were subjected to epoxidation screening. [4]



9 R = i-C_4H_9 **11** R = *c*-C_6H_{11}
10 R = *c*-C_5H_9 **12** R = *c*-C_7H_{13}

Fig. 5.4 *Simple and robust silsesquioxane silanols for bench marking epoxidation kinetics.*

The titanium complexes of readily available trisilanol silsesquioxanes were used, containing different (cyclo)alkyl groups.

Using cyclooctene or 1-octene as substrate, catalytic reactions were performed according to epoxidation protocol 1 (see experimental section), using [alkene] = [TBHP] = 1.0 M, with [Ti] = 0.0010 M; T = 58^{o}C. Graphs showing straight lines result when presented in a second order kinetics plot (fig. 5.5), indicating single site activity. At higher conversion, however, deviations from pure second order kinetics occur.

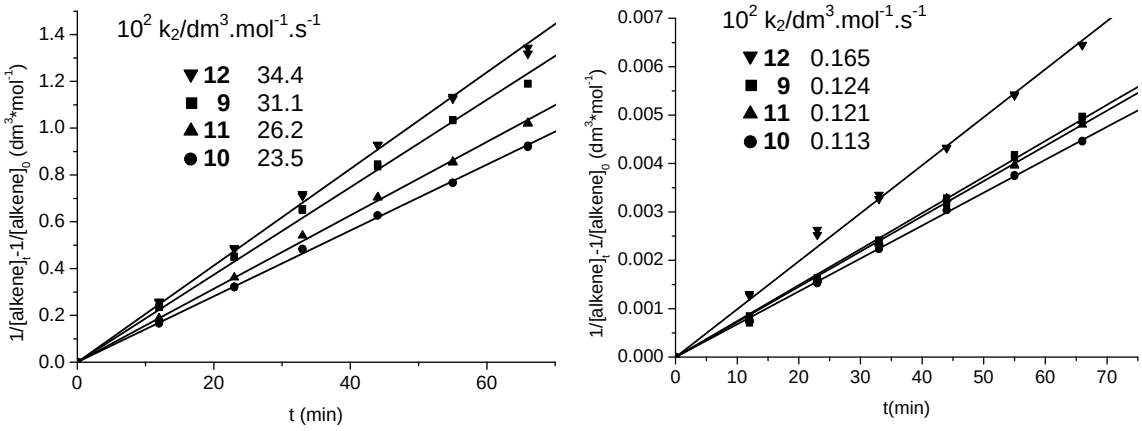


Fig. 5.5 *Second order kinetics for cyclooctene (left) and 1-octene epoxidation by TBHP with* **9-12**. *[conditions: [Ti] = 0.001 M, [TBHP] = [alkene] =1.0 M, T = 58 ^{o}C].*

Although the activity drops for both substrates in the sequence **12-9-11-10**, 1-octene turns out to be a more reluctant substrate, which is epoxidized about 200 times slower, as expected for these electrophilic epoxidations. In several epoxidation experiments that run to high conversion using **9-12**, and especially seen with 1-octene, the reaction was retarded at higher conversion while NMR analysis did not show complex degradation to trisilanol starting materials. Therefore, the influence of the reaction co-product, *tert*-butanol was studied for cyclooctene epoxidation. With a starting concentration of 1.0 M, we still found second order kinetics, but the k_2 value of the catalyst **11** we tested dropped by 45 %. Similar inhibition was also found for THF, triethylamine and *tert*-butanol. This can be explained by the coordinating ability of those compounds. Surprisingly, addition of water (ca 0.1 mmol), did not alter the kinetics, possibly due to its presence as a separate phase.

We also performed the epoxidation of cyclooctene at lower catalyst concentrations. Within the range of 0.2 to 1.0* 10^{-3} M, no significant effect on the rate constant was found, indicating single site behavior (Fig. 5.6).

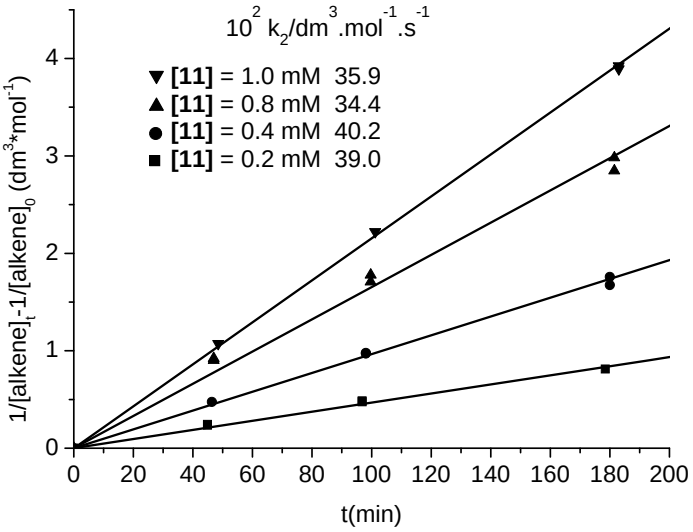


Fig 5.6 *Second-order kinetics plot of epoxidation of cyclooctene by TBHP with four different concentrations of (c-$C_6H_{11})_7Si_7O_{12}$TiOH (**11**). [conditions**:** [Ti] = 0.2 /.1 mM, [TBHP] = [alkene] =1.0 M, T = 58 ^oC].*

In order to account for dimer to monomer shifts that may affect the kinetics in dilution experiments, we determined the aggregation of titanol catalysts **9-12** by vapor pressure osmometry in toluene and THF, see Table 5.1. In the coordinating solvent THF, the amount of monomers increases somewhat on increasing R-group size. This may account for the higher activity of **12**, but the kinetic trends shown in figure 5.5 are not reflected in the osmometric data.

Table 5.1 Aggregation of TiOH catalysts, measured by vapor pressure osmometry[a]

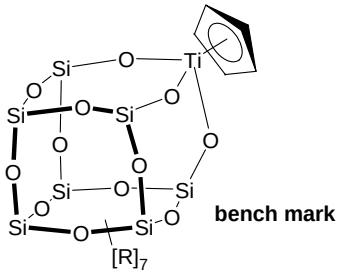
Catalyst	Aggregation/toluene	Aggregation/THF
10	2.0 ± 0.2	2.0 ± 0.2
11	2.0 ± 0.2	1.9 ± 0.2
12	2.0 ± 0.2	1.7 ± 0.2
9	2.2 ± 0.2[b]	2.0 ± 0.2

[a] Conditions: Knauer K-7000: cell temperature; toluene 60 ^oC, THF 45 ^oC; Complex (0.042 mol kg solvent^{-1}), calibrated with $(C_4H_9)_8Si_8O_{12}$ [b] aggregation > 2 unlikely

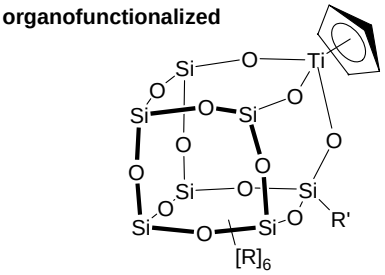
Much desired, full stability of the catalysts cannot be guaranteed, as in repeated catalysis experiments, the yield of epoxide after 30 min. in the case of **11** (or its TiO^{i}Pr congener in protocol 2; see experimental section) gave in their second runs 61 % conversion compared to 78 and 82 % in their first runs respectively, which indicates some deactivation during catalysis. As no leaching to trisilanol was observed, exchange of the side group to a Ti-O-*t*-Bu is most probable, which is also described by Crocker et al[5].

5.2.3. Homogeneous epoxidation of olefins with TBHP by Ti-Cp catalysts.

Early reports[5] and even a more recent one[6] on silsesquioxane Ti-Cp complexes indicated their stability during epoxidation catalysis as evidenced in typically straight kinetic plots. These experiments however, only monitored short reaction times often in combination with high catalyst concentration. As a result, is was reported that the cyclopentadienyl moiety was fully present even after 100 turnovers[7], or not lost while in contact with 1 M hydrochloric acid.[8] These promising features of Ti-Cp, would make it suitable to do quantitative kinetic investigations. We carefully conducted such kinetics, according to experimental protocol 1.



13 R = *i*-C_4H_9
14 R = *c*-C_5H_9
15a R = *c*-C_6H_{11}
16 R = *c*-C_7H_{13}



15d R' = $Cl(CH_2)_3$, R = *c*-C_6H_{11}
15e R' = $NC(CH_2)_3$, R = *c*-C_6H_{11}
15h R' = $H_3CS(CH_2)_3$, R = *c*-C_6H_{11}

Fig. 5.7 *Titanium Cp-silsesquioxanes used for epoxidation of cyclohexene with TBHP: left: benchmark; right: functionalized catalysts*

The Ti-Cp complexes **15a**, **d**, **e** and **h** were chosen and compared with already known tripodal TiCp complexes with R = isobutyl (**13**), cyclopentyl (**14**) and cycloheptyl

(**16**).[9] Earlier hand-made epoxidations of cyclooctene with catalysts **15a-j** with TBHP/catalyst = 500 have shown that **15a**, **d**, **e** and **h** are interesting to examine further: **15a** and **d** being reference materials, **15e** containing the very polar cyano group and also showing the highest activity, and **15h** containing a thioether (Me-S-) group, which can be oxidized to the more polar sulfoxide (Me-S(O)-) or sulfone (Me-$S(O_2)$-) group, which is indeed the case in the reaction with TBHP.

Monitoring the conversion of the substrate reveals a typical activation in the first 100 minutes of catalysis, from which it seems clear that the tripodal Ti-Cp complexes hardly have any intrinsic catalytic activity, but steady conversions resulting in straight lines when plotted with $1/[alkene]_t$-$[alkene]_0$, where $[alkene]_0$ = 1 over t. The full catalyst activity k_2 was obtained from the last four data points presented in fig 5.8.

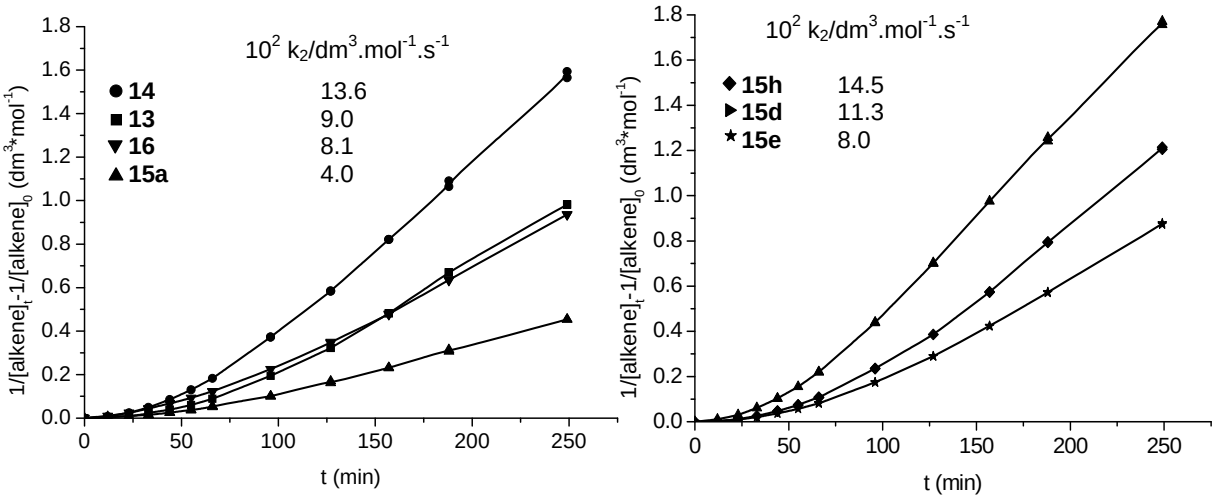
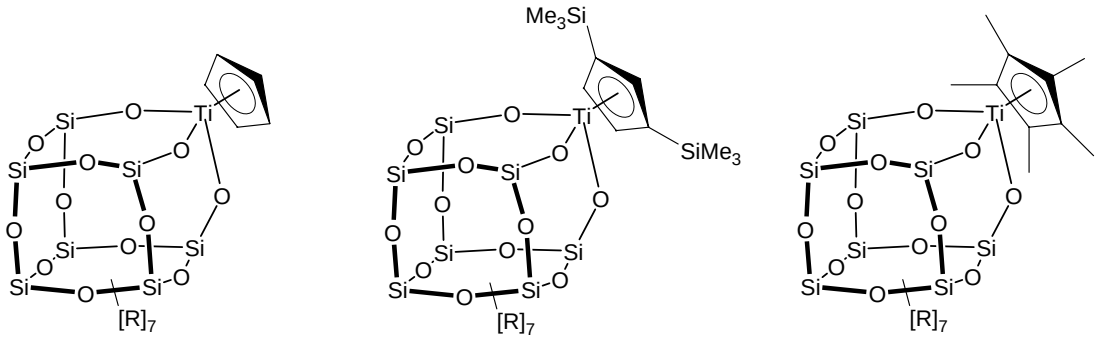


Fig. 5.8 *Second order kinetic plots for cyclooctene epoxidation by TBHP with cyclopentadienyltitanium silsesquioxanes* ***13-16****. [conditions:* *[Ti] = 0.001 M, [TBHP] = [alkene] =1.0 M, T = 58 °C].*

We attribute this onset of activity to the displacement of Cp-moiety by TBHP to form a more active catalyst. However, the maximum activity of these Cp-catalysts is still about one third of that of the corresponding Ti-OH or Ti-O^{i}Pr catalysts. Presumably it is the silsesquioxane Ti-O^{t}Bu, containing more sterically demanding alkoxide group.

Now we wanted to compare the difference of activation behavior of the abovementioned Ti-Cp catalysts. For this we used a different strategy, starting from the normal yield/time plot. The first comparison we made was the activation behavior

of titanium silsesquioxanes with cyclopentadienyl groups of different steric bulk.



15a **17** **18**

Fig. 5.9 *Silsesquioxane titanium complexes (R = c-C_6H_{11}), containing different cyclopentadienyl groups.*

Figure 5.10 shows that complex **17** is the least active and is still activating during the course of the reaction, which is confirmed by the slow protolysis reaction with alcohols (vide supra). Surprisingly, **18** shows no activation period, indicating intrinsic catalytic behavior. An initial activity lower than **15a** was expected due to the more bulky and electron-rich Me_5Cp group.

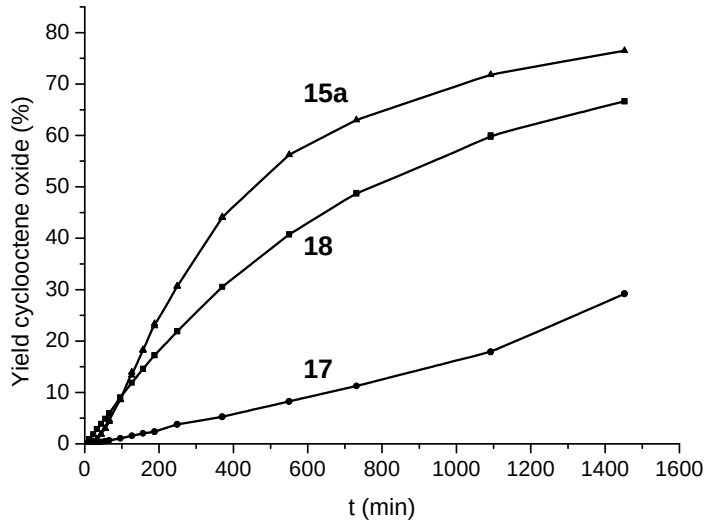


Fig. 5.10 *Epoxidation of cyclooctene by TBHP with (c-C_6H_{11})$_7$$Si_7O_{12}Ti$ with different cyclopentadienyl groups: data points have been omitted for clarity. [conditions**:** [Ti] = 0.001 M, [TBHP] = [alkene] =1.0 M, T = 58 ^oC].*

Now that we have already confirmed that epoxidation catalysis of relatively simple titanol (TiOH) catalysts, is first order in the catalyst, activity can be written as:

$$\frac{d[P]}{dt} = k_2[catalyst]_t[oxidant]_t[alkene]_t \tag{5.1}$$

in which [P] is the epoxide concentration, k_2 can be determined from the maximum slope of the 2nd order kinetics plot, where the catalyst concentration has reached 1 mM.
This makes it a suitable tool to compare the activation behavior of the Ti-Cp catalysts

Regarding TiCp as precatalyst, and its product from reaction with TBHP as the catalyst, assuming first-order activation leads to:

$$[catalyst]_t = [precatalyst]_0 \cdot (1 - e^{-k_{act} \cdot t}) \tag{5.2}$$

with

$$k_{act} = k'_{act} \cdot [oxidant]_0 \tag{5.3}$$

since during the activation of the catalyst, the $[oxidant]_t$ and $[alkene]_t$ are approximately equal to the concentrations at t = 0 (the conversion is less than 5 %)

$$\frac{d[P]}{dt} = k_2[precatalyst]_0(1 - e^{-k_{act} \cdot t})[oxidant]_0[alkene]_0 \tag{5.4}$$

Solving for k_{act}, we get:

$$\log\left(\left(\frac{d[P]}{dt}\right)_{max} - \left(\frac{d[P]}{dt}\right)_t\right) = \log(k_2[oxidant]_0[alkene]_0[precatalyst]_0) - k_{act} \cdot t \tag{5.5}$$

with:

$$\left(\frac{d[P]}{dt}\right)_{max} = k_2[oxidant]_0[alkene]_0[precatalyst]_0 \tag{5.6}$$

The characteristic time for activation of the catalyst, τ is then $1/k_{act}$

Calculating the activation time τ, which is the time necessary to let 1/e = 37 % of the Ti-Cp catalyst remain, we come to values of about 156 min (for **15a**) to 330 min (for **15e** and **16**), which are far beyond the visible onset period of about 80-100 min, as shown in fig. 5.8.

This is due to the fact that the k_2 values obtained from fig. 5.6, are about two times higher than those obtained from the maximum conversion rate in a normal conversion-time plot. When we would use those k_2 values, we would get the expected activation time, which lies typically at 85 min, though shorter times (ca 50 min) are now for **14** and **15h**. Although the method described has its shortcomings, we can conclude that the side chains have no particular influence on the activation of Ti-Cp catalysts.

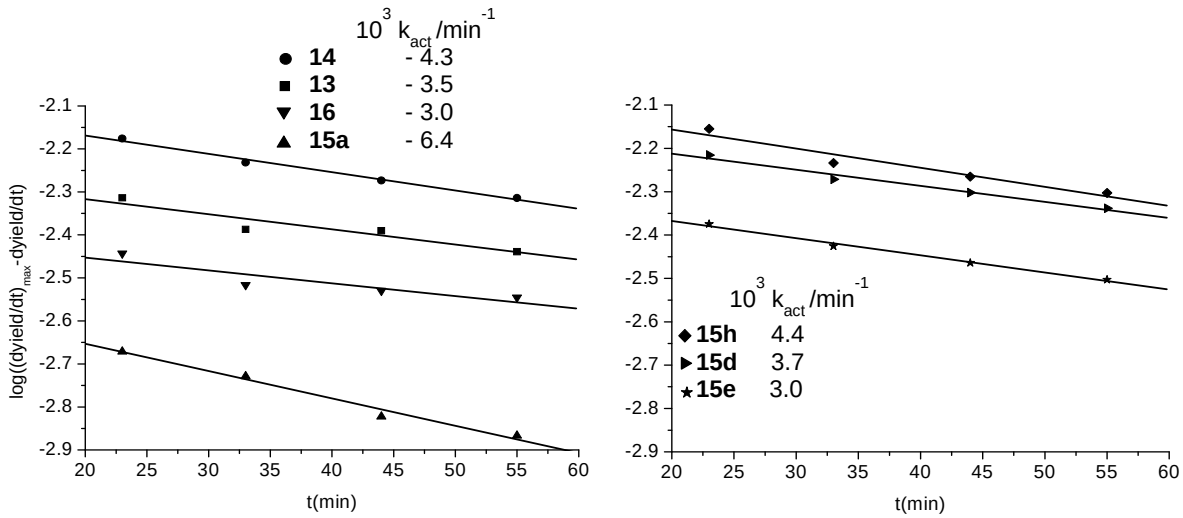
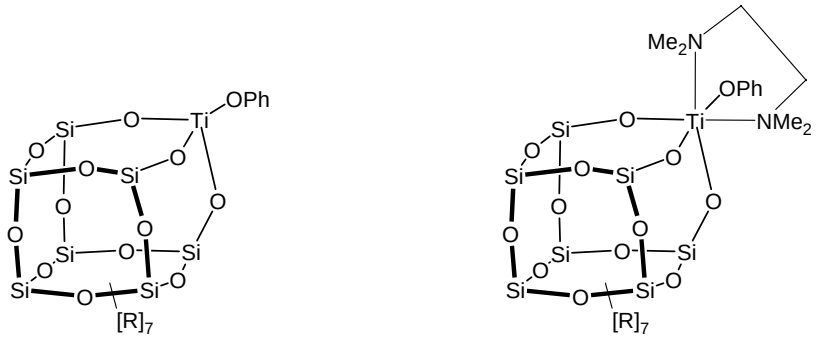


Fig. 5.11 *Determination of the activation constant k_{act} of TiCp silsesquioxanes: k_2 was obtained from fig.5.7.*

*4.2.4. Stability and Catalysis by TMEDA adduct **19**.*

We have tested the catalytic activity of adduct **19** in the TBHP mediated cyclooctene epoxidation and compared it with its parent **18**. (Figure 5.12)



18 **19**

Fig. 5.12 *Silsesquioxane (R = c-C_6H_{11}) titanium phenoxide (**18**) and its TMEDA adduct (**19**).*

As the TMEDA group saturates the coordination sphere, forming a robust complex, one may expect a lower activity. On the other hand, the TMEDA adduct is truly monomeric in solid and solution, which we confirmed by vapor pressure osmometry. One might expect a higher activity, provided that the amine is detached very quickly, leaving a monomeric species, which might be more active than parent **18**. As plotted in Fig 5.13, both catalysts have the same activity, indicating that TMEDA does not inhibit the catalysis, at least when present in a 1:1 ratio with Ti. Even at 20°C, the TMEDA adduct shows full catalytic behavior, indicating a quick detachment of the TMEDA ligand. This is also supported by a rapid decolorization upon addition of the oxidant, which in UV-Vis spectrometry is complete within five minutes at room temperature.

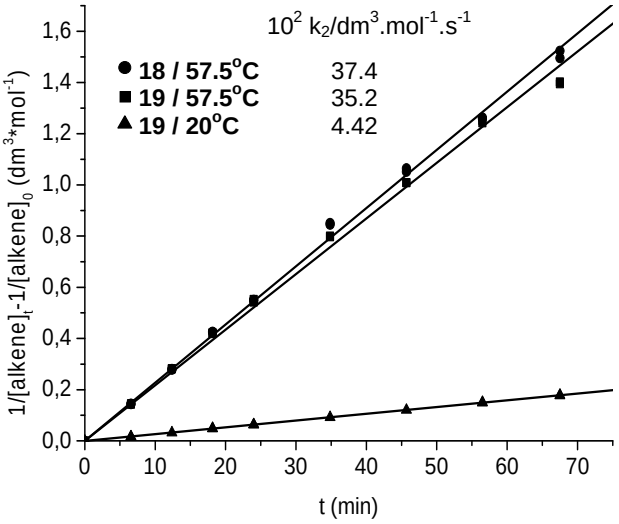


Fig. 5.13 *Second-order kinetics plot of cyclooctene epoxidation by TBHP with free ($(C_6H_{11})_7Si_7O_{12}TiOPh$ **(18)**, and ($(C_6H_{11})_7Si_7O_{12}TiOPhTMEDA$ **(19)** . [conditions**:** [Ti] = 0.001 M, [TBHP] = [alkene] =1.0 M].*

The loss of TMEDA can simply be explained by its oxidation. This was confirmed by test tube experiments with tertiary amines such as Et_3N or TMEDA with TBHP in the presence of titanium catalysts, giving the *N*-oxide or *N,N*-dioxides respectively, which have a much lower affinity towards the Ti-center (chapter 4).

5.3 Conclusions

Dipodal titanium complexes show low catalytic activity with TBHP, which is mostly attributable to leached titanium species. Crosslinking stabilizes the titanium silsesquioxane, but also lowers the catalytic activity. Titanium complexes with a single tripodal ligand and a non-bulky hydroxy group show single-site catalysis, with no influence of monomer-dimer equilibria. The TiCp, except for $TiCp^*$ complexes first need to lose their Cp group in order to form active species. Polarity and bulkiness of the side chains attached to the silsesquioxanes do not lead to higher activity, nor to faster activation. Tripodal Ti-phenoxide and its TMEDA adduct, though monomeric, shows single-site catalysis, with no activation period, which is due to instantaneous oxidative removal of TMEDA during the epoxidation experiment. Unlike all other protic reagents, hydrogen peroxide shows a strong tendency to titanium leaching in all Ti-complexes.

5.5 Experimental Section

GC analyses were determined on a Shimadzu GC-2010 fitted with a 25 m DB-1 column with helium as carrier gas.

Epoxidation Protocols:

Protocol 1: Epoxidation of olefins (cyclooctene, 1-octene) by TBHP.

The reaction was carried out in a Chemspeed ASW1000 automated synthesizer, containing a block with 16 reactor vessels of 13 mL each. All reaction vessels were equipped with a heating jacket, which was connected to a Lauda RM6 Thermostat (- 20 to 90^{o}C) and cold finger reflux condensers. Solutions of alkene (5.0 M in isooctane, 2.0 mL, 10 mmol), TBHP (2.0 M in isooctane, 5.0 mL, 10 mmol), additive (pure isooctane or additive solution, 2.0 mL) was made up to 9 mL. Ten milliliters of catalyst solution was made by dissolving Ti-silsesquioxane (depending on molar mass, 100-200 mg of Ti-silsesquioxane, 0.100 mmol Ti), dissolved in internal standard 1,3,5-trimethylbenzene, (5.75 g) to which isooctane was added till 10.0 mL, giving a [Ti] = 0.010 M. One milliliter of the catalyst solution was transferred to the reaction vessel, containing 9 mL of reactant solution, resulting in a 10 mL reaction mixture, with [Ti] = 0.001 M, [TBHP] = [alkene] =1.0 M. Reaction vessels were heated to 57.5 ^{o}C and vortexed at 600 rpm. At suitable time intervals, samples of 0.1 mL were taken from the reactors and injected to GC vials containing 1.0 mL MeOH. After 24 h, the remaining reaction mixture was transferred into a vial for characterization of the spent catalyst.

The yield for TBHP oxidation of cyclooctene and 1-octene was calculated by the equation: (yield[t=t]) = 100 % * (epoxide [t=t])/(alkene [t=0]).

Protocol 2:

First run: cyclooctene 1100 mg (10.0 mmol), catalyst (53 mg, 0.050 mmol), TBHP (2.31 mmol g^{-1} isooctane solution, 3.65 g, 8.40 mmol), T = 50 ^{o}C, After 24 h, mixture was added to MeOH (60 mL) and allowed to precipitate for 1 h and after filtering and drying, a second run one fifth of the original scale was performed.

Cyclooctene epoxidation by H_2O_2-with **1b**, **3-4**

Catalyst (0.01 mmol Ti) was dissolved in cyclooctene (880 mg, 8.0 mmol) and 1,3,5-trimethylbenzene (86 mg) in 1.5 mL reaction vials fitted with a stirrer bar. H_2O_2(35 % aq, 200 mg, 2.0 mmol) was added and the yield of cyclooctene determined by GC. The yield was calculated by: (yield[t=t]) = 100 % * (epoxide [t=t])/(H_2O_2 [t=0]).

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Summary

Few catalysts have been truly efficient in alkene epoxidation with aqueous hydrogen peroxide. Development of such catalysts is an important goal since with regard to desirability, this oxidant comes only second to oxygen itself. Aim of this theses is to provide a technology push for enabling immobilization of silsesquioxane metal complexes and to exploit these in the context of sustainable catalytic epoxidation.

Currently, the best catalyst in this field is the synthetic, titanium containing zeolite, titanium silicalite-1 (TS-1), which is active for a wide range of oxidation reactions, including epoxidation. For TS-1, activity seems to originate from a combination of a robust active Ti(OSi)n site (n = 3, 4), and its location in a hydrophobic channel or cavity in the MFI (ZSM-5) structure. The resulting catalytic ensemble prevents poisoning of the active site by water as well as unproductive decomposition of the oxidant.

Titanium containing silsesquioxanes provide soluble catalysts that model the active sites of TS-1. As such, they provide an interesting starting point for the development of new epoxidation catalysts. Their scope of application, however, largely relates to the use of less desirable organic oxidants.

First results with silsesquioxane immobilization demonstrated that grafting of functionalized titanium silsesquioxanes on polysiloxanes provided a way to realize the formation of a catalytic ensemble that was capable of performing epoxidation with aqueous hydrogen peroxide. Clearly, the entire system was capable of outperforming the sum of its parts; it is the synergy between active site and its environment that allows hybrid catalysts, and likewise TS-1, or even metalloenzymes to achieve their desirable performance.

Further aiming at catalytic epoxidation employing aqueous hydrogen peroxide, silsesquioxane ligand functionalization was realized to include functional groups that may act as a receptor for peroxide molecules. Following Nature’s concepts, the ultimate goal is to tailor catalytic ensembles with regard to active site, cavity size and precise substrate recognition.

For useful receptors, urea derivatives were aimed at. The fact that urea forms a very stable adduct with hydrogen peroxide while it does not complex water provides a first indication that such receptors can be made. In order to combine substrate receptors with robust silsesquioxane titanates, new routes to silsesquioxane ligands were first developed here, in particular new organofunctionalized trisilanol ligands.

The synthesis of trisilanols of type $(c\text{-}C_6H_{11})_6R'Si_7O_9(OH)_3$ containing a functionalized organic substituent R' was realized by reaction of tetrasilanol $(c\text{-}C_6H_{11})_6Si_6O_7(OH)_4$ with a functional trialkoxysilane $R'(SiOR'')_3$. It was established that relatively small non-polar side chains give the highest yields, whereas amino groups and derivatives thereof give gels, consisting of many different species. Furthermore, functionalization of silsesquioxanes, containing unsaturated side chains was effected through hydroformylation rendering aldehydes, and through a modified Wacker oxidation to create ketone functions. In this way, routes were opened to further functionalization. Selective hydroformylation is possible for silsesquioxanes containing no free hydoxyl groups, including titanium cyclopentadienyl silsesquioxane. The scope of Wacker-type oxidation is more limited.

Following bio-inspired ideas to catalyst design, the synthesis of large, macrocyclic silsesquioxanes titanates was also realized. In this context, the titanium complex of a doubly disilylated tetrasilanol was described. The crystal structure shows an ideally tetrahedrally surrounded titanium atom with highly distorted ligands. This complex contains four unsaturated side groups per titanium, and is utilized in the synthesis of titanium macrocycles. The hydrolytic stability of new titanium complexes was investigated and related to the dentacity of titanate chelation with secondary influence by the macrocyclic cages.

The functionalized trisilanols described in chapter 3 are transformed into cyclopentadienyl titanium complexes. Thorough investigation of its stability towards water, peroxides and alcohols, reveals a base catalyzed loss of the cyclopentadienyl group, which is cleanly substituted by the alkoxy group of the corresponding alcohol. Novel base adducts were formed in the case of electron-withdrawing alkyl group containing alcohol. Their synthetic scope has been described.

The epoxidation of simple olefins with *tert*-butyl hydroperoxide (TBHP) and aqueous hydrogen peroxide has been studied. Though the titanium macrocycle system shows increased stability towards the oxidant, its activity is lower than that of other bidentate

titanium systems. Though increased activity was found with hydrogen peroxide, compared to open systems, leaching of the metal is still the main limitation.

Single-site behavior of titanium hydroxyl silsesquioxanes was found in kinetic experiments in the epoxidation of cyclooctene with THBP. Effects of monomer-dimer equilibria were not found. In the case of titanium cyclopentadienyl silsesquixanes, the activity increased during the epoxidation reaction, which could be attributed to the loss of the cyclopentadienyl group. No clear influence of the incorporated functional side groups in the activity or activation could be found.

Samenvatting

Er zijn nog maar weinig katalysatoren, die echt efficient zijn in de alkeenepoxidatie met waterige waterstofperoxide. Ontwikkeling van dergelijke katalysatoren is een belangrijk doel aangezien dit oxidatiemiddel, op elementaire zuurstof en lucht na, het meest milieuvriendelijk en atoom-efficient is. Het doel van dit proefschrift is het uitbreiden van de technologie om silsesquioxaangebaseerde metaalcomplexen te immobiliseren, gericht op duurzame epoxidatiekatalyse.

De beste katalysator voor alkeenepoxidatie is momenteel een synthetische titaanhoudende zeoliet, titaansilicaliet (TS-1), welke bruikbaar is voor een scala aan oxidatiereacties, waaronder epoxidatie. De activiteit van TS-1 lijkt voort te komen uit een combinatie van een robuuste actieve site (de plaats waar de gekatalyseerde reactie plaatsvindt), $Ti(OSi)_n$ (n = 3, 4), welke zich bevindt in een hydrofoob (waterafstotend) kanaal of holte binnen de MFI (ZSM-5)-structuur. Het resulterende katalytisch ensemble voorkomt deactivatie van de actieve site door water, alsmede onnodige ontleding van het oxidatiemiddel.

Titaanhoudende silsesquioxanen zijn een klasse van oplosbare katalysatoren, die een goed model vormen voor de actieve sites van TS-1. Als zodanig zijn zij geschikt als startpunt voor voor de ontwikkeling van nieuwe epoxidatiekatalysatoren. Hun toepasbaarheid is op dit moment grotendeels beperkt tot het gebruik van (minder gewenste) organische oxidatiemiddelen.

De eerste resultaten van silsesquioxaan immobilisatie laten zien dat het binden van gefunctionaliseerde titaansilsesquioxanen aan siliconenpolymeren een geschikte synthesemethode is voor een katalytisch ensemble, welke goede epoxidatieactiviteit vertoont met waterige waterstofperoxide. Dit systeem functioneert duidelijk beter dan de som der delen: het is de synergie tussen de actieve site en zijn omgeving, dat bovengenoemde “hybride” katalysator, en mogelijkerwijs ook TS-1, en zelfs metalloenzymen zijn gewenste eigenschappen geeft.

Voor ontwikkeling van de epoxidatiekatalyse met waterige waterstofperoxide, is de verdere functionalisering gerealiseerd van silsesquioxanen met organische groepen, die als receptor kunnen dienen om waterstofperoxide te binden. Het uiteindelijk doel is volledig aan de

concepten der natuur te voldoen, waarin net als bij enzymen, het katalytisch ensemble kan worden aangepast, zodanig dat de actieve site, de hydrofobe holte en substraatherkenning elkaar aanvullen.

Ureum-gebaseerde structuren vormen het hierin het hoofddoel. Het feit dat ureum een stabiel adduct vormt met waterstofperoxide, en niet met water, geeft ons de indicatie dat dit geschikt is als receptor. Om de koppeling tussen subtraatreceptor en silsesquioxaan mogelijk te maken, werden nieuwe syntheseroutes ontwikkeld, in het bijzonder silsesquioxaan trisilanolliganden met organische functionele groepen.

De synthese van trisilanolen van het type (c-$C_6H_{11})_6R'Si_7O_9(OH)_3$, met R' als functionele groep werd uitgevoerd met door reactie van tetrasilanol (c-$C_6H_{11})_6Si_6O_7(OH)_4$ met een gefunctionaliseerd trialkoxysilaan $R'Si(OR'')_3$. Deze reactie blijkt de hoogste opbrengst te geven wanneer kleine apolaire zijgroepen worden toegepast. Aminogroepen en derivaten daarvan geven echter een ongedefinieerd gelachtig materiaal. Verder werden functionaliteiten in silsesquioxanen ingebouwd door eerst een simpele onverzadige zijgroep in te bouwen, en deze nadien te hydroformyleren tot aldehydes, of via de Wacker oxidatie om te zetten in ketonen. Deze bieden de potentie om verder te worden gefunctionaliseerd. Selectieve hydroformylering is enkel mogelijk voor silsesquioxanen zonder vrije hydroxylgroepen, inclusief cyclopentadienyltitaanverbindingen. De Wacker-type oxidatie is echter beperkter, zowel qua soorten van silsesquioxanen als vervolgreacties voor verdere functionalisering.

In navolging van door de biologie ingegeven concepten, hebben we silsesquioxanen covalent met elkaar weten te verbinden om zo een macrocyclisch systeem te genereren. Hiervoor werd een titaancomplex met twee gedisilyleerde silsequioxaanliganden gebruikt. Het vrije complex kon worden gekristalliseerd, en zijn structuur worden bepaald. Het complex bevat vier onverzadigde zijgroepen per titaanatoom. Deze kunnen per twee door hydrosilylering aaneen verbonden worden tot een structuur, welke omschreven kan worden als “macrocycle”. De hydrolytische stabiliteit en de stabiliteit tegenover waterstofperoxide tijdens de epoxidatieexperimenten is onderzocht, in relatie met de dentaciteit en chelatie door de macrocycle.

De gefunctionaliseerde trisilanolen, beschreven in hoofdstuk 3 zijn omgezet in titaan-cyclopentadienylcomplexen. Diepgaand onderzoek naar de stabiliteit ten opzichte van water, peroxides en alcoholen onder verschillende omstandigheden geven bewijs voor een basegekatalyseerde vervanging van de cyclopentadienylgroep. In het geval van alcoholen

wordt deze selectief vervangen wordt door de betreffende alkoxygroep. Nieuwe adducten met basen werden gevormd, in het geval dat het betreffende alcohol een electronenzuigende groep bevat. Hierin is ook gekeken naar de synthese en stabiliteit van verschillende base-complexen.

De epoxidatie van enkelvoudige alkenen met *tert*-butylhydroperoxide (TBHP) en waterstofperoxideoplossingen in water is verder bestudeerd met de bovengenoemde systemen. Hoewel titaanmacrocycles een hoger stabiliteit hebben ten opzichte van beide oxidatiemiddelen, is de activiteit met TBHP lager dan het open bidentaatsysteem. Dit in tegenstelling tot waterstofperoxide; waarbij de macrocycles actiever zijn, hoewel ook hier het metaal door de waterstofperoxide uit het silsesquioxaansysteem wordt “uitgeloogd”.

Tenslotte is de kinetiek van de homogene epoxidatie van alkenen met TBHP onderzocht op tripodale titaan-hydroxylsilsesquioxanen, die dimeer zijn en een monomeer TMEDA complex. In al onze experimenten werd ‘single site’ gedrag waargenomen, zonder effecten van monomeer-dimeerevenwichten op de katalyse. Cyclopentadienyltitaansilsesquioxanen geven een toename van de activiteit gedurende het epoxidatieexperiment, welke toe te schrijven is aan het verlies van de cyclopentadienylgroep. Er kon geen duidelijke invloed gevonden worden van functionele zijgroepen op de activiteit en activatie van de complexen.

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AZAP CENGIZ [DE]; WOLF DORIT [DE]; ABBENHUIS HENDRIKUS CORNELIS LOUIS [NL]; GERRITSEN GIJSBERT [NL]; GRELA KAROL [PL]; WILTING JOS B M [NL]; LESZCZYNSKA KINGA [PL]; CZABAN JUSTYNA [PL]; WOJTASIEWICZ ANNA [PL]

POLYSILSESQUIOXANE (POSS)-LINKED IMIDAZOLE-BASED CARBENE AND PHOSPHINE LIGANDS FOR TRANSITION METAL CATALYSTS
AZAP CENGIZ [DE]; WOLF DORIT [DE]; ABBENHUIS HENDRIKUS CORNELIS LOUIS [NL]; GERRITSEN GIJSBERT [NL]; GRELA KAROL [PL]; WILTING JOS B M [NL]; LESZCZYNSKA KINGA [PL]; CZABAN JUSTYNA [PL]; WOJTASIEWICZ ANNA [PL]
Patent filed: 23-05-2010

Curriculum vitae

Gijsbert Gerritsen werd geboren op 22 april 1975 te Nijkerk. In 1987 begon hij zijn middelbare schoolopleiding aan de Chr. Mavo te Nijkerk, welke in 1989 voortgezet werd aan het Christelijk College Nassau-Veluwe te Harderwijk, alwaar hij in juni 1992 zijn HAVO-diploma behaalde. In augustus 1992 is de auteur begonnen aan het Hoger Laboratoriumonderwijs (HLO), richting organische chemie aan de Hogeschool Utrecht. Tijdens zijn bedrijfsstage heeft hij in 1995 aan het Shell Research and Technology Centre Amsterdam (SRTCA) werd gewerkt aan vervangers voor isocyanaten en de in-situ vorming van isocyanaten. Na zijn diploma in 1996 behaald te hebben, begon hij zijn verkorte doctoraalstudie scheikunde aan de Universiteit Utrecht. Zijn afstudeeronderzoek heeft hij uitgevoerd in de vakgroep van prof. Dr. L. Brandsma, alwaar hij ringsluitingsreacties van gesubstitueerde allenen richting pyrrolen en dihydropyridines onderzocht. Tevens werd de selectieve synthese van fosfines door reactie van fosfor met alkalimetalen in vloeibare ammoniak onderzocht. Het diploma (“met genoegen”) werd in augustus 1998 behaald. In mei 2000 is hij zijn onderzoek aan de Technische Universiteit Eindhoven begonnen aan silsesquioxanen voor polymerisatiechemie bij dr. R. Duchateau. Het accent werd in augustus 2001 verlegd naar silsesquioxaansystemen voor titaangekatalyseerde epoxidatie bij dr. H. C. L. Abbenhuis. Het hier verricht onderzoek was deels aanleiding voor Abbenhuis om zijn eigen bedrijf, Hybrid Catalysis B.V. op te richten, alwaar de auteur sinds november 2005 in dienst is.