Silsesquioxanes: realistic homogeneous model systems for various silica surface silanols
Dijkstra, T.W.

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“I was taught that the way of progress is neither swift nor easy.”

Madame Marie Curie
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Introduction

In this chapter some background information is provided in order to place the following chapters in perspective. Silsesquioxanes are demonstrated to be applicable as versatile homogeneous model systems to unravel some of the complexity of heterogeneous and homogeneous supported catalysts. Also, they prove to be valuable in distinguishing between some properties of siliceous materials, including zeolites. The quest for expanding the knowledge of influences of local surface features on reactivity with substrates or catalytic activity will be explained. An overview of the contents of this thesis, which contributes in ending this quest, will be given.

1.1. Silicates

Silicon and oxygen are two of the most abundant elements in the earth’s crust. The Si-O bond and Si-O-Si-O-Si networks are among the strongest known skeletons in silicate chemistry. In silicates all silicon atoms are tetrahedrally coordinated by four oxygen atoms. SiO₄ units are the molecular building blocks from which naturally occurring silicates are constructed. Silicates can exist in the form of chains, layers, rings, or network structures. Three-dimensional silicate networks and zeolites (a special type of crystalline silicates, further explained in section B of this section) contain channels and cavities of molecular dimensions and are used for several applications. Amorphous mesoporous silicas are generally cheap materials and can be used as adsorbents due to their hydrophilic nature. In detergents they are used as filters because of their high specific surface area and when metal ions are present (as in zeolites) they act as softeners as well. Silicate can act as a support for heterogeneous or homogeneous catalysts or can act as catalyst itself. Due to the complicated structure of the siliceous materials, characterization of the surface properties on a molecular level, and elucidating the mechanism when involved in catalytic processes is difficult. An accurate model system for silica surface properties or silicate based catalytic active species could provide such information.

This thesis will deal with homogeneous model systems, experimentally obtained from incompletely condensed silsesquioxanes. The name silsesquioxane denotes that each silicon atom is connected to three oxygen atoms; silsesquioxanes have as general formula (RSiO₃/2)n (n ≥ 4, R = H, organyl, halogen, etc.). When R is small (e.g. H, Me), self assembly into fully condensed cage structures occurs: When R is sufficiently sterically demanding (e.g. cyclopentyl, isobutyl), self assembly into incompletely condensed cage structures occurs (Scheme 1). Incompletely condensed cage structures
Chapter 1

show striking similarities to known morphologies of silica and are considered to be one of the most realistic homogeneous models for silica surface properties or silicate-based catalytically active species. A hydrophobic shell formed by bulky alkyl groups substituted at the corners of the silicate cages makes the molecules soluble in organic solvents. This enables investigation on a molecular level with a wide range of powerful techniques such as multinuclear solution NMR spectroscopy and single crystal diffraction. In the next paragraphs some concepts involving siliceous materials for which silsesquioxanes can be used as models systems will be described. Subsequently the present-day field of incompletely condensed silsesquioxanes and related metallo-silsesquioxanes will be sketched. Some examples will be given in which the usefulness as silica model systems is demonstrated. Finally the contents of this thesis will be outlined in short.

Scheme 1. The condensation of RSiX₃ into silsesquioxanes (X is highly reactive, R is chemically stable). Depending on R the resulting cage structures are fully condensed (route i) or incompletely condensed (route ii).

A. Silica supports

A support possesses several functions but is usually supposed to be catalytically inactive itself. In partnership with the active species it can however participate in the total reaction in important ways. A silica support that is widely used is silica gel. Silica gels have a high surface area which can be obtained in the range 100-800 m²/g. Silica gels are prepared from organic silicates like silicon alkoxide. The main variables in the preparation of silica gels are (1) the kind of alkali metal used, (2) the ratio of SiO₂ to alkali metal oxide, (3) the initial concentration of the soluble silicates, and (4) the acidity.
During the preparation it is important to control the acidity; this ensures that polymerization of silanols into siloxanes is stimulated and particle growth without aggregation is enhanced. Depending on the way the silica gels are further treated, aquagels (pores are filled with water), xerogels (water is removed from the pores by evaporation), aerogel (liquid is removed while collapse or change in the silica structure is prevented), etc. are obtained. Commercially used silica gels contain as main impurities sulphur, sodium, aluminum, iron and titanium. Silica with a small amount of impurities can be obtained by the hydroxylation of purified SiCl₄ at high temperature and is called pyrogenic silica. All silica supports have surface silanol groups present. The number and type of silanol can be directed by altering the calcination temperature or by silylation reactions. The surface properties influence the supported catalytic species directly. When the distance between silanols is small enough, hydrogen bonding can occur which affects the reactivity towards substrates. Metal precursors are not necessarily linked to the surface in a mono-dentate fashion. When silanols are located close to each other also multi-dentate bonding with substrates can occur. Other surface properties that can either stimulate or inhibit catalytic activity are surface defects.

Studying possible surface effects separate from each other would offer a tool to elucidate some of the complexity of a silica surface. Synthesis of accurate (homogeneous) model systems for discrete local surface properties would make this possible.

B. Zeolites

Special classes of mesostructured siliceous materials are zeolite structures. These crystalline aluminosilicates are build from [SiO₄]⁴⁻ and [AlO₄]⁵⁻ tetrahedra that are connected by shared oxygen atoms and form channels, cages or cavities of defined size. Cronstedt first discovered this type of material in 1756, he found that on heating, the mineral he studied (stilbite) lost water rapidly and seemed to boil. He called the material zeolite, from the Greek words zeo (to boil) and lithos (stone). The overall framework charge of zeolites is negative, which can be compensated by cations like protons and alkali metals. Compensation of the negative charge by protons in some cases results in strong Brønsted acidic sites that are capable of catalyzing several organic reactions with high activity. Small modifications during the preparation (i.e. Si/Al ratio, temperature, pH, metal ion content to incorporate in the SiO₂ framework) result in a wide variety of zeolites. An example of a zeolite structure is depicted in Figure 1. Crystalline zeolite type structures with incorporated Si, Al, P, B, Ga, Fe, Ti, Zn, Sn, etc. each have unique chemical and physical properties due to differences in adsorption properties, molecular dimensions, and electronic properties. Finding an explanation for these different properties and ultimately designing tailor-made zeolite catalysts for a given process or reaction (zeolite synthesis has been mainly an empirical field) has inspired many scientists in experimental or computational directions.
Catalysis as a whole comprises heterogeneous, homogeneous, and enzymatic catalysis. Berzelius applied the Greek word catalysis (literally meaning decomposition or dissolution) in 1835 to describe a new phenomenon in chemistry. In 1911 Ostwald redefined this catalytic force that is responsible for carrying out reactions, into catalytic substances which affect the velocities of the chemical reactions and do not influence the thermodynamic equilibrium of reactants and products. Typical in homogeneous and enzymatic catalysis is that catalytic processes take place in one phase. This is not the case in heterogeneous catalysis. In heterogeneous catalysis surface properties, at which the catalytic reactions usually take place, are of crucial importance. The first step in a heterogeneous catalyzed reaction, in the Langmuir-Hinshelwood approach, is adsorption of the reactants on the surface of the catalyst. Subsequently the adsorbed species reacts (often in several consecutive steps) and finally the product desorbs from the surface while regenerating the active sites on the surface. To improve the properties of the catalysts (i.e. lifetime, robustness), catalytically active sites are often dispersed on porous supports such as silica gel or γ-alumina. The overall catalytic activity and selectivity is determined by the composition and structure of the catalyst surface and is very sensitive to details in catalyst preparation. Catalysts can be metal-oxides, metal-sulfides, metal-carbides or organometallic complexes.

Due to complexity of the catalytic system, consisting of multiple active sites, characterization of the structure of the active site and elucidating the mechanism of the catalytic process is difficult. A model catalyst can provide valuable fundamental information and is obtained either from experimental or computational studies; the results are often combined to estimate the value of the recommendations. By using the surface organometallic chemistry (SOMC) approach, developed by Basset et al., relatively well-defined active surface sites are synthesized with a uniform distribution and rather high concentration, which has greatly contributed to the understanding of several heterogeneous catalytic processes. In surface science model systems, (usually) flat oxidized silicon wafers are used as realistic models for industrially applied catalyst supports. These wafers are loaded with the active phase and a
molecular level picture of the active surface is obtained by studying the properties by surface science
techniques. Metals can be deposited on the model support by evaporation but in that case the particle
size distribution is rather broad. Another method is to deposit the active phase by chemical vapor
deposition or deposit the catalysts precursor via wet chemical techniques, followed by drying and
reduction steps. Homogeneous model catalysts are for instance silsesquioxanes.

D. Supported homogeneous catalysts

Heterogeneous catalytic processes are usually applied in bulk chemistry. The large scale of the
processes and the extreme reaction conditions that are used (i.e. high pressure, high temperature) are
not suitable for the production of fine chemicals. Fine chemicals are often thermally unstable and the
complex synthesis routes require moderate reaction conditions in the liquid phase. Well-defined
homogeneous catalysts meet these requirements and ensure high efficiency in stereoregular control of
the products and reduce the formation of byproducts. To facilitate the separation of the homogeneous
catalysts from the products, they can be immobilized on a support. In this way, the positive effects of
catalytic performance and practical use are combined. Recyclable heterogenized catalytic systems can
be obtained in different manners

• When immobilization occurs via grafting, a covalent bond between the catalyst and the inorganic
support is created, which should prevent leaching of the grafted moiety (Figure 2A). Metal
complexes are, for instance, anchored by reaction with silica surface hydroxyls (silanols). For
some metal complexes a more stable bond is ensured when the silanol is first chemically modified
by the introduction of alkoxysilane. A suitable linker is of the type (RO)₃Si-X-L in which L is the
ligand to coordinate to the metal precursor and X is a chemically inert spacer. This anchoring
technique is called tethering (Figure 2B). Another route towards tethered species is via
immobilizing a pre-synthesized catalyst precursor containing an anchorable functionality.

• Homogeneous complexes can be physically encapsulated in mesoporous structures that exist in,
for instance, sol-gel silica or polymer structures (Figure 2C). The host-guest interaction is neither
covalent nor ionic. The guest stays in the host matrix but leaching of the complex through for
instance a channel is possible.

• Physisorption of metal complexes on a pre-treated surface is another immobilization technique
(Figure 2D). The catalytically active compounds interfere with carrier material by van der Waals
interactions. Acids, bases as well as salts, oxides or complexes can be immobilized in this manner.
A major drawback is again the possibility of leaching.

Studying immobilization strategies, stability of the supported catalyst, and electronic/steric effects of the
support on the catalysts performance using homogeneous models would considerably contribute to the
molecular level understanding of supported catalysts.
1.2. Silsesquioxanes

Silsesquioxanes are obtained by polycondensation of trifunctional monomers RSiX$_3$ where R is a chemically stable organic substituent and X is a highly reactive substituent such as chloride or alkoxide. Condensation is usually started by slowly adding water; RSiX$_3$ is hydrolyzed and the resulting silanol groups convert to siloxanes (Scheme 1). By a careful choice of organic substituent condensed or incompletely condensed three-dimensional silicate cages are obtained with usually 6 or 8 (RSiO$_2$)$_n$ units (Scheme 1). The most often used incompletely condensed silsesquioxanes is the tri-silanol R$_7$Si$_7$O$_9$(OH)$_3$ (Figure 3C). Although first reported by Brown et al., Feher and co-workers are considered to be leaders in exploiting the remarkable properties of this silsesquioxane ligand. Synthetic methodologies for silsesquioxane preparation are well-documented and Feher and co-workers have carried out impressive work on both improving existing and developing new silsesquioxane synthesis routes.

Silsesquioxane cage structures can be regarded as small three-dimensional pieces of silica. Their assembly result in rigid structures that resemble for example close-range SiO$_2$ morphologies of (111)β-crystobolite and (001)β-tridymite (Figure 3A and 3B). Incompletely condensed silsesquioxanes not only structurally resemble various silica surface silanol sites. Other homogeneous model systems for silica surface silanols or silica properties are available in vast amount (i.e. R$_3$Si-OH, R$_3$Si-O-SiR$_3$, R$_2$Si(OH)-OSi(OH)R$_2$, R$_2$Si(OH)$_2$) but non of these systems can mimic the local rigidity of silica as silsesquioxanes can.
Figure 3. Structural similarities between silsesquioxanes and silica features: (111) face of β-crytstabolite (A.1 and A.2), (001) face of β-tridymite, several presentation of R$_7$Si$_7$O$_9$(OH)$_3$ (C.1, C.2 and C.3).

During the last decade a wide variety of hetero-silsesquioxanes and metalla-silsesquioxanes have been prepared and described in detail, which are covered in some excellent review articles.$^{8,32,40-45}$ Figure 4 gives an overview of the elements that have been applied in silsesquioxane chemistry. The most recently applied element is indium.$^{46}$

Figure 4. Elements (darker squares) that have been incorporated in silsesquioxane complexes.
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1.3. Silsesquioxanes applied as model systems

In the last two decades, silsesquioxane chemistry has developed into a versatile tool to clarify various issues of supported catalysts. Interesting metalla-silsesquioxanes have been reported that represent surface sites in metal-supported or metal-incorporated silicates that play an important role in industrially applied catalysts. Important characteristics of silica-supported catalysts that can be observed in the corresponding metal-containing silsesquioxane complexes include a rigid, electron-withdrawing siloxide structure and the possibility of adjacent oxygen donors to interact with the metal center. Also some silica surface properties could be imitated by silsesquioxanes. Some representative examples will be given here.

A. Silica supports

Incompletely condensed silsesquioxanes have proven to be realistic homogeneous models for various surface silanol sites found in (partly dehydroxylated) amorphous- and mesoporous silicas and (dealuminated) zeolites (Scheme 2).\(^6\)\(^{47-49}\)

![Scheme 2: Synthesis of various silsesquioxanes and the surface silanol or siloxide sites they represent](image)

**Scheme 2.** Synthesis of various silsesquioxanes and the surface silanol or siloxide sites they represent
As mentioned before, the leading representative of the incompletely condensed silsesquioxanes is the tri-silanol $R_7Si_3O_3(OH)_3$ (Scheme 2: type I). It is a suitable model for vicinal silanol sites, abundantly present in hydroxylated amorphous- and mesoporous silicas. The tri-silanol can model silica-grafted species or the reaction of silica with silylating agents (e.g. $SiMe_3$, $HN(SiMe_3)_2$). Also reaction with other surface modifiers and tethering groups (e.g. $XCH_2CH_2Si(OMe)_3$) can be mimicked.\(^{49}\)

Silsesquioxane tri-silanol can be partially silylated to afford vicinal disilanols (Scheme 2: type III) which models surface sites that are formed upon silylation of silica. In search for model compounds representing isolated silanol functionalities (found in partially dehydroxylated silicas), the trisilanol $R_7Si_3O_9(OH)_3$ was treated with $SiCl_4$ to afford $R_7Si_8O_{13}Cl$ and subsequently hydrolyzed to give the robust, $C_3$-symmetric silanol, $R_7Si_8O_{12}(OH)$ (Scheme 2: type II).\(^{47}\) Strained siloxane functionalities in silsesquioxanes can be obtained by heating tri-silanols in the presence of molecular sieves (to remove the produced water molecules). Next to heating, strained siloxanes can be obtained by addition of dehydroxylating agents such as $SbMe_5$, $O=PCl_3$, or $MoO_2Cl_2$ (Scheme 2: type IV).\(^{6,32}\)

B. Zeolites

Krijnen et al. assigned IR vibrations of zeolite defects by comparing these absorptions with those of several silsesquioxane silanols.\(^{50}\) Boron, aluminium, and gallium silsesquioxane complexes were found to be interesting models for metal sites in zeolites.\(^{51-57}\) Spectroscopic data (IR, NMR) and DFT calculations showed that the alumino-silsesquioxane $\{[(c-C_5H_9)Si_7O_{11}(OSiMe_3)]_2Al\}^+H^+$ contains a strong intramolecular hydrogen bond. This complex proved to be a fairly realistic structural model for a Brønsted acidic aluminosilicate site in zeolite HY (Figure 5).\(^{51,56,59}\) The corresponding Bronsted acidic boron and gallium silsesquioxanes, representing boron- and gallium zeolite sites, were isolated as either the lithium or ammonium salt, $\{[(c-C_5H_9)Si_7O_{11}(OSiMePh_2)]_2M\}^+X^+$ (M = B, $X^+$ = Li$^+$; M = Ga, $X^+$ = HNEt$_3^+$).\(^{51,52,56}\)

![Figure 5. Molecular structures of the Brønsted acidic aluminosilsesquioxane $\{[(c-C_5H_9)Si_7O_{11}(OSiR_3)]_2Al\}^+H^+$ and the zeolitic acidic site it represents](image-url)
C. Supported heterogeneous catalysts

Various processes that can be catalyzed heterogeneously, such as alkene epoxidation, olefin metathesis, and alkene polymerization, have been mimicked using metalla-silsesquioxane complexes. Classic heterogeneous olefin polymerization catalysts such as Ziegler-Natta and Phillips systems were among the first to be simulated by silsesquioxanes. In 1990, Feher reported the synthesis of $\left[[c\text{-C}_6\text{H}_{11}]_7\text{Si}_7\text{O}_{11}\text{(OSiMe}_3)\right]\text{CrO}_2$ (Figure 6). This is the first reported silsesquioxane-based olefin polymerization catalyst precursor and represents the most accurate (homogeneous) model for a Phillips-type pre-catalyst presently known. However, unlike the real Phillips catalyst, this complex is not activated solely by ethylene; trimethyl aluminum is needed to obtain an active catalyst.

![Figure 6. Molecular structure of $\left[[c\text{-C}_6\text{H}_{11}]_7\text{Si}_7\text{O}_{11}\text{(OSiMe}_3)\right]\text{CrO}_2$ (left) and possible corresponding surface structure (right).](image)

D. Supported homogeneous catalysts

Metallocenes are among the most versatile olefin polymerization catalysts known to date. Nevertheless, heterogenization of these well-defined homogeneous olefin polymerization catalysts is crucial for industrial applications. Three methods are commonly used to immobilize homogeneous olefin polymerization catalysts. Grafting or tethering of the catalyst precursor, and immobilization of the catalyst by electrostatic interaction with the supported cocatalyst. These three methods can be mimicked by silsesquioxanes.

**Grafting**

- Maschmeyer and co-workers investigated the interaction of the silsesquioxane tri-silanol $\left[c\text{-C}_6\text{H}_{11}\right]_7\text{Si}_7\text{O}_9(\text{OH})_3$ with $\text{Cp}_2\text{MCl}_2$ and $\text{CpMCl}_3$ complexes ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{Cp} = \text{cyclopentadienyl} = \eta^5\text{C}_5\text{H}_5$) under alkaline conditions. Both the chloride and the cyclopentadienyl substituents showed to react with the silsesquioxane silanols.
Introduction

- Formation of $\mu$-oxo functionalities was reported by Edelmann\textsuperscript{70} where Cp\textsubscript{2}TiCl\textsubscript{2} and Cp\textsuperscript{*}\textsubscript{2}TiCl\textsubscript{2} (Cp\textsuperscript{*} = $\eta^5$-C\textsubscript{5}Me\textsubscript{5}) were reacted to (c-C\textsubscript{6}H\textsubscript{11})\textsubscript{7}Si\textsubscript{7}O\textsubscript{9}(OH)\textsubscript{2}OSiMe\textsubscript{3}. It is suggested that during the course of the reaction some kind of dehydroxylation process takes place.

- To study the stability of the group-IV metal-siloxy bonds, metalla-silsesquioxane species of the type [(c-C\textsubscript{5}H\textsubscript{9})\textsubscript{7}Si\textsubscript{7}O\textsubscript{12}]M(Cp\textsuperscript{*}), [(c-C\textsubscript{5}H\textsubscript{9})\textsubscript{7}Si\textsubscript{7}O\textsubscript{11}(OSiMe\textsubscript{3})]M(Cp\textsuperscript{*})\textsubscript{2}, and [(c-C\textsubscript{5}H\textsubscript{9})\textsubscript{8}Si\textsubscript{8}O\textsubscript{13}]M(Cp\textsuperscript{*})\textsubscript{X} (X = chloride, alkyl; n = 1, 2) were subjected to solutions of MAO (methylalumoxane) in the presence of ethylene.\textsuperscript{47,71} Found was that MAO induces cleavage of the metal siloxy bond (Scheme 3). Hence, the observed catalytic activity was caused by leached catalytic species. Do and coworkers\textsuperscript{72} demonstrated that MAO induces metal-siloxo bond breaking in [(c-C\textsubscript{5}H\textsubscript{9})\textsubscript{7}Si\textsubscript{7}O\textsubscript{12}]M(Cp\textsuperscript{*})\textsubscript{2} is temperature dependent. At elevated temperatures, M-O cleavage is facile and affords a single-site, silsesquioxane-free catalyst. These studies show that silsesquioxanes are suitable model systems in leaching studies.

- Mono(cyclopentadienyl)titanium silsesquioxane dialkyl species Cp\textsuperscript{*}\textsubscript{2}[(c-C\textsubscript{5}H\textsubscript{9})\textsubscript{7}Si\textsubscript{7}O\textsubscript{12}]TiR\textsubscript{2} (Cp\textsuperscript{*} = 1,3-C\textsubscript{5}H\textsubscript{3}(SiMe\textsubscript{3})\textsubscript{2}, R = Me, CH\textsubscript{2}Ph),\textsuperscript{47,71} are realistic models for silica grafted metallocenes and can be activated with ‘non-aluminum’ cocatalysts such as X\textsuperscript{+}[B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}]\textsuperscript{−} (X\textsuperscript{+} = Ph\textsubscript{3}C\textsuperscript{+}, PhN(H)Me\textsubscript{2}\textsuperscript{+}) or B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (Scheme 3).

\begin{equation}
\begin{array}{c}
\text{Scheme 3. MAO-induced M-O cleavage versus borane induced M-C bond breaking in titanium silsesquioxane complexes.}
\end{array}
\end{equation}

Tethering

Studies using silsesquioxanes for modelling catalyst tethering show that these model supports are very suitable for optimizing synthetic strategies.\textsuperscript{73,74} An example of a complex obtained by connecting the active species to a silica surface via a spacer with functionalized cyclopentadiene, is the silsesquioxane tethered fluorenyl(cyclopentadienyl) zirconium dichloride species, [(c-C\textsubscript{5}H\textsubscript{9})\textsubscript{7}Si\textsubscript{7}O\textsubscript{13}CH\textsubscript{2}C\textsubscript{5}Me\textsubscript{4}SiMe\textsubscript{2}O-](Cp\textsuperscript{*})ZrCl\textsubscript{2}.\textsuperscript{73} Complexes of the type [(c-C\textsubscript{5}H\textsubscript{9})\textsubscript{7}Si\textsubscript{7}O\textsubscript{2}Zr(Cp\textsuperscript{*})(C\textsubscript{5}Me\textsubscript{4}SiMe\textsubscript{2}O)\textsubscript{2}]), were shown to form active olefin polymerization catalysts after activation with MAO but unlike observed for grafted species, the metallocene remains attached to the surface by the tethered cyclopentadienyl group.
Chapter 1

Physical Entrapment

- Titanium(IV) complexes of the type $\text{R}_7\text{Si}_7\text{O}_{12}\text{Ti}(\text{Cp})$ were successfully entrapped in MCM-41 mesoporous silica and tested for activity in heterogeneous catalytic epoxidation.\textsuperscript{75,76} An extensive experimental study showed that the heterogenization is influenced by very subtle differences in interactions between the pore walls of the MCM-41 and the impregnated catalyst. It was not possible to find a relation between the morphology of the MCM-41 samples and leaching of the catalyst during reaction. Also was found that if the impregnated catalysts are not water-stable, hydrolysis is possible due the relative high amount of silanols present on the pore walls.\textsuperscript{77} Detailed characterization by UV-Vis, XPS and Raman spectroscopy demonstrated a strong adsorption of the ancillary cyclohexyl ligands of an intact catalytic complex within the MCM-41 host.\textsuperscript{78} A favorable orientation of the Cp ligand ensures a titanium site accessible for both substrate and oxidant.

- Physisorption of $(\text{c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}\text{Ti}(\text{OiPr})$\textsuperscript{79} into a polysiloxane showed catalytic activity for the epoxidation of cyclo-octene with hydrogen peroxide as oxidant. When the same catalyst is tested in solution without the surrounding hydrophobic polymer, only alkylated peroxides can activate the epoxidation reactions. Suggested is that a synergy between the active species and the hydrophobic polysiloxane environment enables activation with hydrogen peroxide.\textsuperscript{80} However, unless the titanium silsesquioxanes is grafted to the polysiloxane, hot filtration results in leaching of the catalyst.
1.4. Scope of this thesis

In the previous section is demonstrated that silsesquioxanes can be successfully applied as model systems to mimic various features in silicate chemistry. The ongoing quest for a better understanding of processes taking place at silica surfaces and supported metal sites in different areas of heterogeneous catalysis (or heterogenized) calls for further development of the silsesquioxane field:

- So far no detailed study has been carried out to investigate the accuracy of silsesquioxanes as homogeneous model systems for silica properties. In almost any article with silsesquioxane complexes representing alleged models for certain silica properties one only refers to the paper published by Feher in which the structural similarities between silsesquioxanes and certain zeolite features are emphasized. Obtained results are hardly ever compared directly with the silica properties they suppose to serve as a model for.

- Until now only some properties of complex silica surfaces could be studied separately by incompletely condensed silsesquioxane model systems (i.e. vicinal and isolated silanols, strained siloxane rings, effect of silylation). Other kinds of silanols occurring on silica surfaces such as geminal silanols (two hydroxyl groups attached to the same silicon atom) or mono-silanols influenced by neighboring non-silanol interactions (i.e. perturbed mono-silanols) have not been modeled by silsesquioxanes yet.

- The mobility of silsesquioxanes (due to their homogeneity) allows aggregation reactions into thermodynamically stable complexes. This results in many cases in metalla-silsesquioxane complexes which do not structurally resemble the silica-supported systems they were intended to serve as a model for. Furthermore, this mobility enables the electronically unsaturated species (the potential active catalysts) to form thermodynamically stable, often inactive complexes. To prevent this mobility, larger and even more rigid silsesquioxane structures should be prepared.

- The synergy of mesoporous material with incorporated metals for some commercially successful systems could be mimicked by silsesquioxanes. Many heterogeneous catalytically active systems are still obtained by trial and error and detailed knowledge of the actual active site should be obtained by mimicking the (suggested) active species by silsesquioxane models.

The aim of this thesis is to contribute to the knowledge of influences of local surface features on reactivity with substrates or catalytic activity:
Chapter 1

In Chapter Two, characterization and thermal behavior of silsesquioxanes with geminal silanols are reported and compared to silica surface geminal silanols. The two silanols of the geminal silsesquioxanes are found to be different in nature both in solution and in the solid state. Depending on the steric and electronic properties of the adjacent silyl ether functionality, the geminal silsesquioxanes undergo intramolecular condensation or intermolecular dehydroxylation.

Chapter Three describes the reactivity of incompletely condensed tri-silanol silsesquioxane starting materials with dichlorosiloxanes. Thus formed intramolecular disilylated products present a new family of silsesquioxanes. The products consist of mono-silanols influenced by neighboring non-silanol features (an additional silicon ring in the proximity of the silanol) and are called perturbed mono-silanols. They represent partly silylated surfaces. The interaction of the siloxane ring with the mono-silanol is investigated. Silsesquioxane tri-silanols were treated with various difunctional reactants in order to create a stable link between two silsesquioxane cages while silanols remain present. This intermolecular connecting of cages is an attempt to diminish the mobility of silsesquioxanes and inhibit formation of aggregates.

Chapter Four gives an overview of the physical characteristics of four different types of silsesquioxane silanols. Already known silsesquioxane model systems for vicinal silanols and truly isolated silanols are compared to the novel silsesquioxane models for geminal silanols and perturbed mono-silanols. A clear distinction will be made between the four types of silanols modeled by silsesquioxanes both in solution and in the solid state. A classification of the hydrogen bonding abilities of the silanols is given. From estimated ion pair acidities a ranking in acidity of the silanols is established. The findings are compared and evaluated with the (indirect) knowledge of the corresponding silica silanol groups.

Chapter Five explores substitution reactions of perturbed mono-silanols, described in Chapter two, with gallium and titanium metal precursors. Mobility of the gallium complexes allows the formation of thermodynamically stable aggregates. No interaction with the additional siloxane ring is observed. Substitution with titanium half-sandwich precursors provides monomeric products that represent soluble model systems for silica-grafted catalysts with neighboring surface defects. Polymerization studies are performed to establish whether silyl groups in the proximity of the active center influences the activation and polymerization process. The catalyst is activated by fluoroaryl-based complexes and formation and stability of the activated species is followed with $^{19}$F NMR spectroscopy.

Chapter Six deals with silsesquioxane tin chemistry. Tin incorporated zeolites show excellent results in chemoselective catalytic oxidation reactions with hydrogen peroxide as oxidant. The proposed active tin species in these processes are mimicked by reacting silsesquioxane starting materials with several tin-precursors. The mobility of the silsesquioxane ligands enables tin to fill its coordination environment and clusters are formed in which tin is electronically saturated. This behavior differs from the successful modelling of titanium silicalite by tanium silsesquioxanes. Some of the prepared tin compounds are tested as catalysts in several (ep)oxidation reactions.
References

Chapter 1

In this chapter the incompletely condensed monosilylated silsesquioxanes \((c-C_5H_9)Si_7O_9(OSiRR')_2(OH)_2\) \((SiRR' = SiMe_3, SiMe_2C(H)CH_2, SiMePh_2)\) were reacted with \(SiCl_4\) in the presence of an amine. The resulting dichloro compounds \((c-C_5H_9)Si_7O_9(OSiRR')O_2SiCl_2\) compounds could be hydrolyzed into the corresponding silsesquioxanes containing geminal silanols, \((c-C_5H_9)Si_7O_9(OSiRR')O_2Si(OH)_2\). At elevated temperatures, different behavior is observed for the geminal silsesquioxanes substituted with \(OSiMe_3\) or \(OSiMe_2C(H)CH_2\) compared to the more bulky and less electron donating \(OSiMePh_2\). Reaction of the geminal dichloride \((c-C_5H_9)Si_7O_9(OSiMe_3)O_2SiCl_2\) with amines afforded the corresponding geminal di-amide, which also appeared susceptible to condensation reactions. NMR and FT-IR studies of the geminal disilanol silsesquioxanes show that the two silanols of the investigated geminal silsesquioxanes are different from each other with respect to hydrogen bonding, both in solution and in the solid state. The relative Brønsted acidities of the geminal silanols could be determined using \(pK_a\) (ion pair acidity) measurements in THF.

2.1. Introduction

Amorphous silicas play an important role in different disciplines of chemistry. Siliceous materials are used for instance as absorbates or filters, in acid-catalyzed reactions or as catalyst supports. Silica has unique properties and reactivity features that stimulates ongoing research to gain better understanding of morphology, porosity and surface characteristics of silica. Both chemical and physical properties of silicas are strongly affected by the nature of their surface sites. The unsaturated surface valencies are satisfied by surface hydroxyl functionalities, which, depending on the calcination temperature, exist in more or less extent as vicinal (hydrogen bonded silanols), geminal (two silanol groups attached to the same silicon atom) or isolated (no hydrogen bonds possible) silanol sites (Figure 1).

Silsesquioxanes and metalla-silsesquioxanes are probably the most realistic homogeneous models for silica surface silanol- and surface metal-sites known to date. An increasing number of these compounds have been prepared that resembled surface silanol sites (isolated and vicinal), Lewis and Brønsted acidic surface sites, or silica-grafted catalysts. Because geminal silanols have not yet been modeled by silsesquioxanes, only data of simple organic silanediols could be used for
studying geminal silica silanol sites. Whereas the weak Brønsted acidity of surface silanols rarely affects catalytic reactions directly, a proper understanding of their chemical nature is essential for the preparation of supported catalysts. Protons of the surface hydroxyls ion-exchange readily with metal cations, a key-step in catalyst preparation that should be related to the Brønsted acidity of the silanol functionality. In this chapter the synthesis of novel silsesquioxanes containing geminal silanols are reported together with a detailed study on their thermal stability, their solution and solid-state characteristics and their relative acidity. Also, reactivity of geminal dichlorides with amines is discussed.

![Figure 1. Schematic presentation of three types of silanol groups occurring on silica surfaces: (a) vicinal silanols, (b) geminal silanols, (c) isolated silanols.](image)

### 2.2. Synthesis

For this study, monosilylated incompletely condensed silsesquioxanes of the type $(c$-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiRR$'$$_2$)(OH)$_2$ were used with sterically and electronically different silylether functionalities (SiRR$'$$_2$ = SiMe$_3$, SiMe$_2$C(H)CH$_2$, SiMePh$_2$). Reaction of these disilanols with an equimolar amount of silicon tetrachloride in the presence of two equivalents of triethylamine afforded in high yield the geminal di-chloro compounds $(c$-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiRR$'$$_2$)O$_2$SiCl$_2$ (SiRR$'$$_2$ = SiMe$_3$, 1; SiMe$_2$C(H)CH$_2$, 2; SiMePh$_2$, 3).

The high selectivity of this reaction was rather unexpected since the reaction of equimolar amounts of R$_7$Si$_7$O$_9$(OSiMe$_3$)(OH)$_2$ (R = c-C$_5$H$_9$, c-C$_6$H$_11$, c-C$_7$H$_13$) and MCl$_4$ (M = Ti, Zr, Hf)$^{18}$ invariably resulted in substitution of all the chloride substituents and formation of the corresponding [R$_7$Si$_7$O$_9$(OSiMe$_3$)]$2$M systems. Likewise, the synthesis of 2,2-dichloro-methylcyclosiloxanes (Me$_2$SiO)$_n$OSiCl$_2$ starting from SiCl$_4$ and $\alpha$,\$\omega$-H(OSiMe$_3$)$_n$OH$^{19}$ could only be achieved by slow and simultaneous addition of the reactants using the dilution principle. Even then a yield higher than 66% could not be achieved.

Compounds 1-3 readily hydrolyze, releasing HCl while forming the corresponding geminal silanols $(c$-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiRR$'$$_2$)O$_2$Si(OH)$_2$ (SiRR$'$$_2$ = SiMe$_3$, 4; SiMe$_2$C(H)CH$_2$, 5; SiMePh$_2$, 6; Scheme 1).

Both the geminal dichlorides (1-3) and geminal silanols (4-6) show the expected pattern in the $^{13}$C- and $^{29}$Si-NMR spectra for a Cs symmetric structure (ratio 1:1:2:2:1 and 1:1:2:1:2 respectively; Figure 2). In addition, the $^{29}$Si-NMR spectra of 1-6 show silicon resonances characteristic for ($\equiv$O)$_2$SiCl$_2$ (± -68 ppm) and ($\equiv$O)$_2$Si(OH)$_2$ (± -89 ppm), respectively (Figure 2).$^{19}$ $^1$H-NMR shows that the two silanols of the geminal silsesquioxanes 4-6 are different in nature. Like the two chlorides in 1-3 (Figure 3), the silanols in 4-6 are exo and endo isomers with respect to the silylether functionality and the hydroxyls occur as
two distinct singlets in the proton NMR spectrum. Compared to the wide range of trialkyl and triaryl silanols $R_3SiOH$, and siloxane diols $R_2Si(OH)OSi(OH)R_2$, the number of geminal silane diols of the type $R_2Si(OH)R_2$ is limited to a few examples where sterically demanding organic substituents like phenyl or $t$-butyl stabilize the silane diols by preventing it to undergo self-condensation into polysiloxanes.\(^\text{14}\)

![Scheme 1. Synthesis of dichloro silsesquioxanes 1-3 and geminal disilanol silsesquioxanes 4-6.](image)

**Figure 2.** $^{29}$Si-NMR spectra of geminal dichloride 1 and geminal disilanol 4.

The molecular structure of 1\(^{20}\) could be determined by single crystal X-ray analysis and is shown in Figure 3, a selection of interatomic distances and angles are given in Table 1. Compound 1' is $C_6$ symmetric in which the two chlorides are $exo$- and $endo$-oriented with respect to the SiMe$_3$ silylether functionality. Atom Si9 is surrounded tetrahedrally and, except for the slightly opened O10-Si9-O12 angle of 112.17(12)$^\circ$, shows no signs of any strain or steric hindrance of the adjacent SiMe$_3$ silylether functionality. As expected for a more electrophilic silicon, the Si9-O10 (1.604(2) Å) and Si9-O12 (1.605(2) Å) are significantly shorter than the average Si-O distance of 1.629(2) Å and result in elongation of the corresponding Si6-O10 (1.645(2) Å) and Si8-O12 (1.655(2) Å) distances. Veith et al.
reported the synthesis and X-Ray structure of [Me$_2$Si(NSiMe$_3$)$_2$]Si[[OSiCl$_2$]O] with geminal silyldichlorides as part of a 6-membered siloxane ring.$^{21}$ Since the two O$_2$SiCl$_2$ units of [Me$_2$Si(NSiMe$_3$)$_2$]Si[[OSiCl$_2$]O] are part of a smaller siloxane ring (6-membered ring instead of a 8-membered ring in 1$'$), the O-Si-O angles are somewhat smaller (109.07(4) and 108.7(2)$^{o}$) than the O10-Si9-O12 angle of 112.17(12)$^{o}$ for 1$. [Me$_2$Si(NSiMe$_3$)$_2$]-Si[[OSiCl$_2$]O] shows slightly shorter Si-Cl bond distances (av. 1.99(9) Å) compared to an average Si-Cl bond distance of 2.03(7) for 1$'$. The average (Cl)-Si-O bond distance of 1.613(4) Å is, however, slightly elongated compared to 1$'$. The Cl-Si-Cl angles are comparable with the angle found in 1$'$; 108.62(1)$^{o}$ and 108.72(9)$^{o}$ for [Me$_2$Si(NSiMe$_3$)$_2$]-Si[[OSiCl$_2$]O] and 108.24(6)$^{o}$ for 1$. These findings confirm that the geminal dichloride is not subject to any strain or steric hindrance of the adjacent SiMe$_3$ silyl ether functionality.

Table 1: Selected interatomic distances and angles for 1$'$.

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Figure 3. Molecular structure of [(c-C$_6$H$_{11}$)$_7$Si$_7$O$_9$O(SiMe$_3$)(O$_2$SiCl$_2$)] (1$'$). Thermal ellipsoids are scaled to enclose 40% of the electron density. Only the cyclopentyl methyne carbon is shown for clarity.
2.3. Thermal behavior

At elevated temperatures (80 °C), the geminal silsesquioxanes 4 and 5 are unstable and undergo intramolecular condensation to yield the closed-cage silsesquioxane mono-silanol \((c\text{-}C_5\text{H}_9)_7\text{Si}_8\text{O}_{12}(\text{OH})\) (Scheme 2). Compound 6 is infinitely stable in the solid state, even when exposed to elevated temperatures (80 °C - 120 °C). However, in solution compound 6 slowly undergoes intermolecular dehydroxylation (even at room temperature), yielding the unprecedented siloxy-bridged dimeric bis-silanol, \(\{(c\text{-}C_5\text{H}_9)\text{Si}_7\text{O}_{9}(\text{OSiMePh}_2)(\text{O}_2\text{Si(OH)}-)\}^2(\mu-\text{O})\) (7). Interestingly, the condensation of 4, 5, and the dehydroxylation of 6 proceed at much lower temperatures than for vicinal silsesquioxanes or on silica surfaces. Vicinal silsesquioxanes, \(R_7\text{Si}_7\text{O}_{10}(\text{OH})_2\text{OR}'\) \((R = c\text{-}C_5\text{H}_9, c\text{-}C_6\text{H}_{11}; R' = \text{H, SiMe}_3, \text{SbMe}_4)\), undergo dehydroxylation affording the condensed \(R_7\text{Si}_7\text{O}_{10}(\text{OR}')\). This reaction requires heating in the presence of molsieves (while heating toluene to reflux), or a dehydrating agent such as \(\text{O=PCl}_3\), \(\text{SbMe}_5\) or \(\text{MoO}_2\text{Cl}_2\). For siliceous materials, calcination temperatures as high as 500 °C are needed to fully dehydroxylate the surface and form isolated silanols and condensed siloxane bonds. For small organic geminal disilanols, this spontaneous condensation behavior has not been reported. Intramolecular condensation can occur when the reaction is catalyzed by an acid, for instance the geminal disilanols \(\text{Me}_3\text{SiOSiMe(OH)}_2\) condenses above 100 °C into \([\text{Me}_3\text{SiOSiMe(OH)}]_2\text{O}\) in the presence of diluted HCl.

Scheme 2. Thermal behavior of 4-6: intramolecular condensation from 4 and 5 into \((c\text{-}C_5\text{H}_9)_7\text{Si}_8\text{O}_{12}(\text{OH})\) and intermolecular dehydroxylation from 6 into \(\{(c\text{-}C_5\text{H}_9)\text{Si}_7\text{O}_{9}(\text{OSiMePh}_2)(\text{O}_2\text{Si(OH)}-)\}^2(\mu-\text{O})\) (7).

Crystals suitable for X-ray analysis could be obtained for 7 and is shown in Figure 4. Selective interatomic distances and angles of 7 are listed in Table 2. Compound 7 consists of two silsesquioxane fragments linked together by a bridging oxygen atom. The Si1-O1-Si10 angle of 171.4(2)° is nearly...
linear and O1 roughly forms the inversion center of the molecule. Similar as observed for the electrophilic Si9 in 1', the lack of an electron donating cycloalkyl group at Si1 and Si10 results in significantly shorter Si-O distances (av. 1.609(4) Å) than the average distance (1.628(4) Å) of the other Si-O bonds in 7. The average Si-O bond lengths and Si-O-Si bond angles are normal within the wide range of Si-O distances and Si-O-Si angles known for silsesquioxanes.

Table 2. Selected interatomic distances and angles for 7.

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<th>Bond distances (Å)</th>
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Figure 4. Molecular structure of 7, thermal ellipsoids are scaled to enclose 40% of the electron density. Only the cyclopentyl methyne carbons are shown for clarity.
2.4. Synthesis of geminal di-amides

A common method to obtain siloxamides is by reacting silylchlorides with an amine. Transformation of the geminal dichlorides \((c\text{-C}_5\text{H}_9)\text{Si}_7\text{O}_9^-(\text{OSiRR'}_2)\text{O}_2\text{SiCl}_2\) 1-3 \((\text{SiRR'}_2 = \text{SiMe}_3, \text{SiMe}_2\text{C(H)CH}_2, \text{SiMePh})\) with amines afforded for 1 and 2 the corresponding geminal di-amides, which appeared susceptible to condensation reactions just like observed for the geminal silanol analogues 4 and 5. Reacting compound 1 with four equivalents of \(\text{iPrNH}_2\) afforded the desired product \((c\text{-C}_5\text{H}_9)\text{Si}_7\text{O}_9^-(\text{OSiMe}_3)\text{O}_2\text{Si}{\text{N(H)\text{iPr}}}^2\) (8) in high yield (Scheme 3). Reaction of the SiMe\_2\text{vinyl} substituted geminal dichloride 2 with \(\text{iPrNH}_2\) resulted in a mixture of starting material, \((c\text{-C}_5\text{H}_9)\text{Si}_7\text{O}_9^-(\text{OSiMe}_2\text{C(H)CH}_2)\text{O}_2\text{Si}{\text{N(H)\text{Pr}}}^2\) and the closed cage \((c\text{-C}_5\text{H}_9)\text{Si}_8\text{O}_{12}\text{N(H)\text{Pr}}\) formed by condensation at ambient temperature. Reaction of 3 with \(\text{iPrNH}_2\) was not selective which is most likely due to steric crowding around the silicon atom. Reactions of 1 with other amines like \(\text{tBuNH}_2\) and \(\text{C}_6\text{H}_5\text{NH}_2\) resulted in a mixture of starting material, mono-substituted product and di-substituted product of which the individual products could not be separated. Reaction of 1 with 2,6-diisopropylaniline showed no sign of substitution of the chlorides at all, probably due to the steric bulk of the amine groups. Compound 8 is stable under argon atmosphere when kept as a solid at ambient temperature. However, when exposed to somewhat elevated temperatures \((50-60 \degree \text{C})\) 8 converts into the closed caged \((c\text{-C}_5\text{H}_9)\text{Si}_8\text{O}_{12}\text{N(H)\text{Pr}}\) (Scheme 3). This condensation process was also observed at room temperature when 8 was kept in solution.

Silazanes of the type \(\text{HN}(\text{SiR}_3)_2\) are commonly used as silylating agents in order to manipulate the characteristics of siliceous supports. \(\text{HN}(\text{SiR}_3)_2\) and thermal behavior of 8.
2.5. Solid state and solution properties of geminal disilanols

To study silica surface properties such as hydrogen bonding, relative acidity or dehydroxylation reactions of various silanols, the infrared stretching vibrations ($\nu_{\text{OH}}$) of the surface silanols are very informative. These bands are well separated from other vibrations and are largely dependent on interactions with neighboring silanols, silyl ethers or metal species. For silica, a broad adsorption around 3530 cm$^{-1}$ (vacuum) is usually assigned to hydrogen bonded silanols close to other silanols acting as a proton acceptor. Absorptions around 3750 cm$^{-1}$ (vacuum) have been assigned to isolated silanols (Figure 5). Stretching vibrations of geminal silanols are usually found in the same region as isolated silanols and still controversy exists whether or not they can be distinguished separately.\cite{27,28} Interestingly, Takei and coworkers\cite{29} reported an additional shoulder at 3600 cm$^{-1}$, suggesting both hydrogen bonded and isolated geminal silanols. Boccuzzi and coworkers found the same phenomenon on silica at low temperatures.\cite{30} Infrared spectroscopy studies on geminal silsesquioxane disilanols could give more insight into the possible vibrations of geminal silanols.

![Figure 5. Isolated (H$_i$) and hydrogen bonded (H$_b$) types of silanols.](image)

When comparing the solid state and solution IR spectra of silsesquioxanes with the IR spectra of silica surface silanols measured in vacuum, one should ensure that the media used to record the IR spectra of the samples does not affect the silanol frequencies. Solid state FT-IR spectra of silsesquioxanes recorded using Nujol mulls are identical to those collected using an ATR (golden gate) devise, indicating that Nujol shows no significant interaction with the silanols. Nujol mulls were preferred as they gave better-resolved silanol stretching vibrations than the ATR device, solution IR spectra were recorded in CCl$_4$. The observed frequencies for silsesquioxanes bearing isolated silanols are close to the value of 3750 cm$^{-1}$ for isolated silica surface silanols in vacuum, indicating that the interaction of CCl$_4$ with silanols is negligible. This is in agreement with early work of Hair et al. on the effect of different solvents on silica-silanol frequencies who showed that CCl$_4$ gives only a small shift of 45 cm$^{-1}$ compared to the value in vacuum, whereas diethylether gives a shift of 430 cm$^{-1}$.\cite{31} As expected, when diethylether was added to the CCl$_4$ solutions of silsesquioxanes, all silanols become hydrogen-bonded (broad vibration band around 3375 cm$^{-1}$) as a result of the strong interaction of the ether with silsesquioxane silanols.

FT-IR spectroscopy studies on 4-6 revealed that both hydroxyl groups in 4-6 are different in nature not only due to their geometric inequivalency, but also with respect to hydrogen bonding. Moreover, the hydroxyl groups are differently bonded in solution and in the solid state. The infrared OH stretching vibrations of CCl$_4$ solutions of 4-6 appear as one broad and one sharp signal (Table 3, Figure 6). The sharp signal at 3700 cm$^{-1}$ is indicative for isolated silanols. The broad vibration around 3600 cm$^{-1}$ is
characteristic for a hydrogen-bonded silanol. Interestingly, in the solid state IR spectra (Nujol mull) no isolated silanol vibrations are observed. Instead, two broad vibration bands are found. The broad vibration band at 3600 cm\(^{-1}\) corresponds with the vibration of the hydrogen-bonded silanol in solution. The broad vibration at 3400 cm\(^{-1}\) is also indicative for a hydrogen-bonded silanol but clearly of a different type than the former one. Any possible weak interaction of CCl\(_4\) with silanol functionalities cannot account for these striking differences observed for the solid state (Nujol) and solution (CCl\(_4\)) infrared spectra.

Table 3. NMR resonances, IR vibrations, and ion pair acidities p\(K_p\) of the geminal silanols 4-6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(^1)H-NMR (ppm) (\delta) Si(OH)(_2)</th>
<th>(^29)Si-NMR (ppm) (\delta) Si(OH)(_2)</th>
<th>IR (Nujol) (\nu) OH (cm(^{-1}))</th>
<th>IR (CCl(_4)) (\nu) OH (cm(^{-1}))</th>
<th>IR (CCl(_4)+Et(_2)O) (\nu) OH (cm(^{-1}))</th>
<th>p(K_p)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2.41, 3.80</td>
<td>-89.43</td>
<td>3515, 3402</td>
<td>3700, 3584</td>
<td>3374</td>
<td>10.2 (± 0.1)</td>
</tr>
<tr>
<td>5</td>
<td>2.37, 3.63</td>
<td>-89.45</td>
<td>3520, 3402</td>
<td>3700, 3591</td>
<td>3373</td>
<td>10.1 (± 0.1)</td>
</tr>
<tr>
<td>6</td>
<td>2.12, 2.23</td>
<td>-89.46</td>
<td>3582, 3438</td>
<td>3699, 3625</td>
<td>3373</td>
<td>9.7 (± 0.3)</td>
</tr>
</tbody>
</table>

p\(K_p\) averages of two indicators; Li\([9-(cyano)fluorenide]\)-2THF and Li\([9-(methoxycarbonyl)fluorenide]\)-2THF, deviation between brackets.

Figure 6. OH-vibrations of the IR spectra of 4-6 in the solid state (Nujol mull) and in solution (CCl\(_4\) and CCl\(_4\)+Et\(_2\)O), isolated hydroxyls (\(H^i\)) and different hydrogen bonded hydroxyls (\(H^b\); intramolecular or intermolecular hydrogen bonded) are indicated.
Small organic molecules bearing vicinal or geminal silanols have been found to form intermolecularly poly-hydrogen bonded networks in the form of ladder-like chains, sheets, layers or more three dimensional solid-state structures. Tilley and coworkers found for a tetrahydroxydisiloxane both intramolecular and intermolecular hydrogen bonds. They demonstrated that a pendant silylether functionality can act as proton acceptor giving rise to the intramolecular hydrogen bonds (Figure 5) that shows a broad OH stretching vibration band at 3438 cm\(^{-1}\) (solid state, KBr) in the FT-IR spectrum.

To better predict the solution structures of 4-6, molecular weight measurements in benzene were carried out, which showed that all three geminal silsesquioxane silanols 4-6 are monomeric in solution. On the basis of the similar hydrophobicity of both solvents (benzene: \(\varepsilon = 2.3\); CCl\(_4\): \(\varepsilon = 2.2\) at 20 °C), 4-6 are assumed to be monomeric in CCl\(_4\) as well. On the other hand, preliminary results of single crystal X-ray analysis show that the structure of 4 is dimeric in the solid state. On the basis of their monomeric structure in solution, the observed hydrogen bonding of 4-6 in solution is most probably an intramolecular interaction of the endo-silanol with the silylether functionality (Figure 7), comparable to the observed intramolecular interaction observed by Tilley. Manners and coworkers investigated the hydrogen bonding of diferrocenylsilanediol both in solution (CCl\(_4\)) and in the solid state. As for 4-6, in solution one sharp signal is found at approximately 3700 cm\(^{-1}\), suggesting isolated silanols and thus, logically, the existence of monomers. However, in the solid state, only broad vibration bands around 3400 cm\(^{-1}\) were observed. Supported by X-ray structure analysis, the vibration bands could be subscribed to hydrogen bonding of one of the silanols to another molecule thus forming dimeric structures, while the other silanol group forms a hydrogen bond to a neighboring dimer. These findings support the proposed intramolecular hydrogen bonds to the silylether functionality in the monomeric solution structures of 4-6, as well as the intra- and intermolecular hydrogen bonding in the dimeric solid-state structures of compounds 4-6. Yet in the case of geminal silsesquioxanes, the silanol not participating in intermolecular hydrogen bonding is more likely to form intramolecular hydrogen bonds to the pendant silylether functionality than to a neighboring dimer (Figure 7) as found for the diferrocenylsilanediol.

![Figure 7](image-url)
When comparing the vibration bands of the hydrogen-bonded silanols of 4 and 6 in CCl₄ solution, hydrogen bonding for compound 4 is strongest because the vibration band shows the strongest shift to lower frequencies (a shift of 41 cm⁻¹ compared to 6). Proton NMR data supports this as the ∆δ of the two silanols in 4 (1.39 ppm) is significantly larger than the ∆δ observed for compound 6 (0.11 ppm). From IR and NMR it is clear that the hydrogen bonding in 5 (∆νOH is 109 cm⁻¹ and ∆δ is 1.26 ppm) is slightly less than in compound 4 but still considerably stronger than in 6. This large difference in hydrogen bonding for 4 and 6 in solution is probably due to both steric and electronic reasons. The SiMe₃ group in 4 is sterically less bulky than the SiMePh₂ group in 6, while it is also the most electron donating one and therefore more capable to stabilize the hydrogen bonded proton. A similar phenomenon was observed in the Brønsted acidic alumino-silsesquioxanes \( \left[ (c\text{-C}_5\text{H}_9)\text{Si}_7\text{O}_{11-}(\text{OSiMe}_3)\text{Al}^+\text{H}^+ \right] \) and \( \left[ (c\text{-C}_5\text{H}_9)\text{Si}_7\text{O}_{11-}(\text{OSiMePh}_2)\text{Al}^+\text{H}^+ \right] \). The more bulky and less electron donating SiMePh₂ substituent in the latter hampers intramolecular hydrogen bonding and renders the complex more acidic than the SiMe₃ substituted complex. The observed difference in hydrogen bonding for 4-5 versus 6 most probably is responsible for the different thermal condensation reactions. The effective intramolecular hydrogen bonds with the pendant silylether functionality in 4-5, might promote the intramolecular condensation into a closed caged structure. The reduced capacity of the bulky, poor electron donating silylether functionality of 6 makes intramolecular hydrogen bonding less preferable and consequently intermolecular dehydroxylation is favored (Scheme 2).

Since the protons of the surface hydroxyls ion-exchange readily with metal cations, there should be a relation between the ion-exchange rate and the Brønsted acidity of the silanol functionalities. It is important to recognize that acidities are strongly solvent dependent. The dissociation constant of an acid depends on the ability of the solvent to solvate the proton, the anion and the undissociated acid. Silsesquioxanes are highly lipophilic and only dissolve in organic solvents with relatively low polarity like THF or hexane. In solvents with a relatively low dielectric constant such as THF (\( \varepsilon_{(25\text{°C})} = 7.4 \)), ion pair dissociation hardly occurs. Hence, acidity measurements in low-polar solvents only give qualitative values about relative acidities in each specific solvent, i.e. one can only determine whether one compound is more or less acidic than another one in a specific solvent. However, this qualitative information is still very significant for ion-exchange reactions and thus for the synthesis of supported catalysts.

Acidity measurements in THF afford relative ion pair acidities for the geminal silsesquioxanes 4-6 (Table 3) by using the overlapping indicator method. This method is described by Bordwell and others, and applied to silsesquioxanes by Feher and Duchateau. Compounds 4 and 5 have almost the same ion pair acidity (10.2 and 10.1 respectively), compound 6 is more acidic than 4 and 5 (pKₐ = 9.7). This agrees with the earlier statements about the less effective intramolecular hydrogen bonding of 6 compared to 4 and 5 due to the more bulky and less electron donating SiMePh₂ substituent of 6.
2.6. Deuteration of the geminal silanols of 4-6

H/D exchange between surface OH groups and adsorbate molecules is a valuable method for the investigation of acid strength of OH groups and the mechanism of acid-catalyzed reactions. From DRIFT (diffuse reflectance IR) and NMR experiments could be concluded that H/D exchange readily takes place with silanols of increased acidic strength, whereas with less acidic silanols only hydrogen bonding with the deuterated adsorbates occurs. Mass-spectrometry of a deuterium treated silica sample can also be used to determine the concentration of surface silanol groups. Of interest to us was whether deuterated products were subject to the same hydrogen bonding abilities as observed for the geminal disilanols 4-6. However, the low acidity of the prepared silsesquioxane geminal disilanols 4-6 prevented H/D exchange with D₂O since no effect could be detected in the IR spectra after addition of D₂O to compounds 4-6. Increasing the temperature to force H/D exchange was not possible due to thermal instability of 4-6. Therefore was decided to react the geminal dichlorides 1 and 3 to D₂O to obtain the deuterated products. Products (c-C₆H₄)₂Si₂O₈(OSiMe₂)O₂Si(OD)₂ and (c-C₆H₄)₃Si₂O₉(OSiMePh₂)O₂Si(OD)₂ were identified by IR measurements in solution (0.1M in CCl₄). Like observed for the IR spectra of the geminal disilanols 4 and 6 in solution, bonded OD₃ groups as well as isolated OD¹ bonds could be distinguished (Table 4). As reference for isolated OD¹ bonds, deuteration of closed cage silsesquioxane (c-C₆H₄)₂Si₆O₁₂Cl with D₂O was also investigated. The vibration band of the isolated Si-OH of (c-C₆H₄)₂Si₆O₁₂(OH) is situated at 3700 cm⁻¹, the vibration band of the isolated Si-OD of (c-C₆H₄)₃Si₆O₁₂(OD) was found at 2730 cm⁻¹. The vibration bands of the isolated Si-OH¹ and Si-OD¹ of the geminal disilanols 4-6 and deuterated analogs (obtained from 1-3) were found at the same positions. This confirms the findings that one of the hydroxyls of the geminal disilanols 4 and 6 is truly isolated. The isotopic ratio R is defined as the wave number ratio for SiOH / SiOD. The isotopic ratio can be calculated by dividing the wave number shift of νOH of the OH-containing compounds with νOD of the deuterated compounds. The results are listed in Table 4. Hydrogen bonded SiOH/SiOD groups show a lower isotopic ratio than non-hydrogen-bonded SiOH/SiOD, which can be explained in terms of differences in reduced mass. The H/D isotopic ratio of the Si-OD¹ isolated groups of the geminal silanols are comparable with the isotopic ratio found for the closed cage isolated Si-OD² group. Experimental studies on isolated silanols occurring at silica, in which a shift from 3748 cm⁻¹ to 2762 cm⁻¹ by deuteration is observed (H/D isotopic ratio of 1.3570), agree with these findings.

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR (CCl₄) νOH (cm⁻¹)</th>
<th>IR (CCl₄) νOD (cm⁻¹)</th>
<th>wavenumber ratio SiOH / SiOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c-C₆H₄)₂Si₂O₈(OSiMe₃)O₂Si(OD)₂, OD¹</td>
<td>3700</td>
<td>2730</td>
<td>1.3553</td>
</tr>
<tr>
<td>(c-C₆H₄)₂Si₂O₈(OSiMe₃)O₂Si(OD)₂, OD²</td>
<td>3584</td>
<td>2647</td>
<td>1.3540</td>
</tr>
<tr>
<td>(c-C₆H₄)₂Si₂O₈(OSiMePh₂)O₂Si(OD)₂, OD¹</td>
<td>3699</td>
<td>2728</td>
<td>1.3559</td>
</tr>
<tr>
<td>(c-C₆H₄)₂Si₂O₈(OSiMePh₂)O₂Si(OD)₂, OD²</td>
<td>3625</td>
<td>2678</td>
<td>1.3536</td>
</tr>
<tr>
<td>(c-C₆H₄)₂Si₆O₁₂(OD)²</td>
<td>3700</td>
<td>2730</td>
<td>1.3553</td>
</tr>
</tbody>
</table>

¹ OD¹ = isolated OD group  
² OD² = bonded OD group
2.7. Concluding remarks and Outlook

Silsesquioxanes containing geminal silanols of the type \((c-C_5H_9)_7Si_7O_9(OSiR'_3)O_2Si(OH)_2\) are readily accessible by reaction of the incompletely condensed silsesquioxanes \((c-C_5H_9)_7Si_7O_9(OSiR'_3)(OH)_2\) with SiCl\(_4\) in the presence of an amine, followed by hydrolysis. At elevated temperatures, the geminal silsesquioxanes with silyl ether functionalities that are best capable of stabilizing the intramolecular hydrogen bond \((OSiMe_3\) and \(OSiMe_2CHCH_2\)), undergo condensation reactions yielding the closed cage silsesquioxane mono silanol \((c-C_5H_9)_7Si_8O_{12}(OH)\). In solution, the geminal silsesquioxane with a more bulky and less electron donating \(OSiMePh_2\) substituent and therefore diminished hydrogen bonding is more inclined to form the thermodynamically stable intermolecular dehydroxylated product, \(\left[(c-C_5H_9)_7Si_7O_9(OSiMePh_2)(O_2Si(OH))\right]_2(\mu-O)\). NMR and FT-IR studies show that the two silanols of the geminal silsesquioxanes are different in nature. In solution one of the silanols is intramolecularly hydrogen bonded while the other is isolated. In the solid state both silanols are hydrogen bonded, one intramolecularly and the other intermolecularly. The SiMePh\(_2\) substituted geminal disilanol is slightly more Bronsted acidic than the \(OSiMe_3\) or \(OSiMe_2CHCH_2\) substituted disilanols, due to less effective intra-molecular hydrogen bonding.

An interesting extension to this work would be investigating the reactivity of silsesquioxane geminal disilanols towards metal substitution. Some preliminary reactions have been performed with the prepared compounds but unfortunately with limiting success. Geminal disilanols \(R_2Si(OH)_2\) \((R = Ph, t-Bu)\) have been used as building blocks for a variety of metallasiloxanes.\(^{52,53}\) Commonly observed products from reaction of \(R_2Si(OH)_2\) with a metalprecursors possess an 8-membered ring (Figure 8). A careful choice of metal precursor to prevent too much steric crowding around the geminal silanol of \(R_2Si_7O_9(OSiR'_3)O_2Si(OH)_2\) and bearing in mind the low acidity of the geminal silanols might result in interesting new model systems for immobilized catalysts on a silica surface.

![Figure 8. Common observed reactivity of \(R_2Si(OH)_2\) with \(ML_n\).](image-url)
2.8. Experimental section

**General Remarks:** Reactions were performed under an argon atmosphere using Schlenk techniques when necessary. Solvents were distilled from K (THF), Na/K alloy (hexanes, C₆D₆) and benzophenon (Et₂O) or dried over 4 Å molecular sieves (NEt₃, CCl₄, CDCl₃, THF-d₈) and stored under argon. ¹H and ¹³C-NMR spectra were recorded on Varian Mercury 400 spectrometers (250MHz, ¹H NMR: 400 MHz, ¹³C NMR: 100.6 MHz). ²⁹Si-NMR spectra were recorded on a Varian Indigo 500 spectrometer (250MHz, ²⁹Si-NMR: 99.3 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (¹H, ¹³C-NMR) or external standards (²⁹Si: SiMe₄ = 0 ppm). All Fourier Transformed IR spectra were recorded at room temperature on a Nicolet Avatar™ 360 spectrophotometer. Samples in solution were prepared under inert atmosphere (glovebox), νOCH values were determined in 0.1M CCl₄ solutions and ΔνOCH in 0.1M CCl₄-solutions containing 0.25M diethylether. Solid-state samples were recorded as Nujol-mulls (prepared under inert atmosphere, glovebox) or recorded directly on a Nicolet Smart DuraSampIR in air for single reflection diamond ATR analysis (golden gate). Molecular weight determinations in benzene were performed in the laboratoria of Prof. J.H. Teuben, University of Groningen. Elemental analyses were carried out at the Analytical department of the University of Groningen (compounds 1', 1 - 3) and the University of Eindhoven (compounds 4 - 6); quoted data are the average of at least two independent measurements. Silsesquioxanes starting materials (c-C₃H₈)₄Si(OH)₂, (c-C₃H₈)₂Si(OSiMe₂)(OH)₂, (c-C₃H₈)₂Si(OH)(OSiMe₂CH₂Cl)(OH)₂, (c-C₃H₈)₂Si(OSiMePh₂)(OH)₂, (c-C₃H₈)₃Si(OH)₂ and (c-C₃H₈)₂Si(OH)₃ were prepared following referred literature procedures.

**PK₆ measurements** - The pK₆ ion pair acidity measurements were carried out using the overlapping indicator method, the used indicators were 9-cyanofluorene (pK₆(DMSO) = 8.3) and 9-(methoxycarbonyl)fluorene (pK₆(DMSO) = 10.4). Lithium salts of the indicators were prepared, isolated, and recrystallized before use. Due to the low solubility of silsesquioxanes in DMSO, THF was used as the solvent instead. UV-Vis measurements for determination of the pK₆ values, were performed on a UV-2401PC spectrophotometer with standard slit width and scan speed.

(c-C₃H₈)₂Si(OH)(OSiMe₂)OSiCl₂ (1): To a solution of (c-C₃H₈)₂Si(OH)(OSiMe₂)(OH)₂ (20.40 g, 21.53 mmol) and 1 equivalent of SiCl₄ (21.53 mmol, 2.47 mL) in 200 mL of hexanes, 2 equivalents of NEt₃ (0.04 mol, 6.00 mL) were slowly added. The resulting suspension was stirred at ambient temperature to complete the reaction. Filtration and removal of the solvent afforded analytically pure 1 as a white powder (19.89 g, 17.40 mmol, 81%). ¹H NMR (CDCl₃): δ 0.18 (s, (CH₃)₂Si, 9H), 0.88-1.14 (m, CH₃C₃H₈Si, 7H), 1.59 (m, CH₃C₃H₈Si, 42H), 1.79 (m, CH₂C₃H₈Si, 14H). ¹³C(¹H) NMR (CDCl₃): δ 1.74 ((CH₃)₂Si), 21.96; 22.23; 22.84; 22.95; 24.15 (7 CH-CH₃, ratio 1:1:2:2:1), 26.92 - 27.62 (CH₂-C₂H₄); ²⁹Si NMR (CDCl₃): δ 9.34 (OSiMe₂), -64.97; -65.17; -66.32; -66.75; -67.85 (7 O₂SiC₃H₈, ratio 1:1:2:1:2), -69.42 (O₂SiCl₂). IR (cm⁻¹, DuraSampIR): 2948 (s), 2865 (m), 1449 (w), 1248 (m), 1132 - 1108 (s), 951 (m), 911 (m), 832 (m), 786 (m), 720 (m). Tmp.: 120±2 °C. Elemental analysis calcd (%) for C₅₀H₃₁Cl₂O₂S₈I₆ (1044.66): C 43.69, H 6.95, Cl 6.79; found C 43.78, H 6.98, Cl 6.89.

(c-C₃H₈)₃Si(OH)(OSiMe₂)OSiCl₂ (1'): The cyclohexyl substituted analogue of 1 was prepared following the same synthetic procedures and was isolated in 84 % yield. Colorless crystals could be obtained from hexane, and were suitable for single crystal structure determination. ¹H NMR (CDCl₃): δ 0.36 (s, (CH₃)₂Si, 9H), 0.94-1.05 (m, (CH₃)₂Si, 9H), 0.88-1.14 (m, CH₃C₃H₈Si, 7H), 1.23 (m, CH₂C₃H₈Si, 21H), 1.64 (m, CH₂C₃H₈H, 35H), 2.07 (m, CH₂C₃H₈H, 14H). ¹³C(¹H) NMR (CDCl₃): δ 2.05 ((CH₃)₂Si), 23.46; 23.66; 24.01; 24.75; 25.42 (7 CH-CH₃, ratio 1:1:2:2:1), 26.88 - 28.01 (CH₂-C₂H₄); ²⁹Si NMR (CDCl₃): δ 10.49 (OSiMe₂), -66.16; -66.39; -67.39; -67.83; -69.24 (7 O₂SiC₃H₈, ratio 1:1:2:1:2), -69.42 (O₂SiCl₂). Tmp.: 167±2 °C. Elemental analysis calcd (%) for C₉₀H₇₄Cl₂O₂S₈I₆ (11142.80): C 47.29, H 7.59, Cl 6.20; found C 47.35, H 7.61, Cl 6.26.
(c-C₅H₅)₂SiO₃(OSiMe₂)CHCH₂O₂SiCl₂ (2): Using the same procedure as for 1, compound 2 was isolated as a white powder in 87% yield. ¹H NMR (CDCl₃): δ 0.25 (s, (CH₂)₃Si-vinyl, 6H), 0.89-1.15 (m, CH₂-C₅H₅Si, 7H), 1.58 (m, CH₂-C₅H₅Si, 42H), 1.80 (m, CH₂-C₅H₅Si, 14H), 5.76-5.83 (dd, 2J = 20.2 Hz, 2J = 3.8 Hz, 1H, trans-SiCHCH₂), 5.94-5.99 (dd, 2J = 14.9 Hz, 2J = 3.8 Hz, 1H, cis-SiCHCH₂), 6.16-6.25 (dd, 2J = 20.2 Hz, 2J = 14.9 Hz, 1H, SiCHCH₂). ¹³C NMR (CDCl₃): δ 0.17 ((CH₃)₂Si-vinyl), 21.94; 22.22; 22.28; 22.93; 24.07 (7CH₂-C₅H₅Si, ratio 1:1:2:2:1), 26.90 - 27.59 (CH₂-C₅H₅Si), 131.64 (CH₃SiMe₂), 139.20 (CH₂CH₂SiMe₂). IR cm⁻¹ (νOSiCl₂): 1378, 1229, 1097. Chapter 2

(c-C₅H₅)₂SiO₃(OSiPh₂MeO₂SiCl₂ (3): Using the same procedure as for 1, compound 3 was isolated as a white extremely viscous solvent in 84% yield. ¹H NMR (CDCl₃): δ 0.72 (s, (CH₃)₂SiPh₂, 3H), 0.84-1.17 (m, CH₂-C₅H₅Si, 7H), 1.53 (m, CH₂-C₅H₅Si, 42H), 1.80 (m, CH₂-C₅H₅Si, 14H), 7.38 (m, CHPh, 6H), 7.63 (m, CHPh, 4H), 7.92 (m, CH₂Ph, 4H). ¹³C NMR (CDCl₃): δ 21.95, 22.25, 22.33, 22.90, 23.96 (7CH₂-C₅H₅Si, ratio 1:1:2:2:1), 26.89 - 27.49 (CH₂-C₅H₅Si, 127.52 (m-C₇H₆), 129.90 (p-C₇H₆), 134.08 (o-C₇H₆), 137.71 (p−p-C₇H₆), 139.20 (CH₂CH₂SiMe₂). ¹⁰Si NMR (CDCl₃): δ 0.73 (OSiMePh₂), -65.68; -68.97; -68.47; -66.52 (7O₂SC₂H₅, ratio 1:1:2:3), -76.81 (O₂SC₂H₅). IR cm⁻¹ (νOSiCl₂): 3515, 3430, 3251, 2948, 2864, 1736, 1587, 1451, 1249, 1085. Tmp: 118±2 °C. Elemental analysis calcd (%) for C₂₆H₂₆Cl₅O₃Si₅ (1056.67): C 43.33, H 6.67, Cl 6.71, found C 43.31, H 6.96, Cl 6.69.

(c-C₅H₅)₂SiO₃(OSiPh₂MeO₂Si(OH)₂ (4): Compound 1 was hydrolyzed by adding 1 mL of distilled water to a solution of 1 (5.00 g, 4.79 mmol) in THF. After stirring at room temperature for 30 minutes, the volatiles were removed in vacuo. The remaining sticky white solid was dissolved in toluene (2 × 20mL) and subsequently pumped to dryness. The same procedure was repeated with hexanes (20 mL) leaving 4 as a free flowing white powder. Recrystallization from hexanes at -20 °C afforded analytically pure 4 (3.09 g, 3.07 mmol, 64%). ¹H NMR (CDCl₃): δ 0.21 (s, (CH₃)₂SiPh₂, 3H), 1.02 (m, CH₂-C₅H₅Si, 7H), 1.57 (m, CH₂-C₅H₅Si, 42H), 1.79 (m, CH₂-C₅H₅Si, 14H), 2.41 (s, Si(OF₂)₂, 1H), 3.80 (s, Si(OF₂)₂, 1H). ¹³C NMR (CDCl₃): δ 1.71 ((CH₃)₂SiO₂, 22.10, 22.19, 22.43, 22.85, 24.21 (7CH₂-C₅H₅Si, ratio 1:1:2:2:1), 26.95 - 27.52 (CH₂-C₅H₅Si), 139.20 (CH₂CH₂SiMe₂). ¹⁰Si NMR (CDCl₃): δ 11.21 (OSiMe₃), -64.81, -65.12, -65.38, -68.38, -67.33 (7O₂SC₂H₅, ratio 1:1:2:2), -89.43 (O₂Si(OH)₂). IR cm⁻¹ (DuraSampIR, vsOH from Nujol-mull): 3542 (vsOH, m), 3402 (vsOH, m), 2949 (s), 2865 (s), 1445 (w), 1252 (m), 1083 (s), 953 (m), 911 (m), 844 (s), 758 (m). Tmp: 154±0.5 °C. Elemental analysis calcd (%) for C₂₆H₂₆Cl₅O₃Si₅ (1017.77): C 45.29, H 7.40, found C 45.01, H 7.21.

(c-C₅H₅)₂SiO₃(OSiMe₂CHCH₂O₂Si(OH)₂ (5): Using the same procedure as for 4, compound 5 was isolated as a white powder in 71% yield. ¹H NMR (CDCl₃): δ 0.28 (s, (CH₃)₂Si-vinyl, 6H), 1.02 (m, CH₂-C₅H₅Si, 7H), 1.58 (m, CH₂-C₅H₅Si, 42H), 1.79 (m, CH₂-C₅H₅Si, 14H), 2.37 (br s, Si(OF₂)₂, 1H), 3.63 (br s, Si(OF₂)₂, 1H), 5.79-5.85 (dd, 2J = 20.4 Hz, 2J = 3.8 Hz, 1H, trans-SiCHCH₂), 5.94-5.99 (dd, 2J = 14.7 Hz, 2J = 3.8 Hz, 1H, cis-SiCHCH₂), 6.16-6.25 (dd, 2J = 20.4 Hz, 2J = 14.7 Hz, 1H, SiCHCH₂). ¹³C NMR (CDCl₃): δ 0.00 ((CH₃)₂Sivinyl), 22.08, 22.19, 22.44, 22.84, 24.09 (7CH₂-C₅H₅Si, 1:1:2:2:1), 26.93 - 27.49 (CH₂-C₅H₅Si), 132.30 (CH₃SiMe₂), 138.97 (CH₅SiMe₂). ¹⁰Si NMR (CDCl₃): δ -0.70 (OSiMe₂vinyl), -64.98, -65.10, -65.36, -66.41, -67.39 (7O₂SC₂H₅, ratio 1:1:2:2), -89.45 (O₂Si(OH)₂). IR cm⁻¹ (DuraSampIR, vsOH from Nujol-mull): 3520 (vsOH, m), 3402 (vsOH, m), 2948 (s), 2864 (s), 1450 (w), 1245 (m), 1082 (s), 951 (m), 911 (m), 865 (w), 832 (m), 790 (m). Tmp: 135 ± 0.5 °C. Elemental analysis calcd (%) for C₂₆H₂₆Cl₅O₃Si₅ (1019.78): C 45.93, H 7.31, found C 45.59, H 7.31.
(c-C₃H₇)₃SiO₃(OSiMe₂)₂O₂Si(OH)₂ (6): Using the same procedure as for 4, compound 6 was isolated as a white free flowing powder in 78% yield. ¹H NMR (CDCl₃): δ 0.73 (s, (CH₃)₃Si-H), 1.05 (m, CH₂-C₃H₇Si), 1.54 (m, CH₂-C₃H₇Si), 1.80 (m, CH₂-C₃H₇), 1.21 (s, Si(OH)₃), 2.23 (s, Si(OH)₃), 1.74 (m, CH₂-Ph), 6.78 (m, CH₂-Ph), 4.74. ¹³C(¹H) NMR (CDCl₃): δ -0.78 (CH₂-SiPh₂), 22.06, 22.25, 22.95, 23.91, 27.75 (7 CH₂-C₃H₇Si, 1:1:2:2:1), 26.93 - 27.48 (CH₂-C₃H₇Si), 127.75 (m-C₃H₇), 129.62 (p-C₃H₇), 134.10 (o-C₃H₇), 137.56 (psio-C₃H₇). ²⁹Si NMR (CDCl₃): δ -6.57. IR (cm⁻¹): 3582 (Si(OH)₃), 3438 (ν(OH)Si), 2974 (s), 2864 (s), 1450 (w), 1245 (m), 1088 (s), 911 (m), 871 (w), 795 (m), 730 (m), 696 (m). Tmp: 138(±0.5)°C. Elemental analysis calcd (%) for C₅₂H₇₁O₁₉Si₄: C 50.93, H 6.95, found C 49.87, H 6.95.

[(c-C₃H₇)₃SiO₃(OSiMe₂)₂O₂Si(OH)]₂(μ-O) (7): A saturated n-heptane (10 mL) solution of compound 6 (1.00 g, 0.88 mmol) was left overnight at room temperature and subsequently stored at -5 °C. After several days the thermodynamically stable condensed product 7 could be isolated in almost quantitative yield. Recrystallization from n-heptane afforded 7 as colorless crystals (0.3 g, 0.13 mmol, 15%) suitable for a single crystal X-ray analysis. ¹H NMR (CDCl₃): δ 0.76 (s, (CH₃)₃Si-H), 0.96 (m, CH₂-C₃H₇Si), 1.51 (m, CH₂-C₃H₇Si, 84H), 1.71 (m, CH₂-C₃H₇), 7.38 (m, CH₂-Ph), 7.63 (m, CH₂-Ph), 8H; ¹³C(¹H) NMR (CDCl₃): δ -0.84 (CH₂-SiPh₂), 21.95, 22.37, 22.89, 23.04, 23.88 (7 CH₂-C₃H₇Si, ratio 1:1:2:2:1), 26.95 - 27.49 (CH₂-C₃H₇Si), 127.57 (m-C₃H₇), 129.31 (p-C₃H₇), 134.23 (o-C₃H₇), 137.88 (psio-C₃H₇). ²⁹Si NMR (CDCl₃): δ -10.26 (OSiMe₂). -65.00, -65.04, -65.82, -66.11, -67.85 (7 O₂SiC₃H₇, ratio 1:1:2:1), -97.76 (O₂Si(OH)), IR (cm⁻¹): ν(OSiCH₃) from Nujol-mull: 3631 (ν(OSiCH₃), m), 2948 (s), 2864 (s), 1450 (w), 1245 (m), 1088 (s), 911 (m), 871 (w), 795 (m), 730 (m), 696 (m). Tmp: 197(±1)°C. Elemental analysis calcd (%) for C₅₂H₇₁O₁₉Si₄: 51.34, H 6.91, found C 50.68, H 6.84.

(c-C₃H₇)₃SiO₃(OSiMe₂)₂O₂Si(N[H]Pr)₂ (8): To a solution of 1 (2.88 g, 2.52 mmol) in 60 mL of THF, 4 equivalents of PrNH₂ (0.86 mL, 10.08 mmol) were slowly added. The resulting suspension was stirred overnight at ambient temperature to complete the reaction. Filtration and removal of the solvent afforded analytically pure 7 as a white solid (2.44 g, 2.24 mmol, 89%). ¹H NMR (CDCl₃): δ 0.39 (s, (CH₃)₃Si-H), 1.25 (m, CH₂-C₃H₇Si, 7H), 1.31 (d, HNC(Η)(CH₂)₂, 6H), 1.53 (m, CH₂-C₃H₇Si), 3.34 (m, HNC(Η)(Me₂), 2H); ¹³C(¹H) NMR (CDCl₃): δ 2.36 ((CH₃)₃Si), 22.83; 22.92, 23.80; 23.88, 25.05 (7 CH₂-C₃H₇Si, 1:1:2:2:1), 27.90 (HNC(Η)(CH₂)₂, 12), 28.37 - 28.24 (CH₂-C₃H₇Si), 42.45, 42.52 (HNC(Η)(Me₂)), 42.52 (HNC(Η)(Me₂)), 63.99, 64.27, 64.82, 66.54, 67.21 (7 O₂SiC₃H₇, 12:1:2:1:2, 69.43 (O₂Si(NH)Pr²). Elemental analysis calcd (%) for C₅₄H₇₄O₂₃N₃: C 48.49, H 8.14, N 2.57, found C 48.36, H 8.06, N 2.49. Condensation product (c-C₃H₇)₃SiO₃(OSiMe₂)₂O₂Si(N[H]Pr)¹ H NMR (CDCl₃): δ 1.00 (m, CH₃-C₃H₇Si), 1.12 (d, HNC(Η)(CH₂)₂, 6H), 1.58 (m, CH₂-C₃H₇Si), 1.80 (m, CH₂-C₃H₇), 14H), 2.31 (m, HNC(Η)(Me₂), 2H); ¹³C(¹H) NMR (CDCl₃): δ 22.26; 22.28 (3/4, CH₃-C₃H₇Si), 27.22 (HNC(Η)(CH₂)₂), 27.02, 27.31 (CH₂-C₃H₇Si), 42.52 (HNC(Η)(Me₂)).

X-Ray crystal structure analyses of 1*: A suitable crystal was selected, mounted on a thin, glass fiber using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° o-scans at 0, 90, and 180° in θ. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied. Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group. The structure was solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F². A hexameric molecule was co-crystallized in the asymmetric unit. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHELXTL 6.12 program library.
X-Ray crystal structure analysis of 7: A colorless crystal (measuring 0.18 × 0.12 × 0.06 mm) was mounted under the cold nitrogen stream (150 K), on a Bruker SMART APEX CCD diffractometer equipped with a 4K CCD detector set 60.0 mm from the crystal (Platform with full three-circle goniometer). Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS), and reduced to \( F_0^2 \). The program suite SHELXTL was used for space group determination (\textit{XPREP}). The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program \textit{DIRDIF}. All refinement calculations were performed using the program packages SHELXL and PLATON.

| Table 5. Crystal data and details of the structure determination of 1\(^t\) ([((c-C\(_6\)H\(_{11}\))\(_7\)Si\(_7\)O\(_9\)(OSiMe\(_3\))O\(_2\)SiCl\(_2\)]\(_2\))\(_2\) and 7 ([([c-C\(_5\)H\(_9\)])\(_7\)Si\(_7\)O\(_9\)(OSiMePh\(_2\))(O\(_2\)Si(OH)-)]\(_2\)\(_\mu\)-O). |
|-----------------|-----------------|
| **1\(^t\)**     | **7**           |
| Empirical formula | C51H91C2O12Si9   | C96H154O27Si18 |
| Formula weight, g·mol\(^{-1}\) | 1219.95          | 2245.82          |
| Crystal system, space group | Monoclinic, P2(1)/c | Triclinic, P2(1)/a |
| Unit cell dimensions | a, Å 11.108(11) | 28.576(2) |
|                      | b, Å 24.629(2) | 13.378(1) |
|                      | c, Å 25.512(2) | 34.010(3) |
|                      | α, ° 90 | 90 |
|                      | β, ° 91.835(2) | 100.324(1) |
|                      | γ, ° 90 | 90 |
| Volume, Å\(^3\)     | 6976.2(12) | 12791.2(17) |
| Theta range for data collection | 1.15 to 28.53 deg | 2.38 – 23.62 deg |
| Z                   | 4               | 4               |
| T, K                | 203(2)          | 110(2)          |
| \( P_{calc} \), g·cm\(^{-3}\) | 1.162          | 1.166          |
| Crystal size, mm    | 0.10 x 0.10 x 0.10 | 0.12 x 0.11 x 0.11 |
| Final R indices [I >2σ(I)] | R1 = 0.0589 | R1 = 0.0707 |
|                      | wR2 = 0.1412 | wR2 = 0.1686 |
| R indices (all data) | R1 = 0.0924 | R1 = 0.0924 |
|                      | wR2 = 0.1609 | wR2 = 0.1609 |
| Goodness-of-fit on \( F^2 \) | 1.050          | 1.114          |
| Limiting indices | -14<=h<=14, 0<=k<=31, 0<=l<=34 | -30<=h<=32, -13<=k<=15, -37<=l<=38 |
| F(000)             | 2612            | 4792            |
| Absorption coefficient | 0.297 mm\(^{-1}\) | 53416 / 19632 [R(int) = 0.1095] |
| Reflections collected / unique | 46145 / 11446 [R(int) = 0.0922] | 0.9741 – 0.9718 |
| Completeness to theta = 25.00 | 90.9 %         | 0.848337 |
| Max. and min. transmission | 1.000000 and 0.848337 | 1.050          |
| Goodness-of-fit on \( F^4 \) | 1.050          | 0.874          |
| Largest diff. peak and hole | 0.817 and -0.488 e. Å\(^{-3}\) | 0.52(8) and -0.39 e. Å\(^{-3}\) |

Special Acknowledgements

Glenn P. A. Yap (Chemistry Department, University of Ottawa, Canada) is kindly acknowledged for solving the crystal structure of ([((c-C\(_6\)H\(_{11}\))\(_7\)Si\(_7\)O\(_9\)(OSiMe\(_3\))O\(_2\)SiCl\(_2\)]\(_2\)). Auke Meetsma (Crystal Structure Center, Chemical Physics, Material Science Center, University of Groningen) is given thanks to for solving the crystal structure of ([([c-C\(_5\)H\(_9\)])\(_7\)Si\(_7\)O\(_9\)(OSiMePh\(_2\))(O\(_2\)Si(OH)-)]\(_2\)\(_\mu\)-O) (7).
References and Notes

20) Only 1', the cyclohexyl substituted analog of 1 gave crystals suitable for an X-ray analysis.
59) Sheldrick, G. M. Multi-Scan Absorption Correction Program.; University of Göttingen, Germany, 2000.
62) Spek, A. L. Program for the automated Analysis of Molecular Geometry (A multipurpose Crystallographic Tool); University of Utrecht, the Netherlands, 2001.
Silsesquioxane Models for Partly Silylated Silica Surfaces in the Proximity of a Silanol

Incompletely condensed silsesquioxanes with a siloxane ring of various size and rigidity in the proximity of a silanol are described in this chapter. Compounds $R_7Si_7O_{17}-(OSiR'_2O)_{n}(OH)$ ($R=c-C_5H_9, c-C_6H_{11}$; $R'=Me, Ph$; $n=1-4$) represent a model system for partly silylated silica surfaces in the presence of silanols. Furthermore they resemble defective sites present on silicate surfaces. Solution and solid state FT-IR spectra show a shift to lower frequency of approximately 150 cm$^{-1}$ compared to a truly isolated silanol $R_7Si_7O_{12}(OH)$, indicating hydrogen bonding of the silanol with the adjacent siloxane ring. In agreement with this, the relative ion pair acidities $pK_{ip}$ of the silanols were lowered by about a factor 10 compared to a truly isolated silanol. This chapter also describes several approaches towards mimicking zeolite pores. In spite of several attempts to force an intermolecular silylation of $R_7Si_7O_{10}(OH)_3$ with dichlorosil(ox)ane, entropically beneficial intramolecular ring formation appeared to be preferred. A successful route in which two silsesquioxane cages were covalently linked while silanols are still available for additional reactions proved to be hydrosilylation by a platinum catalyst of mono-silylated ($c-C_5H_9)_7Si_7O_{9}(OSiMe_2vinyl)(OH)_2$ and fully silylated ($c-C_5H_9)_7Si_7O_{9}(OSiMe_2O)(OSiMe_2H)$ into an asymmetric dimer.

3.1. Introduction

Silica surface silanol groups can react with various organic and inorganic compounds. This gives for example the opportunity to modify the adsorption properties of silica absorbents or to form heterogeneous catalysts after grafting organic groups or catalyst precursors onto the silica surface.\textsuperscript{1,2} Grafting onto silica surfaces can effectively be mimicked by incompletely condensed polyhedral silsesquioxanes. Like observed for silica surfaces, silylation of silsesquioxanes dramatically affects their acidity and reactivity; a drop in acidity and reactivity was observed when going from an incompletely condensed tri-silanol $R_7Si_7O_{10}(OH)_3$ towards a monosilylated di-silanol $R_7Si_7O_{9}(OSiR'_3)(OH)_2$.\textsuperscript{3} This behavior and other differences between various types of silanols will be further discussed in Chapter 4. Starting from the most widely used incompletely condensed silsesquioxanes $R_7Si_7O_{10}(OH)_3$ ($R=c-C_5H_9$, $c-C_6H_{11}$) several silylation reactions have been studied in the past. As a result the number of hydroxyl groups was altered and thus various types of surface silanols could be modelled: vicinal silanols,\textsuperscript{3,5} geminal silanols (Chapter 2 of this thesis), and isolated silanols.\textsuperscript{6}
Monosilylation of \( R_7SiO_3(OH) _3 \) (\( R= c-C_3H_7, c-C_5H_{11} \)) with chlorosilanes in the presence of amine is straightforward and successful for a range of chlorosilanes with different steric and/or electronic properties (Scheme 1). The monosilylated silsesquioxanes, leaving two vicinal silanols, are the most widely used silylated silsesquioxane precursors and the metalated analogues represent models for grafted bipodal silica metal sites.\(^7\)\(^-\)\(^13\) Disilylated silsesquioxanes are much more difficult to obtain, silylation of \( R_7SiO_3(OH) _3 \) (\( R= c-C_3H_7, c-C_5H_{11} \)) with two equivalents of chlorotrimethylsilane resulting in \( R_7SiO_3(OSiMe) _2OH \) has been reported but can only be isolated by fractional crystallization of a mixture of the mono-, di-, and tri-silylated products.\(^4\) The low selectivity for this reaction originates from the fact that the tri-silanol is up to two orders of magnitude more acidic than the di-silanol whereas the di- and mono-silanol show similar acidities.\(^3\) Consequently, the first silylation of a tri-silanol is much more selective than the second one. Complete silylation of the tri-silanol with three equivalents of chlorosilanes has been reported for sterically unhindered chlorosilanes \( CSiMe_3R' \) (\( R = Me, H, ^1^4\) \( CHCH_2, ^1^5\)). Lorenz and Edelmann reported a completely silylated dimeric structure \([((c-C_3H_{11})_2SiO) - (OSiMe_2O)]_2(OSiMe_2O)\) which was obtained by reacting two equivalents of \((c-C_3H_{11})_2SiO(OH) _3\) with three equivalents of the dichlorosilane \( Cl_2SiMe_2\).\(^1^5\) By silylating \( R_7SiO_3(OH) _3 \) first with \( R'3SiCl_2 \), followed by silylation with \( SiCl_4 \), the intermediate \( R_7SiO_3(OSiR' _3)OSiCl_2 \) was formed, hydrolysis afforded the geminal silanols \( R_7SiO_3(OSiR' _3)O-Si(OH) _2 \) which are described in detail in the previous chapter. Another well-known type of silylation reaction forms the corner-capping reactions of the silsesquioxane tri-silanol \( R_7SiO_3(OH) _3 \) with \( XSiCl_3 \) or \( XSi(OEt)_3 \) yielding stable closed caged octameric silsesquioxanes \( R_7SiO_3X \) (\( X= alkyl, alkenyl, aryl, Cl, OH, NR_2, OSi(alkyl)_3 \)).\(^9\)\(^-\)\(^1^6\)\(^-\)\(^2^0\) These silsesquioxanes have been applied to model various monodentate bonded metal silica surface species. The fully condensed framework containing one potentially polymerizable pendant group has also been applied as comonomer in polymers and resins, thus providing interesting hybrid-like materials. All silsesquioxane silylation reactions are summarized in Scheme 1.

**Scheme 1. Silylation of incompletely condensed silsesquioxanes \( R_7SiO_3(OH) _3 \).**
So far, only isolated silanol groups and their reactivity have been studied. The effect of neighboring groups was left out of consideration. Decided was to mimic the effect of neighboring siloxy functionalities on the acidity and reactivity of isolated silanols, as can be found in for example partly dehydroxylated and partly silylated silicas. In this chapter a range of disilylated silsesquioxanes with a remaining silanol are presented. They are obtained from reaction of \( R_7Si_7O_9(OH)_3 \) \((R = \text{c-C}_5H_9, \text{c-C}_6H_{11})\) with several dichlorosil(ox)anes. The influence of the neighbouring siloxane ring, capable of electron donation by its silyl ethers, on the mono-silanol \((\text{i.e. a perturbed silanol})\) was investigated.

A major disadvantage of most metallic silsesquioxane models is their tendency to decompose on hydrolysis, releasing the silsesquioxane ligand(s). Creating a stable link between two silsesquioxane cages will reduce this problem, as the multidentate character of the thus formed ligand will enhance the stability of the corresponding metal complexes. Building homogeneous zeolite-like pores or complex silica surface sites by linking silsesquioxanes intermolecularly, would lead a step closer to reliable mimicking of complex siliceous materials. We were interested whether tuning the substituents and reaction conditions in the reaction of \( R_7Si_7O_9(OH)_3 \) \((R = \text{c-C}_5H_9, \text{c-C}_6H_{11})\) and \( \alpha,\omega\)-dichlorosil(ox)anes would afford solely silsesquioxanes containing an intramolecular siloxy ring or would also allow intermolecularly linked silsesquioxane products to be formed (Figure 1). In this chapter, this route together with several other possible routes to establish a stable link (\( \text{e.g. a siloxane-} \) or carbon-spacer) between two silsesquioxane cages, with silanols available for additional reactions, will be described.

![Figure 1](image.png)

**Figure 1.** Target towards mimicking more complex silica surface sites and zeolite pores: two silsesquioxane cages intermolecularly linked by a spacer and availability of remaining silanols for additional reactions.

### 3.2 Synthesis

Treating \((\text{c-C}_5H_9)_7Si_7O_9(OH)_3\) with 0.95 equivalent of \( \text{Cl}_2\text{SiMe}_2 \) in the presence of \( \text{NEt}_3 \) in THF and stirring at room temperature overnight cleanly yielded the disilylated \((\text{c-C}_5H_9)_7Si_7O_9(\text{OSiMe}_2O)(OH)\) (1). In the same manner, a variety of disilylated silsesquioxanes could be obtained from the reaction of \( R_7Si_7O_9(OH)_3 \) \((R = \text{c-C}_5H_9, \text{c-C}_6H_{11})\) with the dichlorosil(ox)anes \( \alpha,\omega\)-\( \text{ClSiMe}_2\{\text{OSiMe}_2O}\) \((n = 0, 1, 2, 3)\), \( \text{Cl}_2\text{SiPh}_2 \), and \( \text{CISiPh}_2\{\text{OSiPh}_2}\text{Cl} \). From the twelve possible products, eight products could actually be isolated in elemental analytically pure form; \((\text{c-C}_5H_9)_7Si_7O_9(O\{\text{OSiMe}_2O\})_n(OH)\) \((n = 0, 1, 2, 3)\), \((\text{c-C}_5H_9)_7Si_7O_9(O\{\text{OSiMe}_2O\})_2(OH)\) (2), \((\text{c-C}_6H_{11})_7Si_7O_9(O\{\text{OSiMe}_2O\})_4(OH)\) (3), \((\text{c-C}_6H_{11})_7Si_7O_9(O\{\text{OSiMe}_2O\})_2(OH)\) (4),
Interestingly, in some cases, the cyclopentyl substituted silsesquioxane showed considerable divergent reactivity than the cyclohexyl substituted analogue. Whereas reactions with cyclopentyl substituted silsesquioxane (c-C\textsubscript{5}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OSiMe\textsubscript{3})\textsubscript{3}(OH)\textsubscript{3} (5), (c-C\textsubscript{6}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OSiMe\textsubscript{3})\textsubscript{3}(OH)\textsubscript{3} (6), (c-C\textsubscript{5}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OSiPh\textsubscript{2})\textsubscript{3}(OH) (7), and (c-C\textsubscript{6}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OSiMe\textsubscript{3})\textsubscript{3}(OH)\textsubscript{3}·(OH)·(OH)·(OH)·(OH) (8) (Scheme 2). Product 8 is a hydrogen bridged dimeric complex, which is the result of reaction of (c-C\textsubscript{5}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OH)\textsubscript{3} with ClSiMe\textsubscript{2}OSiMe\textsubscript{2}Cl in a 2 to 1 fashion. Reactions of R\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OH)\textsubscript{3} with α,ω-dichlorosil(ox)anes that were not successful, either reacted in a 2 to 1 ratio or 1 to 1 ratio, proved to be unselective and resulted in unidentifiable or mixtures that could not be separated.

Reactivity for cyclohexyl and cyclopentyl substituted trisilanol with ClSiMe\textsubscript{2}OSiMe\textsubscript{2}Cl was different as well. In the case of the cyclohexyl substituted silsesquioxane (c-C\textsubscript{6}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OH)\textsubscript{3}, a clean monomeric product could be obtained (compound 4). However, for the cyclopentyl analogue a pure product could only be acquired when the tris-silanols was present in excess; i.e. when (c-C\textsubscript{5}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OH)\textsubscript{3} was reacted with the dichlorosiloxane in a 2 to 1 fashion instead of the usual 1 to 1 fashion. This reaction resulted in the unprecedented complex (c-C\textsubscript{5}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OSiMe\textsubscript{3})\textsubscript{3}(OH)·(OH)·(OH)·(OH)·(OH)·(OH) (8) of which the proposed structure is shown in Scheme 2. From NMR data and a reactivity study (described in the next paragraph) it is deduced that the remaining silanol group of the intramolecular substituted product coordinates via hydrogen bonds to two silanols of the adjacent silsesquioxane trisilanol (Scheme 2). Attempts to crystallize the complex or separate the di-silylated mono-silanol from the trisilanol by crystallization afforded (c-C\textsubscript{5}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OH)\textsubscript{3} and fully condensed (c-C\textsubscript{5}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9} species. This confirms that the tri-silanol is not silylated and stabilizes its disilylated stable counterpart by intermolecular hydrogen bonding. When (c-C\textsubscript{5}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OH)\textsubscript{3} was reacted with an excess of ClSiMe\textsubscript{2}OSiMe\textsubscript{2}Cl and kept under argon carefully, the product (c-C\textsubscript{5}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OSiMe\textsubscript{3})\textsubscript{2}(OSiMe\textsubscript{2}OSiMe\textsubscript{2}Cl) (9) could be isolated. NMR-data confirm the formation of 9 and a silver nitrate test proved the presence of chloride. The question why the disilylated monosilanol (c-C\textsubscript{5}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OSiMe\textsubscript{2}OSiMe\textsubscript{2}) (OH) and (c-C\textsubscript{6}H\textsubscript{11})\textsubscript{7}Si\textsubscript{3}O\textsubscript{9}(OSiMe\textsubscript{2}O) (OH) are not stable and their counterparts 4 and 1 are, remains unanswered.
Scheme 2. Reaction of incompletely condensed silsesquioxanes 1-8 with methyl or phenyl substituted dichlorosilanes.

Reaction of \((\text{c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{9}(\text{OH})_3\) with the sterically demanding \(\text{ClSiPh}_2\text{OSiPh}_2\text{Cl}\) was not successful and also reaction with \((\text{c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{9}(\text{OH})_3\) was in this case unfruitful. Disilylation of tri-silanols \(\text{R}_7\text{Si}_7\text{O}_{9}(\text{OH})_3\) (\(\text{R} = \text{c-C}_5\text{H}_9, \text{c-C}_6\text{H}_{11}\)) with longer \(\alpha,\omega\)-dichlorosil(ox)anes \(\text{ClSiMe}_2(\text{OSiMe}_2)_n\text{Cl} (n = 2, 3)\) in the presence of amine were straightforward. Although stirring for two nights or moderately heating for one night was required for reactions to go to completion, the expected products 2, 3, 5, and 6 could be isolated in pure form for both cyclopentyl and cyclohexyl substituted silsesquioxanes.

In none of the abovementioned reactions the formation of siloxane bridged bis-silsesquioxanes was observed. Even reactions with the longer \(\alpha,\omega\)-dichlorosil(ox)anes \(\text{ClSiMe}_2(\text{OSiMe}_2)_n\text{Cl} (n = 2, 3)\) in a 2 to 1 fashion resulted solely in the intra-silylated products 2-6 and unreacted \(\text{R}_7\text{Si}_7\text{O}_{9}(\text{OH})_3\) (\(\text{R} = \text{c-C}_6\text{H}_{11}\), \(\text{c-C}_6\text{H}_{11}\)). Apparently, entropic reasons bring about that substituting a second silanol group from the same molecule is more preferable than substituting a more reactive silanol group of a second molecule.
3.3 Identification of disilylated silsesquioxanes; solution-NMR

$^1$H-, $^{13}$C-, and $^{29}$Si-NMR data of compounds 1-8 are shown in Table 1. Products 1 and 7 are C$_2$ symmetric, which can be deduced from the five CH methyne resonances ($^{13}$C-NMR) and five framework-Si resonances ($^{29}$Si-NMR) in a 2:2:1:1:1 ratio. The proton NMR spectra of compound 1 and 7 (in deuterated chloroform) show that the silanols are situated at 3.17 and 2.39 ppm respectively, indicating stronger deshielding of the silanol of 1 compared to compound 7. In the $^{29}$Si-NMR spectrum, the silanol silicon atom can be found at –59.27 ppm for compound 1 and at –58.95 for compound 7. The methyl groups of product 4 (two -OSiMe$_2$O- units in the ring) give rise to a doublet at 0.20 ppm in the $^1$H-NMR spectrum and two singlets, each assigned to two methyls in the $^{13}$C-NMR spectrum. The $^{29}$Si-NMR spectra of 2 and 5 display two resonances (ratio 1 to 2) for the three -OSiMe$_2$O- silicons at –17.5 and –20.0 ppm, respectively. Finally, products 3 and 6, with four -OSiMe$_2$O- units in the additional siloxane ring, show three (3; 2:4:2) and four (6; 2:2:2:2) methyl resonances in the $^1$H- and $^{13}$C-NMR spectra respectively. The $^{29}$Si-NMR spectrum shows two ring-Si resonances (ratio 2 to 2) for both 3 and 6 at about –20 ppm. These NMR spectra correspond with highly fluxional siloxane rings. The chemical shifts of the silanol OH protons in 1-6 are considerably shifted to lower field in $^1$H-NMR spectra compared to silsesquioxanes with a truly isolated silanol. The proton resonance of the silanol of ($c$-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH) can be found at 2.53 ppm, at 2.49 ppm for ($c$-C$_6$H$_{11}$)$_7$Si$_6$O$_{12}$(OH), and at 2.79 ppm for ($c$-C$_6$H$_{11}$)$_7$Si$_9$O$_9$(OSiMe$_3$)$_2$OH. As a comparison, the OH resonance of an isolated silanol of a non-silsesquioxane, SiPh$_3$OH can be found at 2.68 ppm in the $^1$H-NMR spectrum. The hydrogen resonance of the silanol of the disilylated silsesquioxanes are found at lower field ranging from 3.16 ppm for compound 1 to 3.94 ppm for compound 5 (Table 1). This low-field shift for compounds 1-6 can either originate from a decrease in acidity of the silanols or from increased hydrogen bonding with the intramolecular siloxane ring. Truly isolated silanols are barely capable of hydrogen bonding in solution and therefore give rise to sharp OH resonances at higher field than the perturbed mono-silanols of compounds 1-6.

Complex 8 is surprisingly stable and NMR-data (Figure 2, Table 1) indicate one single complex consisting of two cage-structures. The $^1$H-NMR spectrum shows two singlets at 0.22 and 0.19 ppm, these are assigned to the four methyl groups attached to the siloxane ring (in total 12 H). The methyne protons of the cyclopentyl substituents integrate for 14 H compared to the twelve methyl protons of the two -OSiMe$_2$O- units. Two broad bands are found in the $^1$H-NMR spectrum at 3.61 ppm and 2.97, which are assigned to two types of hydroxyls and, according to the relative integrals, correspond to three and one proton respectively. These data suggest a stable complex in which two cages, ($c$-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiMe$_3$O)(OH) and ($c$-C$_6$H$_{11}$)$_7$Si$_9$O$_9$(OH)$_3$, are held together solely by hydrogen bonds (a suggested structure is shown in Scheme 2). In this complex, the three silanols of the tri-silanol participate in hydrogen bonding with the silyl ether functionalities of the siloxane ring of the disilylated complex.
Figure 2. $^1$H-, $^{13}$C- and $^{29}$Si-NMR spectra of (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(O{SiMe$_2$O}$_3$)(O{OH})(OH)$_3$Si$_7$O$_9$(c-C$_5$H$_9$)$_7$ (8).

Table 1. $^1$H-, $^{13}$C($^1$H)- and $^{29}$Si-NMR Data$^a$ of silsesquioxanes 1-8.

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$^a$: $^1$H-, $^{13}$C- and $^{29}$Si-NMR-spectra were recorded in CDCl$_3$.
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Table 1 continued

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<td>-67.38 (4)</td>
<td>(O)(_2)SiC(_3)H(_3)</td>
<td>1.00 (m, 14H)</td>
<td>CH(_2)-C(_2)H(_5)</td>
<td></td>
</tr>
<tr>
<td>22.51</td>
<td>CH(_2)-C(_2)H(_5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.19</td>
<td>CH(_2)-C(_2)H(_5)</td>
<td></td>
<td></td>
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<tr>
<td>0.90</td>
<td>CH(_2)-Si(O)(_2)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>0.45</td>
<td>CH(_2)-Si(O)(_2)</td>
<td></td>
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3.4 Identification of disilylated silsesquioxanes; FT-IR

Infrared spectroscopy is a frequently used technique to study bulk properties of silica surfaces. Especially the OH stretching vibrations of silanol groups (\(\nu_{\text{OH}}\)) offer a great deal of information on the process of dehydroxylation or dehydration of silicas.\(^1\) Here, attention will be focused on OH stretching vibrations of mono-silanolos with and without the presence of an additional siloxane ring. A full comparison of silsesquioxanes bearing different types of silanols (including geminal silanols, described in Chapter 2) with surface silanols will be described in Chapter 4.

The infrared spectra of compound 1-8 were examined both in solution (0.1M in CCl\(_4\)) and in the solid state (Table 2, Figure 3). Solid state spectra were recorded using Nujol mulls. The sharp band at 3700 cm\(^{-1}\) found both in solution and in solid-state FT-IR spectra of (c-C\(_2\)H\(_5\))\(_2\)Si\(_6\)O\(_{12}\)(OH), is assigned to its truly isolated silanol. Similar sharp bands at high frequency have been observed for other silsesquioxide compounds possessing an isolated silanol (Table 2). In the solid state IR spectrum of (c-C\(_2\)H\(_5\))\(_2\)Si\(_6\)O\(_{12}\)(OH), a second vibration band was observed at 3450 cm\(^{-1}\) and assigned to an intermolecularly mono-hydrogen bond of the partly existing dimeric crystalline phase (Figure 3, Table 2). This agrees well with OH stretching vibration FT-IR bands found for silica surfaces. A broad band
having a maximum near 3550 cm\(^{-1}\) is usually assigned to hydrogen bonded silanol groups.\(^{21}\) After extensive thermal treatment of silica, a narrow band at 3750 cm\(^{-1}\) (recorded in vacuum) remains that is assigned to truly isolated silanols.\(^{21}\) Compounds 1-7 show comparable \(\nu_{\text{OH}}\) wave numbers in solution and in the solid state; around 3550 cm\(^{-1}\) for the methyl substituted compounds 1-6, and at approximately 3635 cm\(^{-1}\) for the phenyl substituted compound 7 (Figure 3, Table 2). Compounds 1-6, possessing flexible methyl substituted siloxane rings, show broad OH stretching vibration bands characteristic for the presence of hydrogen bonding. The \(\nu_{\text{OH}}\) vibration band of the phenyl-substituted compound 7 is much sharper than the \(\nu_{\text{OH}}\) vibration band of 1-6 and its frequency (3635 cm\(^{-1}\)) suggests the presence of almost truly isolated silanols. This is supported by the large \(\Delta\nu_{\text{OH}}\) shift in the presence of ether (\textit{vide infra}, Table 2). Probably, the bulky phenyl groups of 7 complicate interaction of the silanol with the silyl ether functionalities unlike the methyl groups of 1-6. The position and broadness of the \(\nu_{\text{OH}}\) bands in solution show that even in solution significant hydrogen bonding with the silyl ethers of the intramolecular siloxane ring is present. Besides the broad \(\nu_{\text{OH}}\) band, the solution IR spectrum of 1 shows an additional high frequency \(\nu_{\text{OH}}\) band, characteristic for an isolated hydroxyl group. Most probably, the siloxane ring in 1 is too small to undergo effectively intramolecular hydrogen bonding with the hydroxyl group. It is assumed that like R\(_7\)Si\(_8\)O\(_{12}\)(OH), 1 forms in the solid state rather dimeric structures stabilized by intermolecular hydrogen bonding than monomeric structures stabilized by intramolecular hydrogen bonding. These intermolecular hydrogen bonded dimeric species partly dissociate in solution. Indeed, molecular weight measurements in benzene of compound 1 show that 1 is dominantly monomeric in solution, just as R\(_7\)Si\(_8\)O\(_{12}\)(OH) (with an unperturbed silanol) and compound 2 (with a perturbed silanol) in solution. On the basis of the similar hydrophobicity of both solvents (benzene: \(\varepsilon = 2.3\); CCl\(_4\): \(\varepsilon = 2.2\) at 20\(^\circ\)C), silsesquioxanes with perturbed or unperturbed isolated silanols are expected to be monomeric in CCl\(_4\) as well.

\textbf{Table 2.} FT-IR values in Nujol and CCl\(_4\), estimated \(pK_{\text{ip}}^*\) values and \(\Delta\nu_{\text{OH}}\) FT-IR values due to a proton acceptor for 1-7 and other silanol containing compounds.

<table>
<thead>
<tr>
<th>compound</th>
<th>siloxane ring size of R(_7)Si(<em>8)O(</em>{12})(O(Si(_R)(_2)O(<em>n))(</em>{n+1}))(OH)</th>
<th>IR (Nujol mull) (\nu_{\text{OH}}) (cm(^{-1}))</th>
<th>IR (CCl(<em>4)) (\nu</em>{\text{OH}}) (cm(^{-1}))</th>
<th>IR (CCl(_4) + Et(<em>2)O) (\Delta\nu</em>{\text{OH}}) (cm(^{-1}))</th>
<th>(pK_{\text{ip}}^*) (THF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n = 0</td>
<td>3564 (3699), 3549</td>
<td>132</td>
<td>9.6 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>n = 2</td>
<td>3561</td>
<td>3594, 3511</td>
<td>49</td>
<td>10.5 ± 0.1</td>
</tr>
<tr>
<td>3</td>
<td>n = 3</td>
<td>3606</td>
<td>3602, 3481</td>
<td>113</td>
<td>10.1 ± 0.1</td>
</tr>
<tr>
<td>4</td>
<td>n = 1</td>
<td>3561</td>
<td>3550</td>
<td>16</td>
<td>10.7 ± 0.3</td>
</tr>
<tr>
<td>5</td>
<td>n = 2</td>
<td>3598, 3516</td>
<td>3602, 3519</td>
<td>40</td>
<td>10.8 ± 0.1</td>
</tr>
<tr>
<td>6</td>
<td>n = 3</td>
<td>3668</td>
<td>3620, 3473</td>
<td>102</td>
<td>9.7 ± 0.3</td>
</tr>
<tr>
<td>7</td>
<td>n = 0</td>
<td>3661</td>
<td>3635</td>
<td>251</td>
<td>11.1 ± 0.4</td>
</tr>
<tr>
<td>8</td>
<td>n = 1</td>
<td>3568, 3198</td>
<td>3207</td>
<td>0</td>
<td>7.9 ± 0.8</td>
</tr>
<tr>
<td>(c-C(_5)H(_9))(_7)Si(<em>8)O(</em>{12})OH</td>
<td>-</td>
<td>3706, 3444</td>
<td>3700</td>
<td>359</td>
<td>8.9 ± 0.4</td>
</tr>
<tr>
<td>(c-C(_6)H(_11))(_7)Si(<em>8)O(</em>{12})OH</td>
<td>-</td>
<td>3716, 3327</td>
<td>3703</td>
<td>360</td>
<td>9.0 ± 0.3</td>
</tr>
<tr>
<td>Me(_3)SiOH</td>
<td>-</td>
<td>-</td>
<td>3694</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ph(_3)SiOH</td>
<td>-</td>
<td>3689, 3337</td>
<td>3685</td>
<td>-</td>
<td>10.8 ± 0.3</td>
</tr>
</tbody>
</table>

*relative ion pair acidities \(pK_{\text{ip}}^*\); averages of two indicators, Li\([\text{9-(cyano)fluorenide}]\)\(-2\)THF and Li\([\text{9-methoxycarbonyl)fluorenide}]\)\(-2\)THF.
Unlike compound 1-7, the dimeric complex 8 shows very different $\nu_{\text{OH}}$ bands in the solution and solid state FT-IR spectra. Two distinct broad vibration bands $\nu_{\text{OH}}$ are found for 8 in the solid state (3568 and 3198 cm$^{-1}$) and only one broad vibration band $\nu_{\text{OH}}$ in solution (3217 cm$^{-1}$). The band located at 3568 cm$^{-1}$ in the solid state is comparable with the frequencies of the intramolecular hydrogen bonded bands found for compounds 1-6, the broad band at 3198 cm$^{-1}$ is indicative for poly-hydrogen bonded bands as observed for the vicinal silanols of $R_7Si(OH)_3$ or $R_7Si(\text{OSIR}_3)(OH)_2$ (Chapter 4 of this thesis). The existence of two types of hydrogen bonded bands in the solid state FT-IR confirm the NMR data shown earlier which also suggested the presence of two types of hydrogen bonded hydroxyl groups. In solution the dimeric complex is much more dynamic and the poly-hydrogen band located at 3217 cm$^{-1}$ that preserve the dimeric character of the complex dominates. Molecular weight measurements in benzene confirm that complex 8 is dimeric in solution.

Figure 3. FT-IR of 1-8 and (c-$C_5H_9$)$_7$Si$_8$O$_{12}$OH recorded in the solid state (Nujol mull) and in solution (0.1M in CCl$_4$).
3.5 Identification of disilylated silsesquioxanes; Brønsted acidities

Although the overall Brønsted acidity of silica surface silanols are usually fairly weak, the differences in Brønsted acidity between various silanol types were found to be large enough to affect the local reactivity. Since the protons of silica surface hydroxyls ion-exchange readily with metal cations, there is a relationship between the ion-exchange rate and the Brønsted acidity of the silanols (Chapter 2 and 4 of this thesis). It has to be stated here that acidities are strongly solvent dependent, the dissociation constant of an acid depends on the ability of the solvent to solvate the proton, the anion and the undissociated acid. Silsesquioxanes 1-8 are highly lipophilic and only dissolve in organic solvents with relatively low polarity like THF or hexane. In solvents with a relatively low dielectric constant such as THF ($\varepsilon_{(20°C)} = 7.6$), ion pair dissociation hardly occurs. Hence, acidity measurements in low-polar solvents only give qualitative values about relative acidities in each specific solvent, i.e., one can only determine whether one compound is more or less acidic than another one in a specific solvent. However, this qualitative information is still very significant for ion-exchange reactions and thus for the synthesis of supported catalysts.

The relative Brønsted acidities of the silanols of 1-8 could be established by two different ways; by the $\Delta \nu_{\text{OH}}$ changes in IR spectra due to addition of a proton acceptor and by ion pair acidities $pK_p$ in THF obtained from UV-VIS using the overlapping indicator method (see Chapter 2). Silsesquioxanes 1-8 were dissolved in neat CCl$_4$ (0.1M) and in CCl$_4$ containing 25% ether as the proton acceptor. In the latter case the $\nu_{\text{OH}}$ vibrations of 1-8 shift towards lower wavenumbers due to hydrogen bond interaction between the silanol and the proton acceptor. These $\Delta \nu_{\text{OH}}$ changes are considered as a measure of the energy of the specific interaction and thus the Brønsted acidity of the silanols (Badger-Bauer relationship$^{23,24}$). When a mono-silanols is almost unperturbed (i.e. compound 7 and ($c$-C$_5$H$_9$)$_7$Si$_8$O$_{12}$(OH)), the effect of adding a proton acceptor is largest (a $\Delta \nu_{\text{OH}}$ shift of 251 and 359 cm$^{-1}$ respectively). Compound 1 has, due to its small additional siloxane ring (in total four silicon ring atoms) the least possible intramolecular hydrogen bonding compared to compounds 2-6. Therefore the silanols of 1 undergoes a relatively large shift towards hydrogen bonded frequencies under influence of the added proton acceptor ($\Delta \nu_{\text{OH}} = 132$ cm$^{-1}$). The $\Delta \nu_{\text{OH}}$ of 2-6 ranges from 16 to 113 cm$^{-1}$ which is considerably smaller than the $\Delta \nu_{\text{OH}}$ shift observed when diethylether was added to CCl$_4$ solutions of unperturbed isolated silanols (Table 2). These $\Delta \nu_{\text{OH}}$ are also smaller than those observed for geminal silsesquioxane silanols ($\Delta \nu_{\text{OH}} > 200$ cm$^{-1}$, Chapter 2 of this thesis). The strong dimeric structure of 8 is not noticeably affected when ether is added to the tetrachloromethane solution of 8, although ion pair acidity measurements with UV-VIS show that complex 8 is considerably more acidic ($pK_p = 7.9$) than compounds 1-7 or $R_7$Si$_8$O$_{12}$(OH) (Table 2). Hence, using $\Delta \nu_{\text{OH}}$ values, derived from addition of a proton acceptor, as a probe for relative Brønsted acidities of the investigated silsesquioxanes silanols are only useful to probe the relative acidities of comparable silanols like the mono silanol containing 1-7 and $R_7$Si$_8$O$_{12}$(OH). The relative ion pair acidities obtained by the overlapping method proved to be much more valuable and also applicable for poly-hydrogen bonded silanols (see also Chapter 4).
Not surprisingly, due to intramolecular hydrogen bonding between the OH and the siloxane ring, the relative ion pair acidities of 1-6 are lower than the unperturbed silanol of $R_7Si_8O_{12}(OH)$ (R = $c$-C$_5$H$_9$ and $c$-C$_6$H$_{11}$) (Table 2). Again, compound 1 with only one -OSiMe$_2$O- unit, and thus ample intra-molecular hydrogen bonding opportunity, is more acidic than silsesquioxanes 2-5 with up to four -OSiMe$_2$O- units. The phenyl substituted 7, in spite of its uninfluenced silanol, has an acidity which is a hundred fold lower than the acidities of $(c$-C$_5$H$_9)_7Si_8O_{12}(OH)$ and $(c$-C$_6$H$_{11})_7Si_8O_{12}(OH)$ ($pK_a$ of 11.1 versus 8.9 and 9.0). Interestingly, when going from a ring-size of six silicon atoms to seven silicon atoms (i.e. from compound 2 to 3 and from compound 5 to 6) the $\Delta \nu_{OH}$ shift increases with about 60 cm$^{-1}$ indicating more efficient hydrogen bonding with the external proton donor. This agrees with the estimated $pK_a$ values. When going from the cyclopentyl substituted compound 2 to compound 3 the $pK_a$ decreases from 10.5 to 10.1. When going from the cyclohexyl substituted compound 5 to compound 6 the $pK_a$ decreases even more (10.8 versus 9.7). The cyclohexyl substituted compound 4 has a Brønsted acidity similar to compound 5 and is even less affected by addition of an external proton donor (for 4 $\Delta \nu_{OH} = 16$ cm$^{-1}$, for 5 $\Delta \nu_{OH} = 40$ cm$^{-1}$). The increased acidity of 3 and 6 and extended hydrogen bonding with an external proton donor compared to 2, 4, and 5 suggests less intra-molecular hydrogen bonding with their silyl ethers. Apparently compounds 2 and 5 with a ring-size of six silicon atoms and three -OSiMe$_2$O- units, and compound 4 with a ring-size of five silicon atoms and two -OSiMe$_2$O- units, possess the most advantageous ring-size, i.e. most effective intramolecular hydrogen bonding and lowest possible Brønsted acidity.

3.6 Towards covalently connected multi-caged functional silsesquioxanes

A major disadvantage of model systems containing mono-, bi-, and terdentate silsesquioxane ligands is their tendency to decompose on hydrolysis, releasing the silsesquioxane ligands. Creating a stable link between two silsesquioxane cages (Figure 1) would reduce this problem as the enhanced chelate character of the thus formed ligand will improve the stability of the corresponding metal complexes. In the field of hybrid materials, bridged poly-silsesquioxanes, a family of organic-inorganic materials prepared by sol-gel processing of multi-functional monomers, are well known. They are prepared in a single step from molecular precursors and a fine degree of control over bulk chemical and physical properties is possible. Mono-functionalized polyhedral silsesquioxanes $(c$-C$_6$H$_{11})_7Si_8O_{12}(X)$ (X = functional group) have been incorporated into polymer chains to modify the local structure and chain mobility in polymeric materials. Controlled linking of two or more silsesquioxane molecules with reactive silanol groups still being present, has not been reported. Several routes to create such materials have been investigated, only a few will be mentioned here. Route A describes direct routes towards siloxane spacers between silsesquioxanes. Route B describes indirect routes via prior protecting two of the three silanols of the starting material $R_7Si_7O_{12}(OH)$.$_3$. Routes C and D describe efforts towards formation of linked silsesquioxanes by metathesis (C) and hydrosilylation (D).
A: Direct route towards siloxane spacers.

As mentioned in paragraph 3.2, deprotonation reaction of \( R_7Si_7O_9(OH)_3 \) (\( R = c-C_5H_9, c-C_6H_{11} \)) with \( \alpha,\omega \)-dichlorosil(ox)anes \( ClSiMe_2\{OSiMe_2\}_nCl \) \( (n = 0, 1, 2, 3) \) solely leads to intramolecular disilylated products, in spite of the 100 fold higher acidity of vicinal trisilanols (i.e. substituting the first silanol) compared to vicinal disilanols (i.e. substituting the second silanol). Changing the ratio of the reagents or the order of putting the reagents together did not make any difference. Neither did changing the polarity of the reaction medium (from THF to toluene) or lowering of the reaction temperature (from ambient temperature to 0 °C). Substituting a second silanol group from the same molecule is more beneficial than substituting a more reactive silanol group of a second molecule because of entropy. Reaction of \( R_7Si_7O_9(OH)_3 \) with 3 equivalents of thallium-ethoxide affords \( R_7Si_7O_9(OTl)_3 \), which upon addition to a solution of 2 equivalents of \( R_7Si_7O_9(OH)_3 \) produces the syn-proportionation product \( R_7Si_7O_9\{OTl\}(OH)_2 \).

Likewise stable anionic frameworks \( [R_7Si_7O_9(O)(OH)]^-[PPh_4]^+ \) were formed when [PPh_4]Cl or other salts were added to \( R_7Si_7O_9(OTl)(OH)_2 \). \( \alpha,\omega \)-Dichlorosil(ox)anes \( ClSiMe_2\{OSiMe_2\}_nCl \) were added in a 2 to 1 fashion to the \( in \text{ situ} \) formed \( R_7Si_7O_9(OTl)(OH)_2 \). But did not result in the expected intermolecular linked species. Only mixtures containing intramolecular products could be detected, apparently thallium exchanges rapidly during reaction, which facilitates the entropic favorable intramolecularly.

B. Indirect route towards siloxane spacers via protection of two silanols. Protecting two silanols of \( R_7Si_7O_9(OH)_3 \) in a reversible manner, establishing a link between two protected cages by substitution of the remaining silanol with a difunctional spacer like \( \alpha,\omega \)-dichlorosil(ox)anes \( ClSiMe_2\{OSiMe_2\}_nCl \) and subsequent deprotection would provide the desired intermolecular species. A feasible candidate seemed to be the dehydrated compound \( R_7Si_7O_9(O)(OH)_4 \) (Figure 4). Regrettably, the described route afforded the desired product only in low yields. Higher yields were reported for the synthesis of the dehydrated silsesquioxane \( (c-C_5H_9)_2Si_2O_4(O)(OSiMe_2)Bu \) by a novel route; in which \( (c-C_5H_9)_2Si_2O_4(OSiMe_2)Bu(OH)_2 \) is reacted slowly with metallic potassium but appeared not applicable to vicinal tri-silanols \( R_7Si_7O_9(OH)_3 \). Reaction of small amounts of dehydrated \( R_7Si_7O_9(O)(OH) \) with \( \frac{1}{2} \) an equivalent of \( \alpha,\omega \)-dichlorosil(ox)anes was not selective; no evidence was found for substitution of the hydroxyl group. Surprisingly, the strained siloxane ring was very stable towards hydrolysis, attempts to open the strained ring with triflic acid were not successful either and decided was to focus the attention to another possible route.

C. Bridging of silsesquioxane cages by metathesis. Olefin metathesis catalyzed by carbene species of molybdenum, tungsten, or ruthenium has been known and utilized for quite some time. Highly functionalized silsesquioxanes have been prepared by cross-metathesis reactions of alkenes
with multi-substituted vinyl-silsesquioxanes. Cross-metathesis of allyl substituted silsesquioxanes catalyzed by ruthenium or rhodium species afforded alkenylene-bridged silsesquioxane ligands. Also, ring closing metathesis of a titanium-containing silsesquioxane bearing two allylic moieties could be catalyzed by a ruthenium catalyst (15 mol%, cat, 54 h, 65 °C). We tried to link two silsesquioxane cages (c-C₅H₉)₇Si₅O₉(OSiMe₂vinyl)(OH)₂ by cross-metathesis with the mentioned catalysts under different circumstances but without success.

D. Bridging of silsesquioxane cages by hydrosilylation. Hydrosilylation is the addition of an Si-H bond across an unsaturated substrate. The Si-H bond is relatively strong and of low polarity and usually hydrosilylation reactions are catalyzed by a platinum compound. For many years H₂PtCl₆ was used, also known as Speier’s catalyst. Nowadays Pt⁰ derivatives, the prototypical example of which is Karstedt’s catalyst Pt₄(H₂C=CHSiMe₂OSiMe₂CH₂=CH₂), have become increasingly popular catalysts. An ideal route towards intermolecularly linked silsesquioxane by hydrosilylation would be the hydrosilylated product of the mono-substituted (c-C₅H₉)₇Si₅O₉(OSiMe₂vinyl)(OH)₂ and the mono-substituted (c-C₅H₉)₇Si₅O₉(OSiMe₂H)(OH)₂. However, while the first reactant can be easily prepared, the second reactant is somewhat more difficult to obtain selectively. Treating (c-C₅H₉)₇Si₅O₉(OH)₃ with ClSiMe₂H, resulted invariably in a mixture of mono-, di-, and tri-silylated silsesquioxanes. Under extreme conditions, i.e. highly diluted in the non-polar solvent toluene with a 10-fold excess of (c-C₅H₉)₇Si₅O₉(OH)₃ compared to ClSiMe₂H at –50 °C, at best 90% purity of the desired mono-silylated product could be achieved. Hydrosilylation of the 90/10 mixture of (c-C₅H₉)₇Si₅O₉(OSiMe₂H)(OH)₂ / (c-C₅H₉)₇Si₅O₉(OSiMe₂H)₂(OH) with (c-C₅H₉)₇Si₅O₉(OSiMe₂vinyl)(OH)₂ in the presence of Karstedt’s catalyst afforded immediately the desired product [(c-C₅H₉)₇Si₅O₉(OH)₂(OSiMe₂CH₂)]₂ but all efforts to successfully separate the wanted product from the unwanted side-products resulting from the disilylated starting material failed (Scheme 3).

![Scheme 3. Hydrosilylation with Karstedt's catalyst.](image-url)
The hydroxyl group of compound 1 was substituted into the more reactive (c-C₅H₅)₃Si₂O₅-(OSiMe₂O)(OSbMe₅) (10). When ClSiMe₂H was allowed to react with 10, the corresponding complex (c-C₅H₅)₃Si₂O₅(OSiMe₂O)(OSiMe₂H) (11) was selectively formed. Hydroisilylation of 10 with (c-C₅H₅)₃Si₂O₅(OSiMe₂,vinyl)(OH)₂ in the presence of Karstedt-catalysts afforded the asymmetric dimer (c-C₅H₅)₃Si₂O₅(OSiMe₂CH₂CH₂SiMe₂O)Si₂O₅(c-C₅H₅)(OH)₂ (12) (Scheme 3). The yield of 12 was low and purification could not achieve complete removal of the platinum catalyst; 12 was isolated as grey powder indicating the presence of metallic platinum. At that time, promising results in other areas of our silsesquioxane research lead us to the decision of postponing this subject for the time being.

3.7 Concluding remarks and outlook

Silsesquioxanes presenting model compounds for partly silylated silica surfaces of the type R₂Si₃O₅(OSiR'₃O)/OH (R= c-C₅H₅; c-C₆H₁₁; R'= Me, Ph; n=0-3) have been prepared. In some cases, unexpected differences in reactivity of cyclopentyl and cyclohexyl starting materials with sil(ox)ane were observed. When tri-silanol and ClSiMe₂OSiMe₂Cl were reacted in a 2 to 1 ratio, the unusual complex (c-C₅H₅)₃Si₂O₅(OSiMe₂O)(OH)·(OH)Si₂O₅(c-C₅H₅)₇ was formed. The dimeric complex is held together by surprisingly strong hydrogen bonds. The fact that crystallization of the dimeric species affords (c-C₅H₅)₃Si₂O₅(OH)₂ and (c-C₅H₅)₃Si₂O₅, suggests a highly flexible and dynamic system which loses its cohesion upon cooling. NMR and FT-IR studies show that a siloxane ring in the proximity of the silanol lowers its acidity considerably due to intramolecular hydrogen bonding of one or more -OSiR'₃O-units with the silanol. An optimum in siloxane ring size was found for compounds with two or three -OSiMe₂O-units. These compounds appeared to possess the most effective intramolecular hydrogen bonding and thus lowest possible Brønsted acidity occurred.

Most efforts to create a stable bridge between two silsesquioxane cages with silanol groups left for further reaction with metal precursors were unsuccessful. Entropy ensures that substituting a second silanol group from the same R₂Si₃O₅(OH)₃ molecule is more preferable than substituting a more reactive silanol group of a second molecule. Platinum-catalyzed hydrosilylation of (c-C₅H₅)₃Si₂O₅-(SiMe₂,vinyl)(OH)₂ and (c-C₅H₅)₃Si₂O₅(OSiMe₂O)(OSiMe₂H) resulted in the asymmetric dimer (c-C₅H₅)₃Si₂O₅(OSiMe₂O)(OSiMe₂CH₂CH₂SiMe₂O)Si₂O₅(c-C₅H₅)(OH)₂. The preferred reactant (c-C₅H₅)₃Si₂O₅-(OSiMe₂H)(OH)₂ could not be selectively prepared since in any attempt di- and tri-silylated side-products were obtained which could not be separated from the desired mono-silylated product. Other routes towards stable siloxane or other types of spacers between silsesquioxane cages were without results. However, still it is believed that achieving linked species while silanols remain for multidentate bonding towards metal species is possible. A recently synthesized compound in our group, ((c-C₅H₅)₃Si₂O₅(O₂Mg)(OH)₂)_2·THF enables a new route towards our goal. This type of compound could serve as a template in which the two silanols are linked by a spacer, subsequent hydrolysis would result in a dimeric covalently linked complex with four silanols left for reaction.
3.8 Experimental section

**General Remarks** - Reactions were performed under an argon atmosphere using Schlenk techniques when necessary. Solvents were distilled from K (THF), Na/K alloy (hexanes, C₂D₆) and benzophenon (Et₂O) or dried over 4 Å molecular sieves (NE₅₅, CCl₄, CDCl₃) and stored under argon. ¹H- and ¹³C-NMR spectra were recorded on Varian Mercury 400 spectrometers (25°C, ¹H-NMR: 400 MHz, ¹³C-NMR: 100.6 MHz). ²⁹Si-NMR spectra were recorded on a Varian Indigo 500 spectrometer (25°C, ²⁹Si-NMR: 99.3 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (¹H, ¹³C-NMR) or external standards (²⁹Si: SiMe₈ = 0 ppm). All Fourier Transformed Infrared spectra were recorded at room temperature on a Nicolet Avatar 360 spectrophotometer. Samples in solution were prepared under inert atmosphere (glovebox), νCH values were determined in 0.1M CCl₄ solutions and δνCH in 0.1M CCl₄ solutions containing 0.25M diethylether. Solid-state samples were recorded as Nujol-mulls (prepared under inert atmosphere, glovebox) or recorded directly on a Nicolet Smart DurasampIR in air for single reflection diamond ATR analysis (golden gate). The pKᵣᵣ ion pair acidity measurements were carried out using the overlapping indicator method (see Chapter 2), 9-cyanofluorene (pKᵣᵣ [DMSO] = 8.3) and 9-(methoxycarbonyl)fluorene (pKᵣᵣ[DMSO] = 10.4) were the indicators used. Lithium salts of the indicators were prepared, isolated, and recrystalized before use. Due to the low solubility of silsesquioxanes in DMSO, THF was used as the solvent instead. UV-Vis measurements for determination of the pKᵣᵣ values, were performed on a UV-2401PC spectrophotometer with standard slit width and scan speed.

Molecular weight determinations in benzene were performed in the lab of Prof. J.H. Teuben, University of Groningen. Elemental analyses were carried out at the Analytical Department of the Technical University of Eindhoven; quoted data are the average of at least two independent measurements. Silsesquioxane starting materials (c-C₃H₇)₃Si₂O₂(OH)₆ (1), (c-C₃H₇)₃Si₂O₂(OSiMe₂O)(OH) (2), (c-C₃H₇)₃Si₂O₂(OsiMe₂vinyl)(OH) (3), (c-C₃H₇)₃Si₂O₂(OC) (OH) (4) were prepared following referred literature procedures.

As an example for the disilylations of R₃Si₂O₂(OH) (R = c-C₃H₇, c-C₅H₁₁), the preparation of (c-C₃H₇)₃Si₂O₂(OSiMe₂O)(OH) (1) is described in detail. A similar procedure was used for compounds 2-8. ¹H-NMR (400 MHz, CDCl₃, 25 °C), ¹³C-NMR (100.6 MHz, CDCl₃, 25 °C) and ²⁹Si-NMR (99.8 MHz, CDCl₃, 25 °C) data of 1-8 are depicted in Table 1.

(c-C₃H₇)₃Si₂O₂(OSiMe₂O)(OH) (1): To a solution of (c-C₃H₇)₃Si₂O₂(OH) (15.00 g, 17.13 mmol) and NE₅₅ (4.8 mL, 34.5 mmol) in 150 mL of THF, 0.95 equivalents of C₂H₅Me₂ (2.10 g, 16.27 mmol) were slowly added. The mixture was stirred at room temperature overnight and then filtered in order to remove most of the formed Et₃N(H)Cl. After evaporation of THF, 100 mL of hexanes was added and the mixture was heated to dissolve the product completely. Upon cooling at air, last traces of Et₃N(H)Cl fell out the mixture as flocks and could be easily removed by filtration. Thorough drying yielded product 1 as a white (slightly hygroscopic) powder (yield 84%). IR (cm⁻¹): 3557 (w), 2947 (s), 2864 (s), 1450 (w), 1257 (w), 1079 (vs), 911 (w), 875 (w), 844 (w), 802 (w), 774 (w), 722 (w). Elemental analysis calcd (%) for C₁₃H₂₇O₂Si₈: C 47.70, H 7.75; found C 47.84, H 7.41.

(c-C₃H₇)₃Si₂O₂(O(SiMe₂O)₃)(OH) (2): white powder, yield 82%. IR (cm⁻¹): 3528 (w), 2948 (s), 2864 (s), 1451 (w), 1259 (m), 1070 (vs), 948 (w), 910 (w), 844 (w), 802 (m), 715 (w). Elemental analysis calcd (%) for C₁₃H₂₇O₄Si₁₀: C 45.60, H 7.65; found C 45.40, H 7.68.

(c-C₃H₇)₃Si₂O₂(O(SiMe₂O)₄)(OH) (3): reaction at 40°C overnight, white wax, yield 81%. A sample suitable for elemental analysis could not be obtained. IR (cm⁻¹): 3567 (w), 2949 (m), 2865 (m), 1451 (w), 1259 (m), 1067 (s), 948 (w), 910 (w), 844 (w), 800 (m), 714 (w).
(c-C₆H₁₁)₃SiO₄(O(SiMe₂O)₂)(OH) (4): white powder, yield 83%. IR (cm⁻¹): 3588 (w), 2919 (s), 2848 (s), 1447 (w), 1261 (m), 1195 (m), 1067 (s), 893 (m), 846 (m), 803 (m), 751 (w). Elemental analysis calcd (%) for C₉₈H₂₀O₂ₓSi₂ (1103.99): C 50.05, H 8.22; found C 49.52, H 7.94.

(c-C₆H₁₁)₃SiO₄(O(SiMe₂O)₂)₃(OH) (5): white powder, yield 66%. IR (cm⁻¹): 3595 (w), 2919 (s), 2848 (s), 1447 (m), 1260 (m), 1196 (m), 1067 (vs), 893 (m), 846 (m), 801 (m), 748 (w). Elemental analysis calcd (%) for C₉₈H₂₀O₂ₓSi₃ (1178.14): C 48.94, H 8.21; found C 48.60, H 8.24.

(c-C₆H₁₁)₃SiO₄(O(SiMe₂O)₂)₃(OH) (6): reaction at 40°C overnight, white powder, yield 60%. IR (cm⁻¹): 3626 (w), 2919 (s), 2848 (s), 1447 (m), 1259 (m), 1195 (m), 1076 (vs), 892 (m), 845 (m), 800 (s), 737 (w). Elemental analysis calcd (%) for C₉₈H₃₂O₂ₓSi₃ (1252.30): C 47.96, H 8.21; found C 47.97, H 8.02.

(c-C₆H₁₁)₃SiO₄(OSiPh₂O)(OH) (7): white powder, yield 81%. IR (cm⁻¹): 3636 (w), 2948 (m), 2864 (m), 1430 (w), 1246 (w), 1093 (s), 948 (w), 911 (w), 717 (m), 699 (m). Elemental analysis calcd (%) for C₉₈H₃₂O₂ₓSi₃ (1071.83): C 53.47, H 7.07, found C 53.33, H 6.85.

(c-C₆H₁₁)₃SiO₄(O(SiMe₂O)₂)₃(SiO₂(C-C₆H₅)) (8): reaction with 2 equivalents of (c-C₆H₁₁)₃SiO₄(OH)₃ and 1 equivalent of ClSiMe₂OSiMe₂Cl, white powder, yield 75%. IR (cm⁻¹): 3534 (w), 3241 (w), 2947 (s), 2864 (s), 1450 (w), 1259 (m), 1092 (vs), 911 (w), 875 (w), 846 (w), 804 (m), 718 (w). Elemental analysis calcd (%) for C₉₈H₃₂O₂ₓSi₁₀ (1881.30): C 47.24, H 7.61; found C 47.63, H 7.56.

(c-C₆H₁₁)₃SiO₄(O(SiMe₂O)₂)₃(OSiMe₂O(SiMe₂Cl)) (9): To a solution of 2.00 g of (c-C₆H₁₁)₃SiO₄(OH) (2.28 mmol) and 3 equivalents of NEt₃ (1.0 mL, 6.9 mmol) in 60 mL of THF an excess of ClSiMe₂OSiMe₂Cl (3 mL, 15 mmol) was added slowly. The mixture was stirred at room temperature overnight and then filtrated in order to remove most of the formed Et₃N(H)Cl. After evaporation of THF, 100 mL of hexanes was added and the mixture was heated to dissolve the product completely. Upon cooling at air, last traces of Et₃N(H)Cl fell out the mixture as flocks and could be easily removed by filtration. Thorough drying yielded product 9 as a white sticky solid. Dissolving a small part of 9 in THF and adding a solution of AgNO₃ immediately gave a white precipitate, indicating the presence of chloride. Yield 81% (1.85 mmol, 2.17 g). ^1H NMR (400 MHz, CDCl₃, 25 °C): δ = 0.14; 0.17 (2 s, O(Si(CH₂)₂O)₂, 12H), 0.22 (s, OSi(CH₃)₂OSiMe₂Cl, 6H), 0.49 (s, OSiMe₂OSi(CH₂)Cl, 6H), 0.96 (m, CH₂-C₆H₅, 7H), 1.52 (br s, CH₂-C₆H₅, 28H), 1.62 (br s, CH₂-C₆H₅, 14H), 1.78 (br s, CH₂-C₆H₅, 14H). ^29Si NMR (100.6 MHz, CDCl₃, 25 °C): δ = -0.85; 1.08 (OSi(CH₃)₂O)₂, 1.08 (OSi(CH₂)₂OSiMe₂Cl, 4.08 (OSiMe₂OSi(CH₂)Cl), 22.38; 22.81; 23.41; 23.64; 24.41 (7 CH₂-C₆H₅, ratio 1:1.22:1), 27.02 – 27.58 (CH₂-C₆H₅). ^29Si NMR (99.8 MHz, CDCl₃, 25 °C): δ = -69.22; -68.01; -67.91; -67.40; -65.53 (7 O₃SiCH₅, ratio 1:2:1:1), -20.87 (OSi(SiMe₂O)₃), -17.93 (OSiMe₂OSiMe₂Cl), 3.62 (OSiMe₂OSiMe₂Cl).

^1H NMR of 9

^29Si NMR of 9
(c-C₅H₅)₃SiO₃(OSiMe₂O)(OSbMe₅) (10): To a solution of 2.00 g of compound 1 (2.15 mmol) in 30 mL THF was added an excess of SbMe₅ (1.00 g, 4.29 mmol). After 3 hours stirring at 55 °C the reaction was complete (no more gas bubbles MeH visible) and after thorough drying, product 10 could be isolated in low yield (2.10 g, 1.89 mmol, 88%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 0.32; 0.37 (2 s, OSi(CH₃)₂O, 6H), 1.04 (s, Sb(CH₃)₅, 12H), 1.19 (m, CH₂-C₅H₅, 7H), 1.51 (m, CH₂-C₅H₅, 14H), 1.76 (m, CH₂-C₅H₅, 28H), 1.95 (m, CH₂-C₅H₅, 14H). ¹³C NMR (100.6 MHz, CDCl₃, 25 °C): δ = 8.61; 12.07; 23.07; 23.10; 23.69; 24.17 (6 CH₃, 2H). NMR spectra of 10.

(c-C₅H₅)₃SiO₃(OSiMe₂O)(OSMe₂H) (11): To a solution of 1.17 g of compound 10 (1.05 mmol) in 40 mL THF was added 1 equivalent of OSiMe₂H (0.10 g, 1.05 mmol) and immediately a precipitate was formed. After 1 hour of stirring the mixture was filtrated and the solvent was removed. The sticky solid was washed with aceton and product 11 could be isolated in good yield (2.10 g, 1.89 mmol, 88%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 0.15; 0.21 (2 s, OSi(CH₃)₂O, 6H), 0.26 (2 s, OSi(CH₅)₂H, 6H), 0.98 (m, CH₂-C₅H₅, 7H), 1.57 (m, CH₂-C₅H₅, 42H), 1.78 (br s, CH₂-C₅H₅, 14H). ¹³C NMR (100.6 MHz, CDCl₃, 25 °C): δ = 0.61; 0.87; 0.94; 1.24 (OSi(CH₅)₂O, OSi(CH₅)₂H), 22.57; 23.18; 23.33; 24.30 (7 CH₂-C₅H₅, ratio 2:2:2:1), 27.16 – 27.80 (CH₂-C₅H₅). NMR spectra of 11.

(c-C₅H₅)₃SiO₃(OSiMe₂O)(OSMe₂CH₂CH₂SiMe₂O)SiO₃(c-C₅H₅)₂|(OH)₂ (12): To a solution of 0.08 g of compound 11 (0.08 mmol) and 0.08 g of (c-C₅H₅)₃SiO₃(OSiMe₂Vinyl)(OH)₂ (0.08 mmol) in 10 mL of hexanes, a catalytic amount of Karstedt’s catalyst was added. After 1 hour stirring at room temperature the hexanes were removed under reduced pressure and the resulting grey powder 12 was spectroscopically identified by NMR. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 0.11 (s, OSi(CH₅)₂O, 6H), 0.15; 0.18 (2 s, OSi(CH₅)₂CH₂, 12H), 0.53 (m, Si-CH₂-CH₂-Si, 4H), 1.00 (m, CH₂-C₅H₅, 14H), 1.57 (m, CH₂-C₅H₅, 84H), 1.79 (br s, CH₂-C₅H₅, 28H), 4.21 (s, SiOH, 2H). ¹³C NMR (100.6 MHz, CDCl₃, 25 °C): δ = -0.84; -0.68 (OSi(CH₅)₂CH₂), 0.51; 0.73; 1.01 (OSi(CH₅)₂O), 9.23; 9.30 (Si-CH₂-CH₂-Si), 22.20 – 24.38 (14 CH₂-C₅H₅), 26.92 – 27.70 (CH₂-C₅H₅). ²⁵Si NMR (99.8 MHz, CDCl₃, 25 °C): δ = -68.08; -67.62; -66.82; -66.66; -66.58; -65.69; -65.58; -65.16; -65.05; -57.00 (14 OSi(CH₅)₂O), -21.97; -18.10 (OSiMe₂O), 9.89; 11.88 (OSiMe₂CH₂).
Silsesquioxane Models for Partly Silylated Silica Surfaces in the Proximity of a Silanol

\[ ^1H \text{NMR of 12} \]

\[ ^{13}C \text{NMR of 12} \]

\[ ^{29}Si \text{NMR of 12} \]

References and Notes


Novel types of silsesquioxane models for silica surface silanols, geminal silanols and isolated silanols in the proximity of a partly silylated silica surface, were described in the previous two chapters. Together with the already known silsesquioxanes possessing vicinal silanols or isolated silanols, four different types of silsesquioxane silanols that can serve as models for the corresponding silica surface silanols are now available. In this chapter the chemical properties of these four different types of silanols are investigated and compared to each other both in the solid state and in solution. Solid state characteristics, obtained by FT-IR and single X-ray diffraction techniques, clearly show the tendency of silsesquioxanes to form aggregates. Information on characteristics in the solution were obtained from solution NMR, solution FT-IR and UV-VIS. A classification of the four silanol types in hydrogen bonding ability and acidity could be made. Information of properties of the different types of silanols occurring on silica surfaces is compared to the data found for the silsesquioxane model systems.

4.1. Introduction

Unsatisfied surface valences of silica oxides are saturated by the chemisorption of water, resulting in formation of hydroxyl groups covalently bound to the SiO$_2$ solid. In 1934, Hofman et al. were probably the first who proposed the presence of silanols on the surface of silicas. Nowadays, it is generally accepted that on a silica surface several kinds of silanols occur that differ considerably in reactivity. Silanols are called vicinal silanols when the hydroxyls are in the vicinity of each other, i.e. when the hydroxyl groups are close enough to form hydrogen bonds (distance between silanols < 2.8 Å). Geminal silanols are silanols in which two hydroxyls are attached to the same silicon atom (from geminate: occurring in pairs or couples, geminus: a twin). Geminal silanols are not necessarily accessible for mutual hydrogen bonding but can interact simultaneously with an adsorbate. A silanol is called isolated when no hydrogen bonding can occur (distance between silanols ~ 5 Å). When the effect of neighboring siloxy functionalities is considered the isolated silanols are no longer truly isolated. These fourth kind of silanols can be found in for example partly dehydroxylated and partly silylated silicas where the perturbed isolated silanols are capable of hydrogen-bonding with siloxy functionalities in their proximity (< 3 Å). There is still debate whether or not a possible fifth type of silanol, triple silanols (O-Si(OH)$_3$), exist on silica surfaces and is therefore not taken into account in this study. The four mentioned types of silanols occurring on silica surfaces are schematically shown in Figure 2.
The average silanol number of silicas with different specific surface area, hydroxylated to a maximum degree, is 4.9 OH groups per square nanometer. The respective concentrations of the silanols can be altered by raising the temperature. Gradual heating of silica in vacuo induces dehydration, where physisorbed water is removed, subsequently two hydrogen bonded hydroxyl groups condenses into a siloxane bridge while releasing a water molecule. At 200 °C, vicinal silanols correspond to about 62% of the total surface silanols. Geminal silanols correspond to approximately 13% of the total surface silanols at 200 °C and isolated silanols correspond to about 25%. With increasing temperature, dehydroxylation proceeds and relatively more isolated silanols are present. This dehydroxylation process can be followed by FT-IR experiments; the stretching vibrations of broad hydrogen bonded bands located around 3500 cm⁻¹ disappear during dehydroxylation whereas the sharp \( \nu_{\text{OH}} \) bands of isolated silanols located around 3700 cm⁻¹ remain with increasing intensity (Figure 1). When silica is heated at about 500 °C under vacuum, silica starts to become increasingly hydrophobic. Heating at about 1200 °C finally results in complete dehydroxylation.

![Figure 1. IR spectra of silica calcined at 100 °C and 700 °C.](image)

Because truly isolated silanols remain after extensive heating of silica samples, the characteristics of this type can be studied individually. At lower temperatures, all the mentioned silanols co-exist on the silica surface and distinguishing between them is rather difficult. Hence, detailed studies on most porous silicious materials and zeolites as well as the supported catalysts thereof are considerably hampered by the heterogeneity of these systems. The molecular surface properties of porous silicious materials and zeolites are best studied by a combination of vibrational spectroscopy (e.g. Fourier transform IR, Raman, diffuse or total reflectance IR and photoacoustic IR) and solid state NMR spectroscopy that provides both qualitative and quantitative data. However, these techniques are bulk measurements and their sensitivity is often inadequate to obtain accurate data of local surface properties. Information on a molecular level is usually obtained by indirect means of investigation. Silanols have a different characteristic behavior when subjected to adsorbates; therefore valuable information can be gained from (FT-IR) spectra before and after adsorption of an adsorbate. Information on a molecular level can also be obtained from computer simulations with the necessary
A Comparising Study of Four Types of Silanols Modeled by Silsesquioxanes

simplifications to make the complex silica system manageable. Another important factor when examining the reactivity of surface hydroxyl groups of silica, is the dependency of the structure of silicas on the method of preparation. Fumed silicas (prepared from the gas phase) possess for instance isolated silanols that are statistically distributed. On the other hand, precipitated silicas (prepared from silicalite solutions) have a lot more complex surface. In the gas phase the lack of steric hindrance gives the molecules more flexibility during condensations, which results in a more ordered skeleton.

The molecular structure of supported catalysts is a key-step for understanding the stability and reactivity of the system. Incompletely condensed silsesquioxanes, with a coordination sphere resembling that of silica surface sites, are realistic homogeneous models for studying local silica surface properties. Silsesquioxane cages have a hydrophobic coat formed by cycloalkyl groups substituted at the corners of the silicate cages. This makes the molecules soluble in organic solvents and enables investigation on a molecular level with a wide range of powerful techniques such as multinuclear solution NMR spectroscopy. The major advantage of such homogeneous models is that different silica surface properties can be studied individually while remaining their accuracy. A complicating factor for a direct comparison between silsesquioxane silanol models and silanols occurring on silica surfaces is the mobility of the silsesquioxanes. This mobility results in thermodynamically most favorable structures both in solution and in the solid state. In the solid phase they are best capable of forming aggregates stabilized by hydrogen bonds. In spite of this behavior, striking similarities between the characteristics on silanol surfaces and their model systems can be found. The first studies where silsesquioxane silanols were applied as models for silica surface silanols date from the late nineteen-eighties. Vicinal tri-silanols (type A.2) are the most commonly used starting materials. Slight modifications in the preparation method or substitution reactions of the starting material provides models for vicinal di-silanols (type A.3 and A.4) and isolated silanols (Type C.1 and C.2). In Chapter 2 of this thesis, the preparation and characteristics of silsesquioxanes with geminal silanols were described (type B). A silsesquioxane model for isolated silanols influenced by a siloxane ring was described in Chapter 3 (type D.1). Another perturbed mono-silanol is the condensation product resulting from a sterically hindered geminal silanol silsesquioxane (Chapter 2), type D.2. In Figure 2, the four kinds of silanols A, B, C and D occurring on silica surfaces and the corresponding silsesquioxane models with their sub-division are summarized.

In this chapter these four kinds of silsesquioxanes silanols will be discussed separately and compared to each other and to their corresponding silica surface silanol groups. Although silsesquioxanes are soluble models, their solid state characteristics can be studied with FT-IR spectroscopy or single X-ray diffraction. In this chapter both solid-state and solution characteristics will be discussed. For geminal silsesquioxanes it was found that characteristics can differ considerably when present in either solid- or liquid-state (Chapter 2). Differences between solid- and solution-state was found to be much less pronounced for mono-silanols (Chapter 3). Solution-state characteristics of the four kinds of silanols could be established by $^1$H-, $^{13}$C- and $^{29}$Si- solution NMR. UV-VIS was used to estimate their relative Brønsted acidities.
<table>
<thead>
<tr>
<th>type</th>
<th>silica surface silanol</th>
<th>silsesquioxane model system</th>
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<tbody>
<tr>
<td>type A:</td>
<td></td>
<td></td>
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<tr>
<td><strong>vicinal silanols</strong></td>
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<tr>
<td>distance close enough to form hydrogen bonds</td>
<td><img src="image1.png" alt="Silica surface silanol" /></td>
<td><img src="image2.png" alt="Silsesquioxane model system" /></td>
</tr>
</tbody>
</table>

| type B:      |                        |                              |
| **geminal silanols** |                        |                              |
| two hydroxyls attached to one silicon atom | ![Silica surface silanol](image3.png) | ![Silsesquioxane model system](image4.png) |

| type C:      |                        |                              |
| **truly isolated silanol** |                        |                              |
| minimum distance to nearest neighbor is 5 Å. | ![Silica surface silanol](image5.png) | ![Silsesquioxane model system](image6.png) |

| type D:      |                        |                              |
| **perturbed isolated silanol** |                        |                              |
| interaction with for instance a siloxane ring. | ![Silica surface silanol](image7.png) | ![Silsesquioxane model system](image8.png) |

**Figure 2.** Four types of silica surface silanols versus corresponding silsesquioxane models: A (vicinal silanols), B (geminal silanols), C (isolated silanols) and D (perturbed isolated silanols).
4.2. Solid-State Properties

Naturally, the most accurate manner to compare silsesquioxane models of various silanols to those occurring on silica surfaces is to study both in the same phase, *i.e.* as solids. Two techniques can provide information of the solid state characteristics of silsesquioxanes; single X-ray diffraction on crystallized silsesquioxanes and FT-IR spectra of the silsesquioxanes recorded as Nujol mulls. Both techniques will be discussed here. To study silica surface properties such as hydrogen bonding, relative acidity or dehydroxylation reactions of various silanols, the infrared stretching vibrations ($\nu_{\text{OH}}$) of the surface silanols are very informative. These bands are well separated from other vibrations and are largely dependent on interactions with neighboring silanols, silyl ethers or metal species. It was found that surfaces of different forms of silica have similar properties and thus can be considered as a whole when compared to silsesquioxane silanols. In contrast to hydroxyl stretching vibrations, informative silanol vibrations like stretching $\nu_{\text{Si-OH}}$ and bending $\delta_{\text{Si-OH}}$ vibrations, occurring at lower vibrations (500 –1500 cm$^{-1}$), are more difficult to assign.$^{15}$ A detailed interpretation in combination with theoretical calculations could be performed for silsesquioxane molecules possessing 354 normal vibrations active in the IR spectra. It was found that most of the bands in the lower regions result from overlapping of a number of IR bands with large intensity.$^{16,17}$ Due to this complexity only stretching vibrations of the hydroxyls $\nu_{\text{OH}}$ will be considered here.

Absorption of hydroxyl vibrations $\nu_{\text{OH}}$ can usually be found in the region 3200–3800 cm$^{-1}$. Next to non-hydrogen bonded hydroxyls (OH$^i$), hydroxyls can be involved in several modes of hydrogen bonding (OH$^H$): poly-hydrogen bonding, mono-hydrogen bonding to another silanol or mono-hydrogen bonding to a silyl ether functionality (Figure 3). Hydrogen bonding shifts the $\nu_{\text{OH}}$ wavenumber to lower values and considerably broadens the absorption band.

While comparing the solid state IR spectra of silsesquioxanes with the IR spectra of silica surface silanols measured in vacuum, one has to ensure that the media used to record the IR spectra (Nujol mull) does not affect the silsesquioxane silanol frequencies (see Chapter 2).

![Figure 3. Poly-hydrogen bonded silanols (i), mono-hydrogen bonded types of silanols (ii and iii) and isolated silanols (ii and iii), with hydrogen bonded H indicated as $H^b$ and isolated H as $H^i$.](image-url)
Vibration bands for poly-hydrogen bonded silanols are situated around 3200 cm⁻¹. Infrared spectroscopy, poly- and mono-hydrogen bonded silanols of silica surfaces can be clearly distinguished. When the surface is flexible enough and vicinal hydroxyls are not constrained in such a manner, also poly-hydrogen bonds can be formed. With infrared spectroscopy, only mono-hydrogen bonds occur (Figure 3). When the surface is flexible enough and vicinal hydroxyls are not constrained in such a manner, also poly-hydrogen bonds can be formed. Flexibility is the major difference between vicinal silanols on a silica surface and vicinal silanols that are part of a silsesquioxane. In silsesquioxanes, the vicinal hydroxyls can form strong hydrogen bonds since the energy required to deform the Si-O-Si angle is less than the energy of H-bonding interaction. The stretching vibration bands of the vicinal tetra-silanol \((c-C_3H_{13})_3Si_6O_7(OH)_4\) and the vicinal tri-silanol \((c-C_3H_{11})_2Si_6O_7(OH)_3\) were found at 3183 cm⁻¹ and 3158 cm⁻¹, respectively (Table 1, Figure 4, type A.1 and A.2). For the vicinal disilanol \((c-C_3H_7)_2Si_4O_5(OSiMe_3)(OH)\) and the vicinal di-silanol \((c-C_7H_{15})_2Si_4O_5(OSiMe_3)(OH)\), the \(\nu_{OH}\) bands were found at slightly higher frequencies (3261 cm⁻¹ and 3327 cm⁻¹). The broadness and frequencies of the observed \(\nu_{OH}\) bands indicate strong poly-hydrogen bonded hydroxyls. This corresponds with the dimeric structures found from crystal structure determinations of vicinal tetra-silanol \((c-C_3H_{13})_3Si_6O_7(OH)_4\), vicinal tri-silanol \((c-C_3H_{11})_2Si_6O_7(OH)_3\) and vicinal di-silanol \((c-C_7H_{15})_2Si_4O_5(OSiMe_3)(OH)\).

### Table 1. Solid state infrared spectroscopy of the stretching vibrations \(\nu_{OH}\) of various silanols.

<table>
<thead>
<tr>
<th>type of silanol</th>
<th>Silsesquioxane compound</th>
<th>(\nu_{OH}) of silsesquioxane (Nujol mull, cm⁻¹)</th>
<th>(\nu_{OH}) of surface silanol analog (vacuum, cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.1: tetra-silanol</td>
<td>((c-C_3H_{13})_3Si_6O_7(OH)_4)</td>
<td>3183</td>
<td>3222</td>
</tr>
<tr>
<td>A.2: tri-silanol</td>
<td>((c-C_3H_{11})_2Si_6O_7(OH)_3)</td>
<td>3158</td>
<td>3222</td>
</tr>
<tr>
<td>A.3: di-silanol</td>
<td>((c-C_3H_7)_2Si_4O_5(OSiMe_3)(OH))</td>
<td>3261</td>
<td>3222</td>
</tr>
<tr>
<td>A.3: di-silanol</td>
<td>((c-C_7H_{15})_2Si_4O_5(OSiMe_3)(OH))</td>
<td>3327</td>
<td>3222</td>
</tr>
<tr>
<td>B: geminal silanol</td>
<td>((c-C_3H_7)_2Si_4O_5(OSiMe_3)(OSiMePh_2)O_2Si(OH)_2)</td>
<td>3515, 3402</td>
<td>3747, 3600</td>
</tr>
<tr>
<td></td>
<td>((c-C_3H_7)_2Si_4O_5(OSiMePh_2)O_2Si(OH)_2)</td>
<td>3582, 3438</td>
<td>3747, 3600</td>
</tr>
<tr>
<td>C: isolated silanol</td>
<td>((c-C_3H_7)_2Si_6O_7(OH))</td>
<td>3706, 3444</td>
<td>3747</td>
</tr>
<tr>
<td>D.1: perturbed mono-silanol</td>
<td>((c-C_3H_{15})_3Si_6O_7(O(OSiMe_2)O)OH)</td>
<td>3561</td>
<td>3400 - 3500</td>
</tr>
<tr>
<td>D.2: perturbed mono-silanol</td>
<td>((c-C_3H_{15})_3Si_6O_7(OSiMePh_2))</td>
<td>3629</td>
<td>3660</td>
</tr>
</tbody>
</table>

**Vicinal silanols.** The stretching vibration bands of the vicinal tetra-silanol \((c-C_3H_{13})_3Si_6O_7(OH)_4\) and the vicinal tri-silanol \((c-C_3H_{11})_2Si_6O_7(OH)_3\) were found at 3183 cm⁻¹ and 3158 cm⁻¹, respectively (Table 1, Figure 4, type A.1 and A.2). For the vicinal disilanol \((c-C_3H_7)_2Si_4O_5(OSiR'_3)(OH)\) (\(\nu\) bands were found at slightly higher frequencies (3261 cm⁻¹ and 3327 cm⁻¹). The broadness and frequencies of the observed \(\nu_{OH}\) bands indicate strong poly-hydrogen bonded hydroxyls. This corresponds with the dimeric structures found from crystal structure determinations of vicinal tetra-silanol \((c-C_3H_{13})_3Si_6O_7(OH)_4\), vicinal tri-silanol \((c-C_3H_{11})_2Si_6O_7(OH)_3\) and vicinal di-silanol \((c-C_7H_{15})_2Si_4O_5(OSiMe_3)(OH)\). Flexibility is the major difference between vicinal silanols on a silica surface and vicinal silanols that are part of a silsesquioxane. In silsesquioxanes, the vicinal hydroxyls can form strong hydrogen bonds since the energy required to deform the Si-O-Si angle is less than the energy of H-bonding interaction. The vicinal hydroxyls on surfaces are constrained by bonds to neighboring lattice sites and generally only mono-hydrogen bonds occur (Figure 3). When the surface is flexible enough and vicinal hydroxyls are not constrained in such a manner, also poly-hydrogen bonds can be formed. With infrared spectroscopy, poly- and mono-hydrogen bonded silanols of silica surfaces can be clearly distinguished. Vibration bands for poly-hydrogen bonded silanols are situated around 3200 cm⁻¹ (corresponding well with the poly-hydrogen bonded silsesquioxane vicinal silanols). Mono-hydrogen bonded silanols (Figure 3) are found in the 3400-3600 cm⁻¹ range, depending on the effectiveness of the bonding. Physically absorbed water on a silica surface also induces poly-hydrogen bonding and a very broad absorption band centered at 3222 cm⁻¹ was assigned to this effect. Rigid silica surfaces with vicinal silanols only capable of mono-hydrogen bonds with neighboring silanols have characteristic wavenumbers around 3550 cm⁻¹.
Geminal silanols. The solid state FT-IR spectra for silsesquioxanes with geminal silanols (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiR'$_3$)$_2$O$_2$Si(OH)$_2$ (SiR' = SiMe$_3$, SiMePh$_2$) also show hydrogen bonded vibrations but clearly of another type than the poly-hydrogen bonded bands of vicinal silanols (Figure 4). In Chapter 2 it was found that the geminal hydroxyls in (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiR'$_3$)$_2$O$_2$Si(OH)$_2$ are different in nature and result in two different vibration bands. The vibration bands at 3515 cm$^{-1}$ (OSiMe$_3$ substituted) and 3582 cm$^{-1}$ (OSiMePh$_2$ substituted) are assigned to intramolecular mono-hydrogen bonds with the silyl ether functionality. Hydrogen bonded bands at frequencies of 3402 cm$^{-1}$ (OSiMe$_3$ substituted) and 3438 cm$^{-1}$ (OSiMePh$_2$ substituted) are assigned to intermolecular mono-hydrogen bonds. This corresponds with dimeric aggregates, which are not likely to occur for geminal silanols present on silica surfaces. Stretching vibrations of geminal silanols on silica surfaces are usually found in the same region as isolated silanols and are hard to distinguish separately. However, in some studies both hydrogen bonded (an additional shoulder at 3600 cm$^{-1}$) and isolated geminal silanols have been suggested.

Isolated silanols. The solid state IR spectrum of (c-C$_5$H$_9$)$_7$Si$_8$O$_{12}$(OH) shows two vibration bands in the $\nu_{\text{OH}}$ region. A sharp band at 3706 cm$^{-1}$ is assigned to a truly isolated silanol. A broad band located at 3444 cm$^{-1}$ is assigned to an intermolecular mono-hydrogen bond which is due to the partly existing dimeric crystalline phase (Figure 4, Table 1). The sharp band corresponds well with the observed OH stretching vibration found for silica surface isolated silanols at 3747 cm$^{-1}$.

Perturbed mono-silanols. Perturbed isolated silanols show comparable $\nu_{\text{OH}}$ wave numbers in solution and in the solid state as described in Chapter 3 of this thesis. Mono-silanol silsesquioxanes containing an additional intramolecular electron donating siloxane ring (Figure 4, type D.1) have one or more overlapping broad stretching vibration bands at wave numbers indicative for the presence of hydrogen bonding (3561 cm$^{-1}$ for (c-C$_6$H$_{11}$)$_7$Si$_7$O$_9$(OSiMe$_2$OSiMe$_2$O)OH, Table 1, Figure 4). Formation of dimeric aggregates in the solid state and thus intermolecular hydrogen bonding is hindered by the intramolecular donating abilities of the silyl ethers of the siloxane ring to the silanol group. In the FT-IR spectrum of amorphous silicates (induced by silicon vacancies) bands at 3400-3500 cm$^{-1}$ were assigned to H-bonded silanols in internal defects. These bands are tentatively used as silica surface analogues for the observed intramolecular hydrogen bonding in type D.1 silsesquioxane silanol models.

The silanols of compound (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiMePh$_2$)(O$_2$Si(OH))$_2$($\mu$-O) (the condensation product from (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiMePh$_2$)O$_2$Si(OH)$_2$ as described in Chapter 2) are also somewhat perturbed since the $\nu_{\text{OH}}$ located at 3629 cm$^{-1}$ deviates from unperturbed silanols. Infrared spectroscopy can differentiate between silanol groups of surface functional groups and internal silanol groups. Molecules physically adsorbed near a surface silanol have shifted stretching frequencies as a result of hydrogen bonding. Bands assigned to internal silanols do not change in intensity or frequency when subject to adsorbates. Perturbed silanols on silica that are located at points of inter-particle contact result in stretching vibration frequencies at 3660 cm$^{-1}$. The steric bulk of (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiMePh$_2$)(O$_2$Si(OH))$_2$($\mu$-O) possessing silanols of type D.2 induces the same effect and consequently the corresponding $\nu_{\text{OH}}$ agrees well with $\nu_{\text{OH}}$ of perturbed silanols on silica.
X-Ray determination

In the solid state, silsesquioxanes possessing vicinal silanols or geminal silanols are dimeric. Isolated silanols and mono-silanols with a small additional siloxane ring in their proximity \(\text{(i.e. } \langle \text{c-C}_5\text{H}_9 \rangle_7\text{SiO}_7\text{O}(\text{OSiMe}_2\text{O})(\text{OH})\text{)}\), Chapter 3) are only partly dimeric and substantial perturbed silanols are monomeric. Selected crystallographic data of vicinal silanols of the type A.1, A.2 and A.3 and D.2 are given in Table 2, their molecular structures are depicted in Figure 4. The average Si-C (cycloalkyl) distance decreases slightly when going from a cycloheptyl to a smaller ring like cyclohexyl or cyclopentyl. The average Si-OH distances are somewhat stretched compared to the average Si-O distances (maximal 0.02 Å), probably due to hydrogen bonding, except for type D.2. Average Si-O-Si and O-Si-O angles lie around 109 and 151 degrees respectively. The Si-O-Si angles are most effected when the silsesquioxane cages is substituted by a silylether.

Oxygen atoms have eight electrons with an electron configuration of \(1s^22s^22p^4\). In SiO\(_2\) constructions this usually results in more or less pronounced \(\pi\)-bonding by overlap of the oxygen lone pairs and the vacant silicon d-orbitals, which could be confirmed by X-ray spectroscopy.\(^{24}\) The silicon surface is in some cases able to act as a strong electron acceptor, charge can be easily transferred into the surface.\(^{25}\) The four oxygen atoms in the SiO\(_4\) tetrahedra compete for the use of the free silicon 3d orbitals and equilibrate in equal Si-O distances with partial covalent character.\(^{26}\) Different crystalline structures of silica are known such as quartz, tridymite, cristobalite, coesite, keatite, and stishovite.\(^{27}\) Experimental structural data on a wide range of silicates (including zeolites) suggest average Si-O bond values of 1.605 Å (range 1.57 – 1.72 Å), average O-Si-O angles of 109.5 ° (range 98-122 °) and equilibrium Si-O-Si angles of 140 ° (range 120 – 180 °).\(^{28}\) These average bonds and angles correspond well with the values observed for silsesquioxanes. However, the ranges in bonds and angles found for silicates are much wider than those for silsesquioxanes.

### Table 2. Selected interatomic distances and angles of some silsesquioxane silanols.

<table>
<thead>
<tr>
<th>type</th>
<th>silsesquioxane compound</th>
<th>av. Si-O (± 0.02 Å)</th>
<th>av. Si- OH (± 0.02 Å)</th>
<th>av. Si-C (± 0.02 Å)</th>
<th>av. O-Si-O (± 3 deg)</th>
<th>av. Si-O-Si (± 7 deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.1</td>
<td>((\text{c-C}<em>7\text{H}</em>{13})_7\text{SiO}_7\text{OH}_4)</td>
<td>1.61(5)</td>
<td>1.62(7)</td>
<td>1.86(2)</td>
<td>108.8(5)</td>
<td>153.3(1)</td>
</tr>
<tr>
<td>A.2</td>
<td>((\text{c-C}<em>6\text{H}</em>{11})_7\text{SiO}_7\text{OH}_3)</td>
<td>1.61(1)</td>
<td>1.62(2)</td>
<td>1.84(8)</td>
<td>108.8(8)</td>
<td>152.5(9)</td>
</tr>
<tr>
<td>A.3</td>
<td>((\text{c-C}_5\text{H}_9)_7\text{SiO}_7\text{OH}_2\text{OSiMe}_2)</td>
<td>1.61(2)</td>
<td>1.63(5)</td>
<td>1.82(6)</td>
<td>108.7(5)</td>
<td>151.1(9)</td>
</tr>
<tr>
<td>A.3</td>
<td>((\text{c-C}_5\text{H}_9)_7\text{SiO}_7\text{OSiMe}_2\text{Bu}_2)</td>
<td>1.61(3)</td>
<td>1.61(5)</td>
<td>1.83(8)</td>
<td>108.9(2)</td>
<td>150.2(5)</td>
</tr>
<tr>
<td>A.3</td>
<td>((\text{c-C}<em>6\text{H}</em>{11})_7\text{SiO}_7\text{OSiMe}_2\text{Ph}_2)</td>
<td>1.61(9)</td>
<td>1.62(5)</td>
<td>1.85(0)</td>
<td>108.3(8)</td>
<td>148.3(0)</td>
</tr>
<tr>
<td>D.2</td>
<td>[\langle \text{c-C}<em>6\text{H}</em>{11}\rangle_7\text{SiO}_7\text{OH}_2\text{OSiMe} \langle\mu-\text{OH}\rangle]</td>
<td>1.62(7)</td>
<td>1.61(8)</td>
<td>1.85(0)</td>
<td>109.0(4)</td>
<td>147.9(6)</td>
</tr>
</tbody>
</table>
Figure 4. Solid state infrared spectroscopy (Nujol Mull) of the stretching vibrations $\nu_{\text{OH}}$ of various silanols with the corresponding molecular structure. In the X-Ray structures, the cycloalkyls groups attached to the corners of the silicate cubes are partly or entirely omitted for clarity.
4.3. Solution State Properties

As observed for silsesquioxanes possessing geminal silanols (Chapter 2), the solution properties of silsesquioxane silanols can differ considerably from the solid state properties. Several techniques can be used to study the behavior of silsesquioxanes in solution. Infrared spectroscopy, solution-NMR and UV-VIS (to study relative Brønsted acidities) will be discussed here.

Solution IR spectra were recorded in CCl₄, a medium in which the interaction of CCl₄ with silanols is negligible. In a study on the effect of different solvents on silica-silanol frequencies was shown that CCl₄ gives only a small shift of 45 cm⁻¹ compared to the value in vacuum, whereas diethyl ether gives a shift of 430 cm⁻¹.²⁹ Silsesquioxanes were dissolved in CCl₄ (0.1M) and in CCl₄ containing 25% ether or tetrahydrofuran as an additional proton acceptor. As discussed in the previous two chapters of this thesis, acidity measurements in low-polar solvents only give qualitative values about relative acidities in a specific solvent. In the presence of a proton acceptor such as diethyl ether, the νOH vibrations shift as a result of hydrogen bonding between the silanol and the electron donor. These ∆νOH changes are considered as a measure of the energy of the specific interaction and thus the Brønsted acidity of the silanols. However, as was observed in Chapter 3, using ∆νOH values as a probe for relative Brønsted acidities of the investigated silsesquioxanes silanols, derived from addition of a proton acceptor, are only useful to probe the relative acidities of comparable silanols like for instance mono-silanols. The relative ion-pair acidities obtained by the overlapping indicator method proved to be much more valuable for comparing the acidities of different types of silanols.

Infrared-spectroscopy and relative Brønsted acidity

<table>
<thead>
<tr>
<th>type</th>
<th>silsesquioxane compound</th>
<th>CCl₄ νOH (cm⁻¹)</th>
<th>CCl₄ + Et₂O νOH (cm⁻¹)</th>
<th>CCl₄ + THF νOH (cm⁻¹)</th>
<th>pKₗp*</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.1</td>
<td>(c-C₇H₁₃)₇Si₆O₇(OH)₄</td>
<td>3225</td>
<td>3225</td>
<td>3255</td>
<td>7.5 (± 0.2)</td>
</tr>
<tr>
<td>A.2</td>
<td>(c-C₉H₁₇)₇Si₇O₉(OH)₃</td>
<td>3217</td>
<td>3217</td>
<td>3255</td>
<td>7.6 (± 0.2)</td>
</tr>
<tr>
<td>A.3</td>
<td>(c-C₇H₃)₇Si₇O₉(OSiMe₂)(OH)₂</td>
<td>3471</td>
<td>3415</td>
<td>3382</td>
<td>9.5 (± 0.1)</td>
</tr>
<tr>
<td>A.3</td>
<td>(c-C₇H₃)₇Si₇O₉(OSiMePh₂)(OH)₂</td>
<td>3453, 3592</td>
<td>3416</td>
<td>3374</td>
<td>9.9 (± 0.2)</td>
</tr>
<tr>
<td>B</td>
<td>(c-C₇H₃)₇Si₇O₉(OSiMe₂)O₂Si(OH)₂</td>
<td>3584, 3700</td>
<td>3374</td>
<td>3347</td>
<td>10.2 (± 0.1)</td>
</tr>
<tr>
<td>B</td>
<td>(c-C₇H₃)₇Si₇O₉(OSiMePh₂)O₂Si(OH)₂</td>
<td>3625, 3699</td>
<td>3371</td>
<td></td>
<td>9.7 (± 0.3)</td>
</tr>
<tr>
<td>C.1</td>
<td>(c-C₇H₃)₇Si₇O₉(OH)</td>
<td>3700</td>
<td>3348</td>
<td>3333</td>
<td>8.9 (± 0.4)</td>
</tr>
<tr>
<td>D.1</td>
<td>(c-C₇H₁₇)₇Si₇O₉(OSiMe₂)O₂Si(OH)₂</td>
<td>3550</td>
<td>3354</td>
<td>3528</td>
<td>10.7 (± 0.3)</td>
</tr>
<tr>
<td>D.2</td>
<td>[(c-C₇H₃)₇Si₇O₉(OSiMePh₂)₂]O₂Si(OH)₃</td>
<td>3626</td>
<td>3391</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*pKₗp averages of two indicators; Li⁺[9-(cyano)fluorenide]·2THF and Li⁺[9-(methoxycarbonyl)fluorenide]·2THF, deviation between brackets.
Type A. According to the broad $\nu$OH bands found at 3225 cm$^{-1}$ (vicinal tetra-silanols) and at 3217 cm$^{-1}$ (vicinal tri-silanols), A.1 and A.2 also form dimeric structures in solution. Vicinal di-silanols ($c$-$C_{5}H_{9}$)$_{7}$Si$_{7}$O$_{9}$-(OSiR$''$)$_{3}$)(OH)$_{2}$ (SiR$''$ = SiMe$_{3}$, SiMePh$_{2}$) are less effectively hydrogen bonded in solution, which is accompanied with a shift of the silanol stretching vibration to respectively 3471 cm$^{-1}$ and 3453 cm$^{-1}$ (Table 3, Figure 5). These values correspond with the observed wave numbers for mono-hydrogen bonds of vicinal silanols on rigid silica surfaces (3550 cm$^{-1}$). Interestingly, the solution IR spectrum of the vicinal di-silanol ($c$-$C_{5}H_{9}$)$_{7}$Si$_{7}$O$_{9}$-(OSiMePh$_{2}$)(OH)$_{2}$ shows a second distinct hydroxyl vibration. The reason for this phenomenon can be found in the large steric bulk of the SiMePh$_{2}$ substituent. Crystal structure data of mono-silylated silsesquioxanes bearing two vicinal silanols reveal that the molecules form bridged dimers via silanol hydrogen bonds (Figure 3) with a symmetry close to $C_{2v}$. In Table 4, intra- and intermolecular oxygen distances of the four silanols groups are displayed for three different silyl-terminated silsesquioxanes; ($c$-$C_{6}H_{11}$)$_{7}$Si$_{7}$O$_{9}$-(OSiMe$_{2}$R)(OH)$_{2}$ ($R$=Me$^{18}$, t-Bu$^{30}$).

Table 4. Solid state configuration of mono-silylated silsesquioxanes with vicinal di-silanol groups with intermolecular silanol ($a$, $a'$) and intramolecular silanol oxygen distances ($b$, $b'$) for three different mono-silylated silsesquioxanes.

<table>
<thead>
<tr>
<th>R$<em>{7}$Si$</em>{7}$O$<em>{9}$-(OSiMe$</em>{2}$R')(OH)$_{2}$</th>
<th>$a$</th>
<th>$a'$</th>
<th>$b$</th>
<th>$b'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R'$ = Ph</td>
<td>2.670</td>
<td>2.670</td>
<td>2.722</td>
<td>2.722</td>
</tr>
<tr>
<td>$R'$ = tBu</td>
<td>2.694</td>
<td>2.748</td>
<td>2.639</td>
<td>2.708</td>
</tr>
<tr>
<td>$R'$ = Me</td>
<td>2.663</td>
<td>2.659</td>
<td>2.692</td>
<td>2.684</td>
</tr>
</tbody>
</table>

As can be seen from Table 4, when going from small silyl ether (i.e. SiMe$_{3}$) to more bulky silyl ethers (i.e. SiMe$_{2}$Bu or SiMe$_{2}$Ph), the difference between intramolecular and intermolecular silanol-oxygen distances becomes larger. This indicates that a more bulky group distorts the symmetry of the hydrogen bonded [OH]$_{4}$ core somewhat. When these observations are extrapolated to the even more sterically hindered OSiMePh$_{2}$ silyl ether functionality in ($c$-$C_{6}H_{11}$)$_{7}$Si$_{7}$O$_{9}$-(OSiMePh$_{2}$)(OH)$_{2}$, one would expect increased distortion or even prevention of formation of the [OH]$_{4}$ core as shown in the picture in Table 4. Clearly, this effect will be largest in solution, which explains the two distinct vibrations in the solution infrared spectrum (Figure 5). One signal around 3600 cm$^{-1}$, indicative for an intramolecular hydrogen bond to the silyl ether functionality and one signal around 3450 cm$^{-1}$, indicative for an intramolecular mono-hydrogen bond between two oxygens (Figure 3). Such intramolecular mono-hydrogen bonds were also found for hexaorgano-trisiloxane, for which chelate rings were observed.

The terminal hydroxyl of these species is capable of forming an intramolecular hydrogen bond; a characteristic wavenumber of 3490 cm$^{-1}$ was found in the gauche conformer diluted in CCl$_{4}$.$^{15}$
Geminal silanols (B). In Chapter 2 it was found that geminal silanol silsesquioxanes exist in solution as monomers in which one of the silanols is intramolecularly hydrogen bonded to the silylether functionality while the other is isolated (Table 3, Figure 5). Unlike the frequencies found for silsesquioxane geminal silanols in the solid state, the ν\textsubscript{OH} bands observed in solution correspond much better with those found for geminal silanols on silica surfaces. For these species both hydrogen bonded (an additional shoulder at 3600 cm\textsuperscript{-1}) and isolated geminal silanols (in the same region as isolated silanols) were suggested.\textsuperscript{22,23}

Mono-silanols (C and D). Truly isolated silanols were compared to perturbed isolated silanols in Chapter 3. In the solution infrared spectrum of (c-C\textsubscript{5}H\textsubscript{9})\textsubscript{7}Si\textsubscript{8}O\textsubscript{12}(OH), at 3700 cm\textsuperscript{-1} one sharp band was found, which is assigned to its truly isolated silanol. The additional broad vibration that was observed in the solid state is absent in solution and indicates that (c-C\textsubscript{5}H\textsubscript{9})\textsubscript{7}Si\textsubscript{8}O\textsubscript{12}(OH) is monomeric when dissolved (Table 3, Figure 5). The perturbed silanols of type D.1 show broad vibrations at similar frequencies (3550 cm\textsuperscript{-1}) in solution and in the solid-state. This indicates significant hydrogen bonding with the silylethers of the intramolecular siloxane ring even in solution. The vibration band found at 3635 cm\textsuperscript{-1} for D.2 is also comparable to the value found in the solid state, confirming the analogy with perturbed silanols on silica sterically shielded from the environment.\textsuperscript{19}

Brønsted Acidity. In Chapter 3 it was concluded that unperturbed silanols like (c-C\textsubscript{5}H\textsubscript{9})\textsubscript{7}Si\textsubscript{8}O\textsubscript{12}(OH) are more acidic than perturbed silanols. When diethyl ether is added as proton-acceptor, the ν\textsubscript{OH} vibrations shift towards lower wave numbers due to hydrogen bond interaction between the silanol and the proton acceptor. For almost unperturbed mono-silanols of type C.1 and D.2, this effect is very pronounced (Δν\textsubscript{OH} shift up to 359 cm\textsuperscript{-1}). In perturbed mono-silanols the intramolecular hydrogen bonding to the siloxane ring hinders the interaction with the proton-acceptor effectively and Δν\textsubscript{OH} can be as small as 16 cm\textsuperscript{-1} (Table 3, see further in Chapter 3). When diethyl ether was added to CCl\textsubscript{4} solutions of geminal silanols, all silanols become hydrogen-bonded as a result of the strong interaction of the ether with silsesquioxane silanols (at 3374 cm\textsuperscript{-1}). This band is located at frequencies comparable to those observed for (almost) unperturbed mono-silanols. It is situated at somewhat lower frequency than observed for vicinal disilanols (3415 cm\textsuperscript{-1}) when ether was added to the tetrachloromethane solutions (Table 3). The strong dimeric structures of silsesquioxanes containing vicinal tri- and tetrasilanols are not noticeably affected when ether is added to the tetrachloromethane solutions, which confirms the earlier conclusion that silsesquioxanes capable of poly-hydrogen bonding are dimeric both in the solid state and in solution. When tetrahydrofuran was added instead of ether to tetrachloromethane solutions of these vicinal tri- and tetrasilanols, a small shift towards lower frequencies was observed (about 40 cm\textsuperscript{-1}), which is addressed to superior proton acceptor capabilities of tetrahydrofuran.

When comparing the ion pair acidity in THF with UV-VIS of the closed cage silsesquioxane (c-C\textsubscript{5}H\textsubscript{9})\textsubscript{7}Si\textsubscript{8}O\textsubscript{12}(OH) containing an isolated silanol (pK\textsubscript{a} = 8.9) with the mono-silanol containing compound (c-C\textsubscript{6}H\textsubscript{11})\textsubscript{7}Si\textsubscript{7}O\textsubscript{9}((OSiMe\textsubscript{2})\textsubscript{2}O)OH (pK\textsubscript{a} = 10.7, Table 3), the latter appears to be less acidic as a result of the electron donating effect of the additional intramolecular siloxane ring. Deprotonation NMR
A Comparising Study of Four Types of Silanols Modeled by Silsesquioxanes

experiments on an equimolar mixture of \((c\text{-}C_5H_9)_7Si_8O_{12}(OH)\), \((c\text{-}C_6H_{11})_7Si_7O_9(\text{OSiMe}_2)_2O(OH)\) and one of the indicators used for the \(pK_a\) determinations in THF-d_8 (Li'[9-(cyano)fluorenide]-2THF), indeed showed a clear preference for deprotonation of the former. The differences in ion pair acidity for geminal silanols and corresponding vicinal disilanols \((c\text{-}C_5H_9)_7Si_7O_9(\text{OSiR'}_3)(OH)_2\) (SiR' = SiMe_3, SiMePh_3) are small. The ion pair acidities for geminal silsesquioxanes are 10.2 and 9.7 and for vicinal di-silanol silsesquioxane 9.5 and 9.9 (both respectively SiMe_3 and SiMePh_2 substituted). Vicinal tetra- and tri-silanols containing silsesquioxanes are much more acidic than all other silsesquioxanes studied. As could be seen from the IR data, silsesquioxanes containing vicinal tri- and tetra-silanol-are capable of poly-hydrogen bonding even in solution, while silsesquioxanes containing vicinal di-silanols give considerably less effective hydrogen bonding in solution (Figure 5). Consequently, the vicinal tetra- and tri-silanols \((c\text{-}C_7H_{13})_7Si_6O_7(OH)_4\) and \((c\text{-}C_5H_{11})_7Si_7O_9(OH)_3\) are up to two orders of magnitude more acidic than the vicinal di-silanols \((c\text{-}C_5H_9)_7Si_7O_9(\text{OSiMe}_3)(OH)_2\) (SiR' = SiMe_3, SiMePh_3; Table 3). This difference in acidity of the tri-silanol \((c\text{-}C_9H_{11})_7Si_7O_9(OH)_3\) and the di-silanol \((c\text{-}C_5H_9)_7Si_7O_9(\text{OSiMe}_3)(OH)_2\) was nicely demonstrated by Feher and coworkers who found that silylation of \((c\text{-}C_5H_9)_7Si_7O_9(OH)_3\) is four orders of magnitude faster than for \((c\text{-}C_5H_9)_7Si_7O_9(\text{OSiMe}_3)(OH)_2\).

**Acidity of silicates.** Zeolites incorporated with for instance aluminum are very Brønsted acidic due to bridging hydroxyls between a silicon and an aluminum atom and are used in several acid-catalyzed reactions. All-silica zeolites or silicates are considerably less acidic. Their weak acidity is usually measured indirectly via observed differences in adsorption of small basic molecules. Calorimetric adsorption experiments by Drago and Chronister nicely demonstrated that poly-hydrogen bonded silanols (Figure 3) on silica gel give rise to very effective hydrogen bonding, which generally results in more acidic systems than mono-hydrogen bonded silanols. Truly isolated silanols on a silica surface are considered moderately acidic and form hydrogen bonds with basic molecules but do not take part in proton-transfer reactions. Strong bases such as NaOH are required to deprotonate the silanol and from these experiments \(pK_a\) of isolated silanols on a silica surface was estimated to be around 7. From different studies on the acidity and reactivity of (rigid) silica surface silanols, it was concluded that isolated silanols are more acidic than mono-hydrogen bonded silanols. This agrees with our findings for the estimated differences in relative ion-pair acidities for silsesquoxane silanols. Poly-hydrogen bonded silanols as occurring in silsesquioxane vicinal tri- and tetra-silanol-are up to three orders of magnitude more acidic than vicinal disilanols. Truly isolated silanols of silsesquioxanes have a \(pK_a\) of 8.9, being approximately 10-fold more acidic than the observed \(pK_a\) for mono-hydrogen bonded vicinal di-silanols and geminal di-silanols of silsesquioxanes.
Figure 5. Solution infrared spectroscopy (0.1 M in CCl$_4$) of the stretching vibrations $\nu_{\text{OH}}$ of various silanols with the corresponding molecular configuration in solution.
NMR-spectroscopy

Solution NMR spectroscopy provides useful information on the molecular structure of silsesquioxanes. Most informative are the $^{13}$C signals of the methyne (CH of the cycloalkyl) attached to the cage silicon atoms and the $^{29}$Si resonances of the framework-Si atoms. These signals are very indicative to see whether a reaction is completed and has resulted in a well-defined product or has ended in a product mixture. Moreover, $^{29}$Si-NMR is very informative with respect to the symmetry of the complex. The most commonly used starting material $\text{R}_7\text{Si}_7\text{O}_9\text{OH}_3$ possesses $C_{3v}$ symmetry. This is concluded from the resonance patterns with a ratio of 3 to 1 to 3 from the seven silicon cage atoms and the cycloalkyl-methyneS attached to them (Table 4, Figure 6). When the tri-silanol is substituted by a silylether functionality resulting in vicinal di-silanols like $\text{c-C}_5\text{H}_9\text{Si}_7\text{O}_9\text{OSiMe}_3\text{OH}_2$, the compound has $C_s$ symmetry and results in Si-cage resonances of 2:1:1:1:2. $C_s$ symmetry could also be observed for geminal silanols and di-silylated silsesquioxane mono-silanols (of type B and D.1). For the closed caged $\text{c-C}_5\text{H}_9\text{Si}_8\text{O}_{12}\text{OH}$ $C_{3v}$ symmetry was found (Table 4, Figure 6). The Si-OH resonances found in the $^1$H-NMR spectra of the four types of silanols clearly show an upfield shift as the silanols become less perturbed by hydrogen bonding.

As can be seen in Figure 6, with $^{29}$Si-NMR, a clear distinguish can be made between the differently coordinated $\text{OSiR}_3$, $\text{O}_2\text{SiR}_2$, $\text{O}_2\text{SiR} \text{OH}$, $\text{O}_3\text{SiR}$, $\text{O}_3\text{Si(OH)}_2$ and $\text{O}_3\text{Si(OH)}_3$. Solid state $^{29}$Si-NMR of silica surfaces can discriminate between silicon atoms bearing two, one or no hydroxyl groups.$^5$ Geminal silanols $\text{O}_2\text{Si(OH)}_2$ are found at –91 ppm which correspond well with the observed $\text{O}_2\text{Si(OH)}_2$ signals at –89.4 ppm for silsesquioxanes with geminal silanols (recorded in CDCl$_3$). Signals at –100 ppm were assigned to mono-silanols $\text{O}_2\text{Si(OH)}$ for silica surfaces which also agrees well with the SiOH resonance at –99.40 for the isolated silanol of $\text{c-C}_5\text{H}_9\text{Si}_8\text{O}_{12}\text{OH}$ (recorded in CDCl$_3$).

Table 4. Symmetry of various silsesquioxane silanols obtained by $^{13}$C- and $^{29}$Si- solution NMR and 1H-NMR Si-OH signals.

<table>
<thead>
<tr>
<th>type</th>
<th>silsesquioxane compound</th>
<th>framework-Si and methyne ratio</th>
<th>symmetry</th>
<th>Si–OH ($^1$H NMR, CDCl$_3$, in ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.2</td>
<td>(c-C$<em>6$H$</em>{11}$)$_3$Si$_7$O$_9$(OH)$_3$</td>
<td>3 : 1 : 3</td>
<td>$C_{3v}$</td>
<td>6.97</td>
</tr>
<tr>
<td>A.3</td>
<td>(c-C$_5$H$_9$)$_3$Si$_7$O$_9$(OSiMe$_3$)(OH)$_2$</td>
<td>2 : 1 : 1 : 1 : 2</td>
<td>$C_s$</td>
<td>3.75</td>
</tr>
<tr>
<td>B</td>
<td>(c-C$_5$H$_9$)$_3$Si$_7$O$_9$(OSiMe$_3$)O$_2$Si(OH)$_2$</td>
<td>1 : 1 : 1 : 2 : 2</td>
<td>$C_s$</td>
<td>2.41, 3.80</td>
</tr>
<tr>
<td>C.1</td>
<td>(c-C$_5$H$_9$)$_3$Si$_7$O$_9$(OH)</td>
<td>3 : 4</td>
<td>$C_{3v}$</td>
<td>2.53</td>
</tr>
<tr>
<td>D.1</td>
<td>(c-C$<em>6$H$</em>{11}$)$_3$Si$_7$O$_9$(O{SiMe$_2$O})$_2$OH</td>
<td>1 : 1 : 2 : 1 : 2</td>
<td>$C_s$</td>
<td>3.59</td>
</tr>
</tbody>
</table>
Figure 6. $^{29}$Si-NMR spectra of silsesquioxane silanols A.2 ((c-C$_6$H$_{11}$)$_7$Si$_7$O$_9$(OH)$_3$), A.3 ((c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiMe$_3$)(OH)$_2$), B ((c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiMe$_3$)O$_2$Si(OH)$_2$), C.1 ((c-C$_5$H$_9$)$_7$Si$_8$O$_{12}$(OH)) and D.1 ((c-C$_6$H$_{11}$)$_7$Si$_7$O$_9$[(SiMe$_2$O)$_2$]OH).
4.4. Concluding remarks

The availability of silsesquioxane models for four types of silanols offered the unique opportunity to study characteristics of different types of silanol one by one. On silica, different surface silanols exist simultaneously. A clear distinguish between four types of silanols modeled by silsesquioxanes could be made both in solution and in the solid state by several techniques. Although solid-state properties of silsesquioxane silanols were thought to be most appropriate for a direct comparison with the (usually) solid state properties of silica surface silanols, in many cases solution characteristics showed interesting analogies.

The mobility of silsesquioxane ligands forms a clear disadvantage as it allows systems to form strong intermolecular poly-hydrogen bonds. This agglomeration is most pronounced in the solid state. Multiple vicinal hydroxyl groups of silsesquioxanes form intermolecular poly-hydrogen bonds both in solution and in the solid state which agree well with poly-hydrogen bonded silanols in flexible silicates or poly-hydrogen bonding resulting from interactions with adsorbed water molecules. When intermolecular interactions between silanols in vicinal di-silanols and geminal di-silanols become sterically hampered, which is more effective in solution, the silsesquioxane cages tend to be monomeric. Intramolecular mono-hydrogen bonding with adjacent silyl ether functionalities or adjacent silanols are observed and correspond with mono-hydrogen bonds found for vicinal silanols on rigid silica surfaces. In solution, one hydrogen of the silsesquioxane geminal silanols is mono-hydrogen bonded to the silyl ether substituent while the other hydroxyl is isolated of nature. This hydroxyl has the same characteristics as the unperturbed silanol of the close caged \( \text{R}_7\text{Si}_7\text{O}_{12}^{(\text{OH})} \) and both correspond well with characteristics found for unperturbed silanols on silica surfaces. Silsesquioxanes possessing perturbed mono-silanols were observed to have the same characteristics in the solid state and in solution. This can be explained by effective intramolecular hydrogen bonding to neighboring siloxy units or steric shielding by bulky substituents. Silsesquioxanes with perturbed mono-silanols were tentatively compared to perturbed silanols (also called internal silanols) on silica that are inaccessible to most reactants. Concluding, silsesquioxane silanols in solution are better models for corresponding silica surface silanols than silsesquioxane silanols in the solid state.

The order in acidity of the various silanols of the model systems agreed well with the predicted order in acidity of silica surface silanols. For the different classes of silanols the order in diminishing acidity proved to be: vicinal tetra- and tri-silanols >>> isolated silanols > vicinal di-silanols ~ geminal silanols ~ perturbed silanols. \( ^{29}\text{Si} \) solution NMR signals of silsesquioxanes due to \( \text{O}_2\text{Si(OH)}_2 \) or \( \text{O}_3\text{Si(OH)} \) species showed remarkable similarity with solid state \( ^{29}\text{Si} \)-NMR signals assigned to these species.
Chapter 4

4.5. Experimental section

General Remarks - Reactions were performed under an argon atmosphere using Schlenk techniques when necessary. Solvents were distilled from K (THF) and benzophenon (Et₂O) or dried over 4 Å molecular sieves (CCl₄, CDCl₃) and stored under argon. ¹H- and ¹³C-NMR spectra were recorded on Varian Mercury 400 spectrometers (25°C, ¹H NMR: 400 MHz, ¹³C NMR: 100.6 MHz). ²⁹Si-NMR spectra were recorded on a Varian Indigo 500 spectrometer (25°C, ²⁹Si-NMR: 99.3 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (¹H, ¹³C NMR) or external standards (²⁹Si: SiMe₃ = 0 ppm). All Fourier Transformed Infrared spectra were recorded at room temperature on a Nicolet Avatar™ 360 spectrophotometer. Samples in solution were prepared under inert atmosphere (glovebox), νOH values were determined in 0.1M CCl₄ solutions and ΔνOH in 0.1M CCl₄-solutions containing 0.25M diethylether or 0.25M tetrahydrofuran. Solid-state samples were recorded as Nujol-mulls (prepared under inert atmosphere, glovebox). The investigated silsesquioxanes silanols (c-C₈H₇O)(OSiMePh₂)(OH)₆, (c-C₈H₇O)(OSiMe₂)(OH)₆, (c-C₈H₇O)₃(OH)₆, and [(c-C₈H₇O)(OSiMe₂)(O₂Si(OH))]₆(µ-O) were described in Chapter 2 of this thesis, the synthesis of (c-C₈H₇O)(OSiMe₂)(O₂Si(OH))₆(µ-O) was performed on a UV-2401PC spectrophotometer with standard slid width and scan speed.

pKₛ measurements - The pKₛ measurements were carried out using the overlapping indicator method (Chapter 2, 3), 9-cyanofluorene (pKₛ(DMSO) = 8.3) and 9-(methoxycarbonyl)fluorene (pKₛ(DMSO) = 10.4) were the indicators used. Lithium salts of the indicators were prepared, isolated, and recrystalized before used. Due to the low solubility of silsesquioxanes in DMSO, THF was used as the solvent instead. UV-Vis measurements for determination of the pKₛ values, were performed on a UV-2401PC spectrophotometer with standard slid width and scan speed.

References

A Comparising Study of Four Types of Silanols Modeled by Silsesquioxanes

Incompletely condensed silsesquioxanes with a siloxane ring of various size and rigidity in the proximity of a silanol were described in Chapter 3. Protonolysis with GaMe₃, exclusively affording dimeric structures \( [R_7Si_7O_9(O\{SiR'\_2O\}_n)(\mu-O)GaMe_2]_2 \) revealed that the siloxane rings are not very suitable for forming monomeric systems with intramolecular coordination of the siloxanes to the Lewis acidic gallium. Substitution reactions of the silanol with \( \text{Cp}''\text{TiBz}_3 \) (\( \text{Cp}'' = \eta^5-C_5H_5(SiMe_3)_2 \)) in a 1:1 ratio, afforded monomeric \( R_7Si_7O_9(O\{SiR'\_2O\}_n)OTi(\text{Cp}'')\text{Bz}_2 \) silsesquioxane complexes. To probe the effect of the siloxane ring on the neighboring -OTi(\( \text{Cp}'' \))\text{Bz}_2 group, the catalytic activity of these complexes in the polymerization of 1-hexene was tested. The presence of an adjacent siloxane ring results in a lower initial polymerization activity in comparison with the analogue without an additional siloxane ring, \( (\text{c-C}_5H_9)_7Si_8O_{12}OTi(\text{Cp}'')\text{Bz}_2 \). Conversely, the stability of the cationic species is considerably improved. Phenyl substituents at the intramolecular siloxane ring facilitated the formation of the cationic species.

5.1. Introduction

Heterogeneous catalysts play a crucial role in the industrial production of polyolefins. For 40 years, the industrial production of polyolefins has mainly been based on classical heterogeneous (Ziegler-Natta and Phillips type) catalysts. Only during the last decade, metallocene, constrained geometry and related olefin polymerization catalysts have been developed to a point that they can be commercialized. Combining the advantages of homogeneous metallocene olefin polymerization catalysts (well-defined single-site catalysts, high activities, stereoregularity of polymerized prochiral olefins) with heterogeneous olefin polymerization catalysts (good morphology, little reactor fouling) might result in commercially interesting heterogeneous single-site catalysts. However, the success of heterogenized catalysts is dependent on a careful choice of support, activators and method of preparation. The increased complexity of the system is subject of ongoing research and has been extensively described in several reviews. Persistent problems are catalyst leaching, resulting in unfavorable polymer morphology, reactor fouling, and loss of activity. Generally, the activity of the supported systems is reduced with respect to that of the homogeneous systems. Detailed structural studies of such systems are required but are hampered by the heterogeneity of the systems.
Chapter 5

Surface organometallic chemistry (SOMC) is an approach that is used to investigate immobilized systems and takes into account the basic rules derived both from organometallic chemistry and from surface science. SOMC syntheses lead to catalytic systems with very high percentages of relatively well defined active catalytic sites in which the whole of the supramolecular species is considered; support, metal and ligands. The SOMC approach, developed and applied by Basset et al.,\textsuperscript{6,7} also successfully applied by the groups of Choplin\textsuperscript{8} and Scott,\textsuperscript{9} has greatly contributed to the understanding of several heterogeneous catalytic processes. Recent studies on for example supported Zr(CH\textsubscript{2}CMe\textsubscript{3})\textsubscript{4}, Cp\textsuperscript{2}Zr(CH\textsubscript{3})\textsubscript{2} and Cp\textsubscript{2}Zr(CH\textsubscript{3})\textsubscript{2} on partially dehydroxylated silica has clearly shown the high value of this approach.\textsuperscript{5} Though, questions that cannot be solved using this approach are for example detailed structural properties of the active site or the reasons for low polymerization activity of these heterogeneous systems compared to their homogeneous counterparts. Silica surfaces are poorly defined and, depending on the calcinations temperature, contain different types of surface silanols and (strained) siloxane moieties. Furthermore, roughness of the surface leads to local surface defects that can dramatically affect the reactivity of the surface functional groups as well as the local structural properties of an immobilized metal site. Grafting of silyl- or alkyl functionalities has been applied to further alter the surface properties of silicas.

One step further in modeling heterogeneous catalysts is by using silsesquioxane-based model systems. The use of silsesquioxane model systems proved to be an excellent tool for distinguishing between several aspects of immobilization on silica. Different immobilizing methods (grafting, tethering, electrostatic interaction) and activators (alumoxanes, fluoroaryl-based boranes/borates) have been examined separately.\textsuperscript{10,11} Chapter 3 of this thesis describes how local defects such as possible interactions of neighboring siloxane-oxygens to Lewis acidic catalyst sites can be modeled by silsesquioxanes. Siloxane interactions were mimicked by introducing multiple siloxy functionalities in the proximity of silanols, the resulting silsesquioxanes were of the type R\textsubscript{7}Si\textsubscript{8}O\textsubscript{12}(OH) (R = c-C\textsubscript{5}H\textsubscript{9}, c-C\textsubscript{6}H\textsubscript{11}; R’= Me, Ph; n=0-3). In this chapter, the influence of the neighboring siloxane ring, capable of electron donation by its silyl ethers, was investigated by studying bonding properties and catalytic activity of Lewis acidic gallium and titanium complexes based on these silsesquioxanes. The stability and olefin polymerization activity of the cationic titanium silsesquioxane complexes were compared with the un-influenced metalated analogue, resulting from metalation reaction of the truly isolated silanol of the closed caged octameric silsesquioxane R\textsubscript{7}Si\textsubscript{8}O\textsubscript{12}(OH). The latter proved to be useful models for titanium complexes immobilized on a silica surface, but this is the first time that neighboring effects (i.e. partly silylated silica surface) on the stability and activity of an immobilized catalyst has been taken into account.
5.2. Protonolysis with GaMe₃

Differences in the IR νOH vibration frequencies and pKₐ values gave a qualitative picture of the relative capacity for hydrogen bonding of the siloxane rings in R₇Si₇O₉(OSiR'₂O)ⁿ⁺¹(OH) (R = c-C₅H₉, c-C₆H₁₁; R' = Me, Ph; n = 0-3) with the adjacent hydroxyl group (Chapter 3). To study the electron donating capacity of the siloxane rings further, protonolysis of three representative R₇Si₇O₉(OSiR'₂O)ⁿ⁺¹(OH) silsesquioxanes with the strong Lewis acidic metal precursor GaMe₃ were carried out. Several examples of gallium silsesquioxanes¹²-¹⁴ and polycyclic gallium siloxides¹⁵,¹⁶,¹⁷,¹⁸ are reported in literature. All of these systems show a strong tendency to form tetra-coordinated gallium sites by forming aggregates. Smaller molecules like Ph₃SiOH and Me₃SiOH, when reacted with GaMe₃, are known to form stable dimeric structures possessing a Ga₂(µ-OR)₂ four-membered ring.¹⁸ A monomeric gallium amide has been reported recently to which tetrahydrofuran is coordinated¹⁹, the crystal structure of Cl₂(THF)GaN(H)SiMe₃ revealed that the tetra-coordinate gallium center adopts a distorted tetrahedral geometry. Gallium-zeolites have lead to interesting catalytic properties, for instance the conversion of small alkanes into aromatic hydrocarbons²⁰ in which dehydrogenation of alkanes into alkenes is the crucial first step.²¹ The catalytic activity of proton-poor zeolites Ga-MFI (almost no Brønsted acid groups present) is believed to be caused by Lewis acid-base pair formation of gallium sites and neighboring zeolite oxygen anions.²² In principal, the donating abilities of the additional siloxane ring of R₇Si₇O₉(OSiR'₂O)ⁿ⁺¹(OH) might prevent the formation of aggregates and if so, would provide a model of a Lewis acid influenced by a neighboring electron donor.

**Scheme 1:** Synthesis of gallium substituted dimeric aggregates 1-4 from (c-C₅H₉)₇Si₆O₁₂(OH) and disilylated silsesquioxanes (c-C₅H₉)₇Si₇O₉(OSiMe₂O)(OH), (c-C₅H₉)₇Si₇O₉(OSiPh₂O)(OH), (c-C₅H₉)₇Si₇O₉(OSiMe₂O)(OH) and (c-C₆H₁₁)₇Si₇O₉(OSiMe₂O)(OH) from Chapter 3.
Equimolar amounts of GaMe₃ were reacted with silsesquioxanes containing a truly isolated silanol or an isolated silanol in the presence of an additional siloxane ring, (c-C₅H₉)₃Si(OSiMe₂)O(OH) and compounds (c-C₅H₉)₃SiOₙ(OSiMe₂)O(OH), (c-C₅H₉)₃Si(O(OSiPh₂)₂O(OH)) and (c-C₅H₉)₃SiOₙ(O(SiMe₂)Oₙ)₂O(OH) (Chapter 3). This resulted in thermally stable gallium dialkyl products 1-4 (Scheme 1): [(c-C₅H₉)₃Si(OSiO)₂(OGaMe₂)]₂ (1), [(c-C₅H₉)₃SiOₙ(OSiMe₂)O(OGaMe₂)]₂ (2), [(c-C₅H₉)₃SiOₙ(OSiPh₂)O(OGaMe₂)]₂ (3) and [(c-C₅H₉)₃SiOₙ(O(SiMe₂)Oₙ)₂(OGaMe₂)]₂ (4). NMR-spectroscopic investigation showed no sign of interaction of the additional siloxane ring with the oxygen of the Si-O-Ga bond. No symmetry-changes or significant shift of methyl-signals (¹H or ¹³C) attached to the gallium atom or to the silicon atoms of the ring could be detected. Clearly, also for these silsesquioxane complexes the electron deficiency of Ga is satisfied more effectively by formation of dimeric species in which the siloxy groups are bridging between the two tetrahedrally surrounded Ga centers than by coordination of oxygens from the adjacent silyl ether ring. For small molecules this tendency to form tetrahedrally surrounded gallium complexes and obtain a stable [µ-(RO)GaMe₂]₂ fragment is common.¹⁸,²³-²⁶

The dimeric gallium complexes 1-4 showed once more the major disadvantage of silsesquioxane model systems, being the mobility of the silica cages, which allows the formation of thermodynamically stable dimeric aggregates. This clustering hampered accurate investigation of the siloxane-ring interactions with gallium.

Crystals suitable for diffraction could be obtained for compound 3, in Figure 1 the crystal structure is shown and a selection of bond lengths and angles is depicted in Table 1. Crystal structures of other silsesquioxanes with [µ-(=SiO)GaMe₂]₂ fragments have been reported. [(c-C₅H₉)₃Si(OSi)²]₂[GaMe₂]₂ possessing three [µ-(=SiO)GaMe₂]₂ fragments resulted from reaction of (c-C₅H₉)₃SiOSi(OH)₃ with three equivalents of GaMe₃, [(c-C₅H₉)₃Si(OSiPh₂)O)(GaMe₂)]₄ possessing two [µ-(=SiO)GaMe₂]₂ fragments resulted from reaction of (c-C₅H₉)₃Si(O(OSiPh₂)O(OH)₂ with two equivalents of GaMe₃.¹³ The average Ga-O distance is 1.99(3) Å for [(c-C₅H₉)₃Si(OSi)²]₂[GaMe₂]₂ and 1.97(4) for [(c-C₅H₉)₃Si(OSiPh₂)O](GaMe₂)]₄. Compared to these bond distances the [µ-(=SiO)GaMe₂]₂ fragment of 3 shows almost an identical Ga-O average bond length (1.97(7) Å). No abnormalities in the sense of steric strain or a distorted geometry were found.¹⁷ H- and ¹³C-NMR spectra of 3 show one gallium-methyl peak situated at normal high-field resonances (¹H: δ 0.28 ppm; ¹³C: -2.85 ppm), indicating that the methyls are equivalent in solution. Apparently the [µ-(=SiO)GaMe₂]₂ fragment is not influenced by adjacent moieties and shows no indication of interacting with the O-SiPh₂-O fragments. This was not unexpected since characterization of the starting silsesquioxane complex (c-C₅H₉)₃SiO₇(OSiPh₂O)O(OH) in Chapter 3 of this thesis, revealed that the steric strain of the aryls complicates interaction of the silanol with the silyl ether functionalities.

In Lewis acidic metalasilsesquioxane complexes, the distance between the silicon and the oxygen bonded to the Lewis acidic metal site often gives a qualitative indication of the oxophilicity of the metal center.²⁷-²⁹ Hence, the Si1-O1 distance (1.617(3) Å) of 3 compared to the Si-O distances of other reported silsesquioxane-gallium structures with [µ-(=SiO)GaMe₂]₂ fragments (1.622(2) Å for [(c-C₅H₉)₃Si(OSiPh₂)O](GaMe₂)]₄ and 1.618(3) Å for [(c-C₅H₉)₃Si(OSiO)₂](GaMe₂)]₄) show no divergent oxophilicity.
Grafted Metal Complexes from Models for Partly Silylated Silica Surfaces

![Molecular structure of [(c-C5H9)7Si7O9(OSiPh2O)(OGaMe2)]2 (3). Thermal ellipsoids are scaled to enclose 40% of the electron density. Only the methyne carbon of the cyclopentylrings is shown for clarity.](image)

**Figure 1.** Molecular structure of [(c-C5H9)7Si7O9(OSiPh2O)(OGaMe2)]2 (3). Thermal ellipsoids are scaled to enclose 40% of the electron density. Only the methyne carbon of the cyclopentylrings is shown for clarity.

**Table 1.** Selected interatomic distances and angles for 3.

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>C1-Ga1-C2</th>
<th>Si5-O10-Si8</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga1-C2</td>
<td>1.932(0)</td>
<td>Si6-O10-Si8</td>
<td>144.6(3)</td>
</tr>
<tr>
<td>Ga1-C2</td>
<td>1.931(1)</td>
<td>Si7-O12-Si8</td>
<td>145.7(3)</td>
</tr>
<tr>
<td>Ga1-O1</td>
<td>1.999(1)</td>
<td>Si-O-Si</td>
<td></td>
</tr>
<tr>
<td>Ga-Oaw</td>
<td>1.977(7)</td>
<td>av</td>
<td></td>
</tr>
<tr>
<td>Ga1-Ga1’</td>
<td>2.995(1)</td>
<td>av</td>
<td></td>
</tr>
<tr>
<td>Si1-O1</td>
<td>1.617(3)</td>
<td>av</td>
<td></td>
</tr>
<tr>
<td>Si1-O2</td>
<td>1.616(4)</td>
<td>av</td>
<td></td>
</tr>
<tr>
<td>Si1-O3</td>
<td>1.636(4)</td>
<td>av</td>
<td></td>
</tr>
<tr>
<td>Si5-O10</td>
<td>1.626(5)</td>
<td>av</td>
<td></td>
</tr>
<tr>
<td>Si7-O12</td>
<td>1.630(4)</td>
<td>av</td>
<td></td>
</tr>
<tr>
<td>Si8-O10</td>
<td>1.641(5)</td>
<td>av</td>
<td></td>
</tr>
<tr>
<td>Si8-O12</td>
<td>1.629(4)</td>
<td>av</td>
<td></td>
</tr>
<tr>
<td>Si8-C43</td>
<td>1.865(6)</td>
<td>av</td>
<td></td>
</tr>
<tr>
<td>Si8-C49</td>
<td>1.845(7)</td>
<td>av</td>
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</tr>
<tr>
<td>Si-Oaw</td>
<td>1.624(7)</td>
<td>av</td>
<td></td>
</tr>
</tbody>
</table>
5.3. Protonolysis with Ti{η^5-C_5H_3(SiMe_3)_2}Bz_3(TiCp"Bz_3).

To see whether siloxanes are capable to donate electrons at all, we studied a half-sandwich system in which dimerization is prevented by steric bulk as well as a charged metal center. The monomeric titanium half-sandwich products (c-C_5H_9)_2Si_2O_3(OSiMe_3)(OTiCp"Bz_3) (5) (Cp" = η^5-C_5H_5), (c-C_5H_11)_2Si_2O_3(OSiMe_3)(OTiCp"Bz_3) (6) and (c-C_5H_9)_2Si_2O_3(OSiPh_2O)(OTiCp"Bz_3) (7) are slowly formed in situ at room-temperature upon protonolysis of Cp"TiBz_3 with silsesquioxanes (c-C_5H_9)_2Si_2O_3(OSiMe_3)(OTiCp"Bz_3) (OH), (c-C_5H_11)_2Si_2O_3(OSiMe_3)(OH), and (c-C_5H_9)_2Si_2O(OSiPh_2O)(OH) (Chapter 3, Scheme 2) and were followed by NMR (Figure 2). During the reaction, one of the benzyls is protonated and toluene is formed; the methylene protons of the remaining benzyl groups attached to the metal-center become diastereotopic and this results in an AB spin system in the ^1H-NMR spectrum (Figure 3). The ^1H and ^13C values of the methylene group of the benzyls show normal chemical shifts compared to (c-C_5H_9)_2R_3SiO_2(OSiCp"Bz_3) and SiPh_3OTiCp"Bz_3 (Table 2). Alike was observed for (c-C_5H_9)_2R_3SiO_2(OSiCp"Bz_3) and SiPh_3OTiCp"Bz_3, the absence of a high-field shift of benzyl ortho phenyl protons in 5-7 excludes significant η^2-bonding of the benzyl group. The silsesquioxanes 1-6 show many similarities with Ph_3SiOH and (c-C_5H_9)_2R_3SiO_2(OH) in the reactivity towards Cp"TiBz_3. Forcing a second equivalent of the silsesquioxanes L-SiOH to react with L-SiOTiCp"Bz_3 to obtain L-SiOTiCp"Bz_3(OSiL) appeared impossible. Furthermore, treatment of (c-C_5H_9)_2R_3SiO_2(OSiMe_3)(OH), (c-C_5H_11)_2R_3SiO_2(OSiMe_3)(OH), and (c-C_5H_9)_2R_3SiO(OSiPh_2O)(OH) with Cp"ZrBz_3 resulted in non-selective reactions and NMR spectra of these mixtures indicated formation of Cp"[L-SiO]_2-ZrBz_3, similar as was observed for (c-C_5H_9)_2R_3SiO_2(OH).

Scheme 2: In situ synthesis of titanium half sandwich silsesquioxanes 5-7

Table 2. ^1H- and ^13C- NMR spectroscopic investigation of the methylene group of CH_2Ph of 5-7, (c-C_5H_9)_2R_3SiO_2(OSiCp"Bz_3) and SiPh_3OTiCp"Bz_3 in C_6D_6.

<table>
<thead>
<tr>
<th>compound</th>
<th>^1H ppm</th>
<th>J_C-H (Hz)</th>
<th>^13C ppm</th>
<th>J_C-H (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.30, 2.46</td>
<td>9.9</td>
<td>85.42</td>
<td>125</td>
</tr>
<tr>
<td>6</td>
<td>3.46, 2.39</td>
<td>9.9</td>
<td>85.76</td>
<td>125</td>
</tr>
<tr>
<td>7</td>
<td>3.14, 2.32</td>
<td>9.9</td>
<td>84.92</td>
<td>124</td>
</tr>
<tr>
<td>(c-C_5H_9)_2R_3SiO_2(OSiCp&quot;Bz_3)</td>
<td>3.45, 2.12</td>
<td>9.6</td>
<td>86.83</td>
<td>127</td>
</tr>
<tr>
<td>SiPh_3OTiCp&quot;Bz_3</td>
<td>3.29, 2.37</td>
<td>10.1</td>
<td>86.10</td>
<td>125</td>
</tr>
</tbody>
</table>
5.4. Polymerization of 1-hexene and 4-methyl-1-pentene

Polymerization of 1-hexene and 4-methyl-1-pentene with the described titana-silsesquioxane alkyl complexes were performed under inert atmosphere (glove-box). The poor stability of monodentate siloxy systems toward substitution by aluminum alkyls forced us to use boron based activators instead of MAO or other aluminum based activators. Initially, experiments were carried out as described by Duchateau for \((c-C_5H_9)_7Si_7O_9(OTiCp''Bz_2)\) and \(SiPh_3OTiCp''Bz_2\). The titanium bis(benzyl) complexes \(5, 6\) and \(7\) (10 µmol, formed \textit{in situ} from \((c-C_5H_9)_7Si_7O_9(OSiMe_2O)(OH)\), and product 5.
(c-C_5H_9)_7Si_7O_9(OSiMe_2O)_2(OH) and (c-C_5H_9)_7Si_7O(OSiPh_2O)(OH) and Cp^+TiBz_3 in toluene-d_8) were activated with B(C_6F_5)_3 (40 µmol) and 1-hexene was polymerized in 24 hours in low yield (Table 3, type a). The somewhat more sterically demanding 4-methyl-1-pentene substrate was polymerized with B(C_6F_5)_3 in even lower yield (below 5%). All the obtained polymers were analyzed by NMR spectroscopy (end-group analysis from the 'H-NMR spectra) and gel permeation chromatography (GPC) and summarized in Table 3. From ^13^C-NMR spectra could be deduced that poly(1-hexene) and poly(4-methyl-1-pentene) were atactic. When the complexes were activated with [Ph_3C]^+[B(C_6F_5)_4] -, equimolar amounts were sufficient for activation and activity increased considerably (Table 3, type b) for both 1-hexene and 4-methyl-1-pentene polymerization. When SiPh_3OTiCp^+Bz_2 is activated with [CPh_3]^+[B(C_6F_5)_4] -, a somewhat higher activity than the investigated silsesquioxane titanium complexes is found, while the activity when activated with B(C_6F_5)_3 was much lower.

The silicate structure of the silsesquioxanes as well as the possibility of the additional siloxane ring of 5, 6 and 7 to effect the active species are of importance for the efficiency of the polymerization process. Particularly for the activated (c-C_5H_9)_7Si_6O_2 OTiCp^+Bz_2 and 7, polymerizations were observed to be strongly exothermic, suggesting a tempering influence on the rate of polymerization due to the siloxane ring present in complexes 5 and 6. Decided was to diminish the exotherm (to prevent a polymerization runaway) by cooling the 10 mL reaction vessel by placing it in a beaker filled with toluene. The exotherm (indicative for polymerization activity) was followed in time. In a typical experiment two reaction vessels were placed in a beaker filled with toluene (one containing a thermometer), one reaction vessel was quenched and worked up just after the maximum temperature was reached, the other reaction vessel was quenched and worked up after six hours (Table 3, type c and c'). This experiment was also performed for Cp^+TiBz_3 as a blank to exclude polymerization due to leached catalysts. Since the differences between the polymerization of 1-hexene and 4-methyl-1-pentene and the resulting polymer characteristics were small, only 1-hexene was examined in this experiment.

![Figure 3](image-url)

**Figure 3.** exotherm in time during 1-hexene polymerization of 5-7, (c-C_5H_9)_7Si_6O_2 OTiCp^+Bz_2, SiPh_3OTiCp^+Bz_2 and Cp^+TiBz_3 activated with [B(C_6F_5)_3][CPh_3]^+
Table 3. Polymerization of 1-hexene and 4-methyl-1-pentene (4M1P) with titano-silsesquioxanes 5-7, (c-C₅H₄)₂Si₆O₁₄OTiCp'Bz₂ and Ph₂SiOTiCp'Bz₂ activated with two different fluoro-aryl based activators.

<table>
<thead>
<tr>
<th>catalytic system</th>
<th>substrate</th>
<th>yield (g)</th>
<th>%</th>
<th>Mₙ d</th>
<th>Mₙ e</th>
<th>Mₚ e</th>
<th>Mₚ/Mₙ e</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 + B(C₄F₉)₅ a</td>
<td>1-hexene</td>
<td>1.39</td>
<td>(21)</td>
<td>24744</td>
<td>5912</td>
<td>13857</td>
<td>2.3</td>
</tr>
<tr>
<td>5 + [CPh₃]⁺ [B(C₄F₉)₄] b</td>
<td>1-hexene</td>
<td>4.75</td>
<td>(71)</td>
<td>4135</td>
<td>3483</td>
<td>8240</td>
<td>2.4</td>
</tr>
<tr>
<td>5 + B(C₄F₉)₅ a</td>
<td>4M1P</td>
<td>0.36</td>
<td>(5 )</td>
<td>45952</td>
<td>4666</td>
<td>9249</td>
<td>2.0</td>
</tr>
<tr>
<td>5 + [CPh₃]⁺ [B(C₄F₉)₄] b</td>
<td>4M1P</td>
<td>5.45</td>
<td>(82)</td>
<td>3094</td>
<td>2532</td>
<td>5646</td>
<td>2.2</td>
</tr>
<tr>
<td>6 + B(C₄F₉)₅ a</td>
<td>1-hexene</td>
<td>0.64</td>
<td>( 10)</td>
<td>7742</td>
<td>4428</td>
<td>10431</td>
<td>3.1</td>
</tr>
<tr>
<td>6 + [CPh₃]⁺ [B(C₄F₉)₄] b</td>
<td>1-hexene</td>
<td>5.75</td>
<td>( 86)</td>
<td>3208</td>
<td>2922</td>
<td>6804</td>
<td>2.3</td>
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<tr>
<td>6 + B(C₄F₉)₅ a</td>
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<td>0.09</td>
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<td>10940</td>
<td>3304</td>
<td>5885</td>
<td>1.8</td>
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<tr>
<td>6 + [CPh₃]⁺ [B(C₄F₉)₄] b</td>
<td>4M1P</td>
<td>5.57</td>
<td>( 84)</td>
<td>1740</td>
<td>1757</td>
<td>3789</td>
<td>2.2</td>
</tr>
<tr>
<td>7 + B(C₄F₉)₅ a</td>
<td>1-hexene</td>
<td>2.79</td>
<td>( 42)</td>
<td>2524</td>
<td>1265</td>
<td>2052</td>
<td>1.6</td>
</tr>
<tr>
<td>7 + [CPh₃]⁺ [B(C₄F₉)₄] b</td>
<td>1-hexene</td>
<td>4.64</td>
<td>( 70)</td>
<td>1737</td>
<td>1765</td>
<td>4809</td>
<td>2.7</td>
</tr>
<tr>
<td>7 + B(C₄F₉)₅ a</td>
<td>4M1P</td>
<td>0.23</td>
<td>( 3)</td>
<td>4544</td>
<td>3070</td>
<td>6229</td>
<td>2.0</td>
</tr>
<tr>
<td>7 + [CPh₃]⁺ [B(C₄F₉)₄] b</td>
<td>4M1P</td>
<td>4.99</td>
<td>( 75)</td>
<td>2953</td>
<td>2100</td>
<td>4500</td>
<td>2.143</td>
</tr>
</tbody>
</table>

R₂SiO₂OTiCp'Bz₂ + B(C₄F₉)₅ a | 1-hexene  | 0.53      | ( 8)| 5060 | 2820 | 9838 | 3.5     |

R₂SiO₂OTiCp'Bz₂ + [CPh₃]⁺ [B(C₄F₉)₄] b | 1-hexene  | 4.95      | ( 74)| 2457 | 2380 | 6310 | 2.7     |

R₂SiO₂OTiCp'Bz₂ + B(C₄F₉)₅ a | 4M1P      | 0.08      | ( 1)| 5554 | 2078 | 5899 | 2.8     |

R₂SiO₂OTiCp'Bz₂ + [CPh₃]⁺ [B(C₄F₉)₄] b | 4M1P      | 5.65      | ( 85)| 1753 | 1843 | 3924 | 2.1     |

Si₆O₂OTiCp'Bz₂ + B(C₄F₉)₅ a | 1-hexene  | 0.26      | ( 4)| 13634| 6316 | 12544| 2.0     |

Si₆O₂OTiCp'Bz₂ + [CPh₃]⁺ [B(C₄F₉)₄] b | 1-hexene  | 5.93      | ( 89)| 15568| 5908 | 11266| 1.9     |

Si₆O₂OTiCp'Bz₂ + B(C₄F₉)₅ a | 4M1P      | 0.12      | ( 2)| 8920 | 2528 | 5819 | 2.3     |

Si₆O₂OTiCp'Bz₂ + [CPh₃]⁺ [B(C₄F₉)₄] b | 4M1P      | 4.83      | ( 73)| 13466| 5080 | 9201 | 1.8     |

Cp'TiBz₂ + [B(C₄F₉)₄] a [CPh₃]⁺ b | 4.15      | (62)      |   | 3793 | 5485 | 22349| 2.0     |

a. 10 µmol catalyst, 40 µmol cocatalyst, reaction stopped after 24 hours, no cooling
b. 10 µmol catalyst, 11 µmol cocatalyst, reaction stopped after 24 hours, no cooling
c/d/ 10 µmol catalyst, 11 µmol cocatalyst, reaction followed in time over 6 hours, Mₙ and Mₚ determined just after maximal activity / temperature with and after 6 hours, moderate cooling by solvent buffer outside reaction vessel
d. Determined by endgroup analysis from ¹H-NMR-spectroscopy
e. Determined from GPC measurements
The yield of the polymers (over 90% in all cases) suggests that the maximum in the temperature curve is reached when almost all 1-hexene is consumed and thereafter the temperature decreases because of starvation. No deactivation of the catalysts could be observed. The catalytic performances of the tested metallo-silsesquioxanes and the characteristics of the isolated polymers are comparable to polymers obtained from homogeneous half-sandwich catalysts activated by perfluoroaryl boranes and borates and can not be fully related to heterogeneous single-site catalysts. However, results showed that silyl groups of the additional siloxane ring of 5, 6 and 7 in the proximity of the active center hampers the activation and/or polymerization process considerably. Initiation of the polymerization process for the unhindered \((\text{c-C}_5\text{H}_9)\text{Si}_6\text{O}_{12}\text{OTiCp"Bz}_2\) takes places after about 35 minutes, for 7 after 50 minutes and for 5 and 6 initiation takes place after two hours (Figure 3). The closed cage titanium-silsesquioxane \((\text{c-C}_5\text{H}_9)\text{R}_7\text{Si}_6\text{O}_{12}\text{OTiCp"Bz}_2\) is activated most readily (Figure 3), which is probably due to the lack of steric strain around the metal center. Activation of 7 with one -OSiPh_2O- moiety in the additional siloxane ring, is much easier than activation of 5 and 6 with respectively one or two -OSiMe_2O- moieties in the siloxane ring, which might well be due to a stabilizing effect of the phenyl ring with the cationic metal center. Distinguishing between steric and electronic effects of the siloxane ring on the activation rate was not possible at this point.

5.5. Spectroscopic investigation of cation formation.

After compounds 5, 6, 7 and \((\text{c-C}_5\text{H}_9)\text{R}_7\text{Si}_6\text{O}_{12}\text{OTiCp"Bz}_2\) were formed \textit{in situ} in toluene-\(d_8\), 1 equivalent of B(C_6F_5)_3 in toluene-\(d_8\) was added to the cooled solution (below 0 °C). The NMR-tubes, sealed with a Teflon tap, were stored in a container with liquid nitrogen before use. The formation of ionic species was followed in time at 25 °C by NMR spectroscopy; most informative were the \(^{19}\text{F-NMR}\) spectra. In all cases borane B(C_6F_5)_3 is not fully consumed due to an equilibrium between borane and borate (Scheme 3). For silsesquioxanes 5-7, conversion of titanium bisalkyl into cationic species reaches a maximum after a few minutes and stays more or less constant in time (Figure 4). The maximum conversion of B(C_6F_5)_3 observed when reacted to 5 is about 30%, when reacted to 6 about 15% and when reacted to 7 approximately 45%. This indicates that cation formation is easiest for 7, which possesses phenyl groups in the siloxane ring that might be capable of stabilizing the cationic metal center by \(\pi\)-interaction. Silsesquioxanes 5 and 6, possessing the much less sterically demanding -OSiMe_2O- groups in the proximity of the metal, are activated with more difficulty. Of these two, activation of 6 having the longer (flexible) siloxane ring is the most problematic. The conversion of unhindered \((\text{c-C}_5\text{H}_9)\text{Si}_6\text{O}_{12}\text{OTiCp"Bz}_2\) titanium bisalkyl, when exposed to the B(C_6F_5)_3 activator, into cationic species shows as was observed for 5-7 the largest consumption of B(C_6F_5)_3 in the first minutes (about 30% conversion after 30 minutes). But, where consumption of borane stayed more or less constant for 5, 6 and 7, the consumption of borane in the presence of \((\text{c-C}_5\text{H}_9)\text{Si}_6\text{O}_{12}\text{OTiCp"Bz}_2\) slowly continues to rise and reaches 55% conversion after a day (Figure 4).
Grafted Metal Complexes from Models for Partly Silylated Silica Surfaces

Figure 4. Conversion of $\text{B(C}_6\text{F}_5\text{)}_3$ (■) with 5, 6, 7, and (c-$\text{C}_5\text{H}_9$)$_7\text{Si}_7\text{O}_{12}(\text{OSiMe}_2\text{O})(\text{OTiCp}^+\text{Bz}_2)$ into solvent separated ion pairs (●), contact ion pairs (◆) and in the neutral $\text{C}_6\text{H}_5\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2$ and L-SiOTiCp$^+\text{Bz}(\text{C}_6\text{F}_5)$ (▲).
Chapter 5

The $^{19}$F-NMR spectra revealed for all four complexes two types of borates. From the difference in chemical shift between the peak positions of the $F_{\text{meta}}$ and $F_{\text{para}}$ of the aryl-fluorines could be concluded that both non-coordinating solvent separated ion pairs and coordinating contact ion pairs were formed (Table 4). From Figure 4 it can be deduced that while activating 5, 6 and (c-C$_5$H$_9$)$_7$Si$_8$O$_{12}$($\text{OTiCp'Bz}_2$), at first solvent separated ion pairs are formed and thereafter at a somewhat slower rate contact ion pairs. Activation of complex 5 seems to result simultaneously into formation of solvent separated and contact ion pairs. For 5 and 7, the ratio of formed solvent separated ion pairs slowly decreases after the sudden rise in the beginning until it reaches an almost constant level (for 5 from a maximum of 11% to 8%, for 7 from a maximum of 30% to 5%). For 6, conversion into the solvent separated ion pair slowly rises up to 10% after one hour, then decreases somewhat until it remains constant at 8%. Measurable formation the contact ion pair commences only after one hour and slowly reaches a constant ratio of about 3%. During the borate-formation process from reaction with 5-7 and borane, the concentration of the contact ion pairs increases with the same amount as the concentration of the solvent separated ion pairs decreases while the borane consumption is fairly unaffected. This suggests that contact ion pair formation proceeds via the solvent separated ion pairs (Scheme 3). For (c-C$_5$H$_9$)$_7$Si$_8$O$_{12}$($\text{OTiCp'Bz}_2$) the formation of solvent separated ion pairs abruptly rises in the beginning and very slowly decreases (from 20% to 13% in a day), independently from the slow increase of contact ion pair formation. Furthermore, uptake of borane continues slowly and thus both ion pairs seem to be formed directly from the borane.

Table 4. $^{19}$F-NMR data of the ion pairs resulting from reaction of 5, 6, 7 and (c-C$_5$H$_9$)$_7$R$_7$Si$_8$O$_{12}$($\text{OTiCp'Bz}_2$) with B(C$_6$F$_5$)$_3$.

<table>
<thead>
<tr>
<th>silsesquioxane</th>
<th>ion pair</th>
<th>$^{19}$F$_{\text{ortho}}$ (ppm)</th>
<th>$^{19}$F$_{\text{para}}$ (ppm)</th>
<th>$^{19}$F$_{\text{meta}}$ (ppm)</th>
<th>$\Delta\delta$-(F$_m$-F$_p$) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>[(c-C$_5$H$_9$)$_7$Si$<em>8$O$</em>{12}$($\text{OSiMe}_2$O)OTiCp'Bz]$^+$ / B(C$_6$F$_5$)$_3$] - solvent separated</td>
<td>-53.23</td>
<td>-87.64</td>
<td>-90.28</td>
<td>2.64</td>
</tr>
<tr>
<td>5</td>
<td>[(c-C$_5$H$_9$)$_7$Si$<em>8$O$</em>{12}$($\text{OSiMe}_2$O)OTiCp'Bz]$^+$ / B(C$_6$F$_5$)$_3$] - coordinated</td>
<td>-53.23</td>
<td>-84.00</td>
<td>-88.15</td>
<td>4.15</td>
</tr>
<tr>
<td>6</td>
<td>[(c-C$<em>6$H$</em>{11}$)$_7$Si$<em>8$O$</em>{12}$($\text{OSiMe}_2$O)OTiCp'Bz]$^+$ / B(C$_6$F$_5$)$_3$] - solvent separated</td>
<td>-53.35</td>
<td>-87.65</td>
<td>-90.22</td>
<td>2.57</td>
</tr>
<tr>
<td>6</td>
<td>[(c-C$<em>6$H$</em>{11}$)$_7$Si$<em>8$O$</em>{12}$($\text{OSiMe}_2$O)OTiCp'Bz]$^+$ / B(C$_6$F$_5$)$_3$] - coordinated</td>
<td>-53.35</td>
<td>-83.81</td>
<td>-87.99</td>
<td>4.18</td>
</tr>
<tr>
<td>7</td>
<td>[(c-C$_5$H$_9$)$_7$Si$<em>8$O$</em>{12}$($\text{OSiPh}_2$O)OTiCp'Bz]$^+$ / B(C$_6$F$_5$)$_3$] - solvent separated</td>
<td>-53.30</td>
<td>-87.62</td>
<td>-90.35</td>
<td>2.73</td>
</tr>
<tr>
<td>7</td>
<td>[(c-C$_5$H$_9$)$_7$Si$<em>8$O$</em>{12}$($\text{OSiPh}_2$O)OTiCp'Bz]$^+$ / B(C$_6$F$_5$)$_3$] - coordinated</td>
<td>-53.30</td>
<td>-84.03</td>
<td>-88.08</td>
<td>4.05</td>
</tr>
<tr>
<td>(c-C$_5$H$_9$)$_7$R$_7$Si$<em>8$O$</em>{12}$ ($\text{OTiCp'Bz}_2$)</td>
<td>[(c-C$_5$H$_9$)$_7$R$_7$Si$<em>8$O$</em>{12}$($\text{OTiCp'Bz}_2$)]$^+$ / B(C$_6$F$_5$)$_3$] - solvent separated</td>
<td>-53.41</td>
<td>-87.40</td>
<td>-90.19</td>
<td>2.79</td>
</tr>
<tr>
<td>(c-C$_5$H$_9$)$_7$R$_7$Si$<em>8$O$</em>{12}$ ($\text{OTiCp'Bz}_2$)</td>
<td>[(c-C$_5$H$_9$)$_7$R$_7$Si$<em>8$O$</em>{12}$($\text{OTiCp'Bz}_2$)]$^+$ / B(C$_6$F$_5$)$_3$] - coordinated</td>
<td>-53.41</td>
<td>-84.04</td>
<td>-88.15</td>
<td>4.11</td>
</tr>
</tbody>
</table>
For all four investigated compounds $^{19}$F-NMR spectra also showed the slow appearance of resonances characteristic for neutral fluorinated aryl-species. The most likely explanation is that aryl-scrambling between the borate and the titanium complex caused the formation of deactivated PhCH$_2$B(C$_6$F$_5$)$_2$ and L-SiOTiCp'Bz(C$_6$F$_5$) (Scheme 3). The peak positions found in the $^{19}$F spectra correspond with the values found for alkyl-exchange observed by Qian and Ward. For 5-7, this aryl-scrambling increases very slowly in time. This process is the most significant for 5 (up to 5% aryl-scrambling) and is nearly neglectable for 6 and 7. For (c-C$_5$H$_9$)$_7$Si$_8$O$_{12}$(OTiCp'Bz)$_2$, at first the concentration of formed aryl-scrambling products increases slowly but after a few hours the ratio increases substantially up to a concentration of 20% after a day and rising. The amount of cationic species formed from 5-7, the consumption of borane and the in low rate formed inactive PhCH$_2$B(C$_6$F$_5$)$_2$ and L-SiOTiCp'Bz(C$_6$F$_5$) stays almost constant as from an hour. For a prolonged period of time for 5-7, this equilibrium of co-existing boranes (i.e. B(C$_6$F$_5$)$_3$ and PhCH$_2$B(C$_6$F$_5$)$_2$) and borates (i.e. contact and solvent separated ion pairs) appears to be stable. On the other hand, for (c-C$_5$H$_9$)$_7$Si$_8$O$_{12}$(OTiCp'Bz)$_2$, the equilibrium of co-existing boranes and ion pairs is not stable and ends most likely solely in deactivated boranes. Apparently, the -OSiR$_2$O- unit(s) of 5-7 in the proximity of the cationic metal center stabilize the ion pairs after a state of equilibrium is reached.

Scheme 3: formation of solvent separated and contact ion pairs of titanium silsesquioxanes with B(C$_6$F$_5$)$_3$ and degeneration process (alkyl scrambling)
The formation of the active species with the other fluoroaryl activator used in our studies, $\text{[Ph}_3\text{C]}^+ [\text{B(C}_6\text{F}_5)_4]^-$, was also subject of spectroscopic investigation. Compounds 5-7 and $(\text{c-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}^- (\text{OTiCp}^\text{Bz}_2)$ were formed in situ in bromobenzene-$d_5$ and 1 equivalent of $\text{[Ph}_3\text{C]}^+ [\text{B(C}_6\text{F}_5)_4]^-$ was added to the cooled solution. In this case $^{19}\text{F}$-NMR could not give much information since the activation process is an irreversible reaction and the nature of the anion $\text{[B(C}_6\text{F}_5)_4]^-$ is not affected. $^1\text{H}$-NMR showed in all cases immediate disappearance of the AB pattern coming from the diastereotopic CH$_2$ of the starting compounds. Instead, peaks indicative for $\text{Ti(CH}_2\text{C}_6\text{H}_5)$ (two broad peaks around 3.9 ppm and 2.2 ppm) and $\text{CPh}_3(\text{CH}_2\text{C}_6\text{H}_5)$ (3.8 ppm) were observed. In time, no significant changes in $^{19}\text{F}$- or $^1\text{H}$-NMR indicating degeneration of the ionic species were found. However, in spite of instantaneous ion exchange, maximum activity for the polymerization of 1-hexene could only be observed after initiation times up to two hours (Figure 3 in paragraph 5.4). Apparently, the siloxy units complicate the substrate to coordinate to the active center and start the polymerization reaction. Once this barrier is taken, polymerization proceeds until all monomer has been consumed.

5.6. Concluding remarks

Substitution reactions of the silanol with the metal-precursors $\text{GaMe}_3$ and $\text{Ti}[\text{t}-\text{C}_5\text{H}_3(\text{SiMe}_3)_2]\text{Bz}_3$ ($\text{TiCp}^\text{Bz}_3$) in a 1 to 1 ratio, afforded dimeric [L-OGaMe$_2$]; and monomeric L-OTiCp$^\text{Bz}_2$. The Lewis acidity of OGaMe$_2$ and the tendency to form stable tetrahedrally surrounded gallium complexes was found to be stronger than the weak donating abilities of the siloxane ring. The monomeric titanium halfsandwich precursors provided soluble models for silica-grafted catalysts with neighboring surface siloxy oxygens. Olefin polymerization with a borane activator showed considerable lower initial activities in comparison with the analogue without an additional siloxane ring, $(\text{c-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}(\text{OTiCp}^\text{Bz}_2)$. Spectroscopic investigation of activation with $\text{B(C}_6\text{F}_5)_3$ in time showed an equilibrium of co-existing solvent separated- and contact ion pairs, borane starting material and deactivated borane. The apparent stabilizing effect of the –OSiR$^2$O- containing titanium silsesquioxanes causes after some time an equilibrium state which appears to be stable. On the other hand, this co-existing equilibrium of boranes and borates is not stable for the unperturbed $(\text{c-C}_5\text{H}_9)_7\text{Si}_8\text{O}_{12}(\text{OTiCp}^\text{Bz}_2)$ and ends most likely solely with deactivated boranes. Changing the methyl-substituents of the siloxane rings for phenyls facilitated formation of the active species. From the exotherm in time of the polymerization of 1-hexene with $\text{[Ph}_3\text{C]}^+ [\text{B(C}_6\text{F}_5)_4]^-$ as activator could be concluded that initiation for catalysts possessing –OSiR$^2$O- units can take up to 2 hours. Because spectroscopic investigation of the ion formation indicated an instantaneous ion exchange resulting in activated species, suggested was that the siloxy units complicate the substrate to coordinate to the active center and start the polymerization reaction. At this point can be concluded that silyl groups in the proximity of the active center have a stabilizing effect on the active species and influence the activation and polymerization process considerably but distinguishing between steric and electronic effects is not possible.
5.7. Experimental Section

General Remarks: Reactions were performed under an argon atmosphere using Schlenk techniques when necessary. Solvents were distilled from K (THF), Na/K alloy (hexanes, toluene, C6D6) and benzophenon (Et2O) or dried over 4 Å molecular sieves (NEt3, CCl4, CDCl3, toluene-d8, BrC6D6) and stored under argon. 1H- and 13C-NMR spectra were recorded on Varian Mercury 400 spectrometers (25°C, 1H NMR: 400 MHz, 13C NMR: 100.6 MHz). 29Si- and 19F-NMR spectra were recorded on a Varian Indigo 500 spectrometer (25°C, 29Si NMR: 99.3 MHz, 19F NMR: 470.4 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (1H, 13C NMR) or external standards (29Si: SiMe4 = 0 ppm, 19F: CF3COOH = 0 ppm). Elemental analyses were carried out at the Analytical Department of the University of Groningen (compounds 1-4); quoted data are the average of at least two independent measurements. Starting materials: Silsesquioxane starting materials R2Si/3O6(OH)37 (R = c-C3H7, c-C5H11) and (c-C3H7)3SiOc2(OH)38, were prepared following referred literature procedures. The synthesis of the other silsesquioxane starting compounds, (c-C3H7)2Si-O3(OSiMe2O)(OH), (c-C3H7)3SiO(OSiH2O)(OH), (c-C3H7)3Si-O3(OSiMe2O2)(OH) and (c-C3H7)3SiO2(OSiMe2O2)(OH) are described in Chapter 3 of this thesis. TiCp2(CH2Ph)2, B(C6F5)340 and [B(C6F5)3][Ph2C]41 were synthesized according to published procedures. MALDI-TOF Analyses: MALDI-TOF spectra of compounds 1-4 were recorded at the Department of Polymer Chemistry Eindhoven with a Voyager STR Spectrometer of Applied Biosystems. Samples were recorded in reflector mode with matrix trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile and Sodium as cation. Samples were prepared as follow: 25 µg/ml Sodiumtrifluoroacetate + 25 µl on target. GPC Analyses: The molecular weights, number average molecular weights and molecular weight distributions of the 1-hexene and 4-methyl-1-pentene polymers were measured by gel permeation chromatography (GPC) at the Department of Polymer Chemistry, Eindhoven. GPC was carried out using a WATERS Model 510 pump, Model 486 UV detector (at 254 nm), and Model 410 refractive index detector (at 40°C). Injections were done by a WATERS Model WISP 712 autoinjector, injection volume used was 50 µL. The Polymer Laboratories columns used were: gel guard (5µm particles) 50*7.5 mm guard column, followed by 2 gel mixed-C (5µm particles) 300*7.5 mm columns (40°C) in series, referred to as the standard column set. Tetrahydrofuran (Bisolve, stabilised with BHT) was used as eluent at a flow rate of 1.0 ml/min. Calibration has been done using polystyrene standards (Polymer Laboratories, M = 580 to M = 7.1*105). Data acquisition and processing were performed using WATERS Millennium32 (v3.2) software. Samples are filtered over a 13 mm * 0.2 µm PTFE filter, PP housing (Alltech) .

\[[(c-C3H7)2SiOc2(OGaMe3)]_2\] (1). A solution of 1.59 g (c-C3H7)2SiOc2(OH) (1.73 mmol) in 30 mL of toluene was cooled to -40 °C. To this cooled solution 4.44 g of GaMe3 in toluene was added (0.39 mmol GaMe3 / g toluene; 1.73 mmol) and the mixture was allowed to warm to room temperature. Then, the mixture was stirred vigorously and heated to reflux until all CH3Si was visibly removed, to complete the reaction the mixture was subsequently stirred for two hours at 60 °C. The product was observed to be less soluble in toluene than the starting materials. The mixture was pumped to dryness and by adding hexanes (5 mL) and subsequent evaporating the volatiles, final traces of toluene were removed. The dry residue could be isolated in almost quantitative yield (1.71 g, 0.84 mmol, 97%). A sample suitable for elemental analysis was obtained by dissolving 1 in hot methylcyclohexane (30 mL) and slow cooling to room temperature. 1H NMR (400 MHz, CDCl3, 25 °C): δ = 0.31 (s, 12H, Ga-C(Ph)), 1.18 (m, 14H, CH2-C(Ph)), 1.47 (m, 28H, CH2-C3H7), 1.67 (m, 56H, CH2-C3H7), 1.90 (m, 28H, CH2-C3H7). 13C NMR (100.6 MHz, CDCl3, 25 °C): δ = -3.52 (Ga(Ph)), 22.84; 22.88 (14 · CH-C3H7, ratio 3:4), 27.69; 28.03 (14 · CH-C3H7). 29Si NMR (99.8 MHz, CDCl3, 25 °C): δ = 103.07 (2 · O3SiOGaMe3), -66.54; -66.50; -65.99 (14 · O3SiC3H7, ratio 3:1:3). MALDITOF (Na+): m/z (%) = 939(3), 1039(2). Elemental analysis calcd (%) for C4H13Ga2O2Si8: C 43.74, H 6.84; found C 43.35, H 6.84.
(c-C₅H₅)₃Si=O(SiMe₂O)(OGaMe₂)₂ (2). Using the same procedure as for 1 with the exception that a longer reaction time was allowed (16 hours stirring at 60 °C instead of 2 hours), (c-C₅H₅)₃Si=O(SiMe₂O)(OH) was reacted with GaMe₃. Compound 2 could be isolated in almost quantitative yield (98%). A sample suitable for elemental analysis was obtained by dissolving 2 in hot methycyclohexane and slow cooling to room temperature. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 0.36 (s, 6H, CH₃-Si), 0.38 (s, 12H, GaCH₃), 0.53 (s, 6H, CH₃-Si), 1.21 (m, 14H, CH₂-C₅H₅), 1.48 (m, 28H, CH₂-C₅H₅), 1.70 (m, 56H, CH₂-C₅H₅), 2.01 (m, 28H, CH₂-C₅H₅). ¹³C NMR (100.6 MHz, C₆D₆, 25 °C): δ = 2.49 (Ga(CH₃)₂), 0.87; 1.28 (Si(CH₃)₂) 22.95; 23.13; 23.51; 23.76; 25.56 (14 · CH₂-C₅H₅, ratio 1:1:2:2), 27.28; 27.48; 28.10; 28.51 (14 · CH₂-C₅H₅). ²⁰Si NMR (99.8 MHz, C₆D₆, 25 °C): δ = -67.28; -65.99; -64.61; -64.38 (12 · O₂Si(CH₃), ratio 2:2:1:1), -59.47 (2 · Si-OGaMe₂), -17.32 (2 · O₂SiMe₂). MALDITOF (Na⁺): m/z (%) = 1078(5), 1177(5). Elemental analysis calcd (%) for C₇₀H₁₅₀Ga₂O₆Si₁₀ (2060.85): C 45.46, H 7.34; found C 45.54, H 7.40.

[[c-C₅H₅]₃Si=O(OSiPh₂O)(OGaMe₂)]₂ (3). Using the same procedure as for 1, reaction of (c-C₅H₅)₃Si=O(OSiPh₂O)(OH) with GaMe₃ afforded compound 3 in almost quantitative yield (97%). Suitable crystals for diffraction were obtained by dissolving 3 in hot methycyclohexane (30 mL) and slow cooling to −10 °C. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 0.28 (s, 12H, GaCH₃), 1.08 (m, 14H, CH₂-C₅H₅), 1.60 (m, 84H, CH₂-C₅H₅), 1.92 (m, 28H, CH₂-C₅H₅), 7.18 (m, 4H, p-CH₂-C₅H₅), 7.42 (m, 8H, m-CH₂-C₅H₅), 7.83 (d, 4H, o-CH₂-C₅H₅), 8.03 (d, 4H, o-CH₂-C₅H₅). ¹³C NMR (100.6 MHz, C₆D₆, 25 °C): δ = -2.85 (Ga(CH₃)₂), 23.06; 23.20; 23.67; 23.82; 25.14 (14 · CH₂-C₅H₅, ratio 1:1:2:2), 27.39; 27.98; 28.49 (CH₂-C₅H₅), 127.85 (m-CH₂-C₅H₅), 127.93 (m-CH₂-C₅H₅), 134.74 (p-CH₂-C₅H₅), 135.08 (p-CH₂-C₅H₅), 148.37 (o-CH₂-C₅H₅), 149.66 (o-CH₂-C₅H₅), 152.55 (C-CH₅). ²⁰Si NMR (99.8 MHz, C₆D₆, 25 °C): δ = -66.65; -69.44; -64.11; -63.87 (12 · O₂Si(CH₃), ratio 2:2:1:1), -59.07 (Si-OGaMe₂), -44.23 (O₂SiPh₂). MALDITOF (Na⁺): m/z (%) = 939(3), 1039(2). Elemental analysis calcd (%) for C₆₀H₁₀₆Ga₂O₆Si₁₀ (2309.13): C 50.97, H 6.90; found C 50.39, H 6.90.

[[c-C₅H₅]₃Si=O(O(SiMe₂O)₉)(GaMe₂)]₂ (4). Using the same procedure as for 1, reaction of (c-C₅H₅)₃Si=O(O(SiMe₂O)₉)(OH) with GaMe₃ resulted in compound 4 in almost quantitative yield (98%). A sample suitable for elemental analysis was obtained by dissolving 4 in hot methycyclohexane (30 mL) and slow cooling to −30 °C. ¹H NMR (500 MHz, C₆D₆, 50 °C): δ = 0.19-0.38 (m, 48H, CH₂-Si), 0.19-0.38 (s, 12H, GaCH₃), 1.01 (m, 14H, CH₂-C₅H₅), 1.30 (m, 28H, CH₂-C₅H₅), 1.68 (m, 56H, CH₂-C₅H₅), 2.12 (m, 28H, CH₂-C₅H₅). ¹³C NMR (125 MHz, C₆D₆, 50 °C): δ = 0.56 (Ga(CH₃)₂), 1.17-1.49 (Si(CH₃)₂), 23.85; 24.70; 24.78; 25.55; 25.70 (14 · CH₂-C₅H₅, ratio 1:2:1:2), 27.24-28.34 (CH₂-C₅H₅). ²⁰Si NMR (99.8 MHz, C₆D₆, 50 °C): δ = -70.39; -69.53; -68.27; -67.77 (12 · O₂Si(CH₃), ratio 2:1:2:1), -60.26 (Si-OGaMe₂), -20.92; -20.08 (O₂SiMe₂). MALDITOF (Na⁺): m/z (%) = 1274(6), 1373(5). Elemental analysis calcd (%) for C₆₀H₁₀₆Ga₂O₆Si₁₀ (2702.16): C 46.23, H 7.98; found C 46.06, H 8.05.

(c-C₅H₅)₃Si=O(SiMe₂O)OTiCp⁺(CH₃Ph₂) (5). To a solution of TiCp⁺(CH₃Ph₂) (0.024 g, 45 µmol) in 0.5 mL of C₆D₆, 1.1 equivalent of a solution of (c-C₅H₅)₃Si=O(SiMe₂O)(OH) (0.503 g, 50 µmol) in 0.5 mL of C₆D₆ was added at room temperature. After two days at room temperature, NMR indicated that product 5 was formed quantitatively. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ = 0.19 (s, 3H, OSi(CH₃)O), 0.27 (s, 18H, Si(CH₃)₂), 0.33 (s, 3H, OSi(CH₃)O), 1.21 (m, 7H, CH₂-C₅H₅), 1.52 (m, 14H, CH₂-C₅H₅), 1.69 (m, 28H, CH₂-C₅H₅), 1.93 (m, 14H, CH₂-C₅H₅), 2.46 (d, 2H, CH₂Ph, 1JHH = 9.9 Hz), 3.30 (d, 2H, CH₂Ph, 1JHH = 9.9 Hz), 5.06 (m, 2H, CH₂C₅H₅), 6.09 (m, 2H, p-CH₂-C₅H₅), 6.97 (m, 1H, C₅H₅(SiMe₂O)), 7.22 (s, 4H, o-CH₃), 7.23 (s, 4H, m-CH₃). ¹³C [¹H] NMR (100.6 MHz, C₆D₆, 25 °C): δ = 1.04 (Si(CH₃)₂, 0.69 (OSi(CH₃)O), 1.38 (OSi(CH₃)O), 23.07; 23.81; 24.00; 25.58 (7 · CH₂-C₅H₅, ratio 2:2:1:1), 27.40; 28.15 (CH₂-C₅H₅), 85.42 (CH₂Ph, 1JHH = 125 Hz), 122.82; 125.69; 127.49; 128.51 (C₅H₅), 131.24 (C₅H₅(SiMe₂O)), 133.95 (C₅H₅(SiMe₂O)), 137.82 (p-CH₃-C₅H₅), 150.01 (C₅H₅(SiMe₂O)). ²⁰Si NMR (99.8 MHz, C₆D₆, 25 °C): δ = -66.92; -66.45; -65.28; -64.08; -64.00 (O₂Si(CH₃), ratio 2:1:2:1:1), -16.43 (OSi(CH₃)O), -6.89 (2 Si(CH₃)₂).

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(c-C6H11)3SiO2(O(SiMe3)2)OTiCp′′(CH2Ph)2 (6). To a solution of TiCp′′(CH2Ph)2 (0.024 g, 0.045 µmol) in 0.5 mL of C6D6, 1.1 equivalent of a solution of (c-C6H11)3SiO2(O(SiMe3)2)OH (0.045 g, 0.045 µmol) in 0.5 mL of C6D6 was added at room temperature. After two days at room temperature, NMR showed that product 6 was formed quantitatively. 1H NMR (400 MHz, C6D6, 25 °C): δ = 0.20 (s, 6H, Si(CH3)2), 1.03 (m, 7H, CH2-C6H5), 1.27 (m, 28H, CH2-C6H11), 1.65 (m, 42H, CH2-C6H11), 2.39 (d, 2H, CH2Ph, JHH = 9.9 Hz), 3.46 (d, 2H, CH2Ph, JHH = 9.9 Hz), 6.56 (m, 2H, CH2(SiMe3)), 6.91 (m, 2H, δC-H), 7.06 (m, 1H, CH2(SiMe3)), 7.25 (s, 1H, CH2(C6H5)), 7.26 (s, 1H, CH2(C6H5)). 13C{1H} NMR (100.6 MHz, C6D6, 25 °C): δ = 27.33 – 28.87 (7 · 2C, OSi(C6H5)), 85.76 (CH2(C6H5), Jcd = 125 Hz), 122.82 (C6H5), 125.38 (C6H5), 125.61 (C6H5), 128.29 (C6H5), 133.02 (C6H5(SiCH3)), 133.84 (C6H5(SiCH3)), 137.82 (ipso-C6H5), 149.96 (C6H5(SiCH3)). 29Si NMR (99.8 MHz, C6D6, 25 °C): δ = -69.57, -69.17, -68.99, -68.45, -66.86 (O3SiXC6H5, ratio 2:2:1:1:1), -70.31 (2 OSi(CH3)2O, -6.87 (2 Si(CH3)3).

X-ray crystal structure analyses of 3: A suitable crystal measuring (0.20 × 0.20 × 0.20 mm) was selected, mounted on a thin, glass fiber using paraffin oil and cooled to the data collection temperature (203 K). Data were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ω. Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied. Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group. The structure was solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F2. A methylcyclohexane molecule was cocrystallized in the asymmetric unit. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in the SHELXTL 6.12 program library.
Table 5. Crystal data and structure refinement for \([c-C_{5}H_{9}]_{7}Si_{7}O_{9}(OSiPh_{2}O)-OGaMe_{2}\) (3).

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Special Acknowledgements

Glenn P. A. Yap (Chemistry Department, University of Ottawa, Canada) is kindly acknowledged for solving the crystal structure of \([c-C_{5}H_{9}]_{7}Si_{7}O_{9}(OSiPh_{2}O)-OGaMe_{2}\) (3). Wieb J. Kingma (Polymer Department of Chemistry, University of Eindhoven) is given thanks to for analyzing the poly(1-hexene) and poly(4-methyl-1-pentene) samples. Marion A. van Straten (Polymer Department of Chemistry, University of Eindhoven) is kindly acknowledged for performing MALDI-TOF analyses on the prepared gallium complexes 1-4.

References and notes

Silsesquioxane Tin compounds; Models for Heterogenous Oxidation Catalysts

Tin incorporated in zeolite frameworks shows excellent chemoselective catalytic activity in oxidation reactions with hydrogen peroxide. In this Chapter, the proposed active tin species, being an isolated tetra-siloxy tin species embedded in the zeolite framework, is attempted to be mimicked by tin containing silsesquioxanes. Incompletely condensed silsesquioxanes \( R_7Si_7O_9(OH)_{3} \) and \( R_7Si_7O_9(OSiMe_3)(OH)_2 \) were reacted with common tin-precursors such as \( SnCl_4 \), \( Sn(N(SiMe_3)_2)_2 \), \( Cl_2Sn(acac)_2 \) and \( [Cl_3SnOEt.EtOH]_2 \) which afforded several silsesquioxane tin compounds with tin being in oxidation state II or IV. Tin (IV) tends to form clusters to fill its coordination environment. A unique trimeric cluster stabilized by bridging hydroxyl groups was formed when the product of reaction of \( R_7Si_7O_9(OH)_{3} \) and \( SnCl_4 \) was slowly hydrolyzed. Some of the prepared tin compounds were tested as catalysts in oxidation reactions such as Baeyer-Villiger, Meerwein-Pondorf-Verley-Oppenauer and epoxidation reactions.

6.1. Introduction

Organotin compounds show interesting reactivity for a wide range of applications.\(^1\) Tri-organotin species \( R_3SnX \) are biologically active, with careful choice of \( R \) group (with respect to toxicity) they are successfully used in for instance anti-fouling paints for marine transport vessels.\(^2\) Tri- and di-organotin compounds have been successfully tested for their in vitro activity against tumors.\(^3\) In organic chemistry organotin compounds are widely used as reagents or catalysts in organic reactions. In a recent review by Chandrasekhar, several non-silsesquioxane tri-, di- and mono-organotin derivatives are described.\(^4\) A review on cyclo-stannasiloxanes of different ring size and their potential in ring-opening polymerization reactions compared to related heterocycles is presented by Beckmann and Jurkschat.\(^5\) Ring-opening polymerization of cyclic (di)esters, such as \( \varepsilon \)-caprolactone or lactide are initiated by tin chlorides and tin alkoxides.\(^6,7\) Organotin-oxometalate coordination polymers have been reported as catalysts for the epoxidation of olefins\(^8\) which mimic mixed metal oxides like \( SnO_2 \)-supported molybdenum oxides, catalyzing the oxidation of small alcohols.\(^9,10\) Some simple silsesquioxane tin compounds have been described by Feher and Edelmann and their coworkers. Feher reacted the incompletely condensed silsesquioxanes \( R_7Si_7O_9(OH)_{3} \) (\( R = c-C_6H_{13}, \, c-C_7H_{13} \), c-C\(_7\)H\(_{15}\)) with methyltrichlorostannane (MeSnCl\(_3\)) in the presence of NEt\(_3\) and isolated corner-capped tri-siloxy-mono-alkyl tin complexes \( R_7Si_7O_9(O_2SnCH_3)_3 \).\(^11\) In order to obtain structural evidence for the octameric \( (c-C_6H_{13})_8SnO_{11}(OH)_{2} \) with exo oriented silanols, the silanols were converted into Si-O-SnPh\(_3\).\(^12\)
More recently Edelmann reacted the monosilylated \((c-C_6H_{11})_7SiO_9(OSiMe_3)(OH)_2\) and the disilylated \((c-C_6H_{11})_7SiO_9(OSiMe_3)_2(OH)\) with respectively \(Cl_2SnR_2\) \((R = Me, n-Bu)\) and \(Cl_3SnR\) \((R = Me, CH_2Ph)\) in the presence of amine and isolated the corresponding di-siloxy-di-alkyltin and mono-siloxy-tri-alkyltin complexes.\(^{13}\) So far no catalytic experiments were performed with silsesquioxane tin complexes.

The role of organotin compounds applied as efficient modifiers in heterogeneous catalysis has been modeled by the surface organometallic chemistry approach by the group of Basset.\(^{14}\) At room temperature tetra-alkyl tin is physisorbed via hydrogen bonding of the alkyls with surface silanol groups.\(^{15}\) Above 100 °C tetra-alkyl tin reacts with silanols of partially dehydroxylated silica into Si-O-SnR\(_3\) or \((\text{Si-O})_x\text{SnR}_{4-x}\) \((x = 2, 3)\) depending on the nature of the support, at even higher temperatures consecutive reactions were observed.\(^{16}\) When this type of reaction takes place at the surface of zeolite pores, the diameter and thus the shape-selective properties of the pores can be altered.\(^{17,18}\) A molecular model of \((\text{Si=O})\text{SnBu}_2\) surface species has been reported in which dibutyl dichloride tin reacts with tri-silanol silsesquioxane.\(^{19,20}\) Tin incorporated silicalites were investigated as catalysts in oxidation reactions and found to be active for the hydroxylation of phenol in dilute \(H_2O_2\) as oxidant.\(^{21,22}\) Sn-ZSM-12 and Sn-Al-\(\beta\) catalyze the oxidation of various substituted aryls with moderate selectivity and \(H_2O_2\) selectivities\(^{23,24}\) supposedly due to the presence of isolated Sn\(^{4+}\) ions located within the channels of the molecular sieves.\(^{25}\) For tin incorporated in aluminum free zeolites-\(\beta\) an unexpected high activity and selectivity was found for the catalytic Baeyer-Villiger oxidation of cyclic ketons into the corresponding lacton (diluted \(H_2O_2\) as oxidant), when compared to titanium or aluminum incorporated in zeolite-\(\beta\).\(^{26,27}\) Also Sn-exchanged hydrotalcite proved to be an active and selective catalysts for the liquid phase Baeyer-Villiger oxidation of cyclic ketones using \(H_2O_2\) as oxidant.\(^{28}\) Oppenauer oxidation of alcohols by ketones and the opposite reaction, i.e. the reduction of carbonyl compounds by alcohols (the Meerwein-Pondorf-Verley reaction), could be catalyzed by aluminum free Sn-\(\beta\) as well. The stronger Lewis acidity compared to Ti-\(\beta\) without residual Bronsted acidity as it is the case for Al-\(\beta\), allows Sn-\(\beta\) to perform at low ratios alcohol/ketone and gives higher activity and selectivity than either Ti-\(\beta\) or Al-\(\beta\).\(^{29,30}\) The proposed active species in these oxidation reactions are tetrahedrally coordinated tin species within the framework (Figure 1), as could be deduced from \(^{119}\text{Sn}\) MAS NMR\(^{29}\) and \(^{18}\text{O}\)-labeling experiments.\(^{27}\) We were interested whether a silsesquioxane model compound of the proposed active species (Figure 1) would possess the same Lewis acidic properties as observed for Sn-\(\beta\), thus manifesting comparable activity and selectivity in oxidation reactions and confirming the proposed active species.

![Figure 1. Tetrahedrally surrounded Sn(IV) incorporated within a zeolite framework as suggested active species in catalytic oxidation (left) and possible silsesquioxane structures that can mimic this (right).](image-url)
Titanium-silicate-1 (TS-1) is industrially applied as catalyst in (ep)oxidation reactions. Approaches to mimic the active site of these species by silsesquioxanes model systems proved to be successful. The discovery of titanium-containing crystalline silicates in 1983, which showed remarkable activity as Lewis acid catalysts of selective oxidation reactions with H₂O₂, was considered as a breakthrough in this field. Many papers on this subject have been published since which considered the precise aggregation and coordination of the active Ti IV species in titanium-silicates and the search for (heterogeneous) systems with similar catalytic properties. A general consensus is that the most active and selective sites are isolated, mononuclear, 4-coordinate Ti(IV) centers located in the hydrophobic pores of silicate and are grafted tripodally to the silica-surface. The postulation of titanium sites possessing tripodal geometry to be the active site in epoxidation catalysis could be successfully tested by preparation of soluble analogues based on silsesquioxanes. The activity of a number of titanium compounds with different denticity based on (partly silylated) incompletely condensed silsesquioxanes R₃Si₃O₃(OH)₃ (R = c-C₃H₉, c-C₆H₁₃, c-C₇H₁₃) has been reported by Abbenhuis et al., Maschmeijer et al., and Crocker et al. (summarized in Figure 2). Concluded was that tripodal bonded titanium complexes are the most active catalysts in epoxidation of alkenes with alkyl hydroperoxides as oxidant. Found was that steric crowding around the Ti IV center or, when possible, formation of Lewis base adducts of the Ti IV species influences the activity in a negative sense. In aqueous media, the bidentate bonded titanium complexes are easily hydrolyzed which makes these catalysts unsuitable in catalytic oxidation reactions. On the contrary, tripodal titanium complexes were suitable for epoxidation of alkenes in aqueous media and when a hydrophobic pore was simulated by grafting the catalyst on 3D netted polysiloxanes, hydrogen peroxide could be successfully used as oxidant instead of the usual alkyl peroxide.

**Figure 2.** Synthesis of tridentate (A), bidentate (B) and monodentate (C) titanium silsesquioxane complexes, dimerization (A: slow, B: fast) is dependent on bulkiness of L.
In an attempt to mimic the suggested active tin species incorporated in a zeolite framework, this chapter will describe efforts to synthesize silsesquioxane tin compounds where tin is tetrahedrally surrounded by oxygens (Figure 1). Testing the catalytic abilities towards oxidation reactions of the model systems could verify the proposed active species in heterogeneous catalysis.

6.2. Synthesis and identification of various tin-oxo species

The dimeric product \([ (c-C_5H_9)_7Si_7O_7(OSiMe_3)O_2Sn]_2 \) (1) resulting from the reaction of \((c-C_5H_9)_7Si_7O_7(OSiMe_3)(OH)_2 \) with 1 equivalent of Sn(N(SiMe_3)_2)_2 (Scheme 1) could be identified crystallographically (Figure 6, Table 1 in Section 6.3). Evaporation of the hexanes mother liquor only resulted in the condensed decomposition product \((c-C_5H_9)_6O_9Si_6 \), detected by NMR spectroscopy. Suggested is that the dimeric structure \([ (c-C_5H_9)_7Si_7O_7(OSiMe_3)O_2Sn]_2 \) immediately converts to a condensed decomposition product when traces of moisture are present (Scheme 1). The observed instability of the Sn(II) complex held us back to convert the Sn(II) dimeric complex by oxidation into a Sn(IV) complex (in which a possibly active tetra-siloxy tin species would be obtained).

**Scheme 1.** Synthesis of \([ (c-C_5H_9)_7Si_7O_7(OSiMe_3)O_2Sn]_2 \) (1) and \([ (c-C_5H_9)_7Si_7O_7(OSiMe_3)O_2Sn]_2Sn^IV \) (2) and decomposition under influence of moisture.
A direct synthetic route towards a tin$^{IV}$ tetra-siloxy silsesquioxane complex is the reaction of [(c-C$_5$H$_5$)$_7$Si$_7$O$_5$(OSiMe)$_3$(OH)$_7$] with SnCl$_4$. Half an equivalent of SnCl$_4$ was added to a cooled solution of [(c-C$_5$H$_5$)$_7$Si$_7$O$_5$(OSiMe)$_3$(OH)$_7$], after four equivalents of NEt$_3$ were added and the whole was stirred overnight at ambient temperature, the homoleptic [[(c-C$_5$H$_5$)$_7$Si$_7$O$_5$(OSiMe)$_3$(OH)$_7$]Sn$^{IV}$] (2) could be isolated (Scheme 1). $^{13}$C-NMR shows seven distinct signals for the methine carbons of the cyclopentyls indicating a non-symmetric complex. However, the lability of the Sn-O bond in bis-silsesquioxane species 2, when exposed to H$_2$O, induces the unexpected formation of the closed caged (c-C$_5$H$_5$)$_9$O$_5$Sn. For this reason, in spite of the successful formation of the demanded tetrahedrally surrounded tetra-siloxy tin complexes, performing catalytic oxidation experiments are not an option. The condensation reaction of 1 and 2 into (c-C$_5$H$_5$)$_9$O$_5$Sn is induced by the splitting of the Sn-O bonds under influence of H$_2$O. Interestingly, the opposite phenomenon, being opening of fully condensed silsesquioxanes, was observed by Feher who described the base-catalyzed cleavage and homologation of (c-C$_5$H$_5$H$_1$)$_9$O$_5$Sn into (c-C$_5$H$_5$H$_1$)$_9$O$_5$Sn(OH)$_4$ and (c-C$_5$H$_5$H$_1$)$_9$O$_5$Sn$_3$OH. $^{43}$

More stable siloxy-tin(IV)-silsesquioxane complexes can be obtained by starting from dihalotin$^{IV}$-acetylacetonate precursors. Acetylacetonato-like donors represent an important class of chelating ligands in the field of coordination chemistry. $^{144}$ When (c-C$_5$H$_5$)$_7$Si$_7$O$_5$(OH)$_7$ and (c-C$_5$H$_5$)$_7$Si$_7$O$_5$-(OSiMe)$_3$(OH)$_7$ were reacted to Cl$_3$Sn(acac)$_2$ (acac = acetylacetonate) in the presence of NEt$_3$ the corresponding products(c-C$_5$H$_5$)$_7$Si$_7$O$_5$-(OSiMe)$_3$(OH)$_7$Sn(acac)$_2$ (3) and (c-C$_5$H$_5$)$_7$Si$_7$O$_5$(OH)O$_2$Sn(acac)$_2$ (4) (Scheme 2, Figure 3) could be isolated in high yield. Somewhat elevated temperatures were required to complete the reaction ($80^\circ$C). Both complexes 3 and 4 are stable when subject to moisture. Surprisingly, during the formation of product 4 there is no indication that the third silanol is involved in the reaction and the $^1$H-NMR for 4 shows a sharp OH peak at 4.91 ppm. In an extensive theoretical IR study of the silsesquioxane complex (c-C$_5$H$_5$)$_7$Si$_7$O$_5$(OH)O$_2$Sn(n-Bu)$_2$ sustained by experimental data was found that the Sn metal atom has some interaction with the OH since the $\nu_{OH}$ stretching frequency was somewhat shifted to higher resonance values. $^{19,20}$ In our opinion this interaction is fairly weak according to the sharp OH peak in the $^1$H-NMR. When (c-C$_5$H$_5$)$_7$Si$_7$O$_5$(OH)O$_2$SnMe$_2$ (5) was prepared from (c-C$_5$H$_5$)$_7$Si$_7$O$_5$(OH)$_7$ and Cl$_2$SnMe$_2$ in the presence of NEt$_3$, a similar sharp OH signal was observed in the $^1$H-NMR (5.16 ppm).

Unlike 1 and 2, (c-C$_5$H$_5$)$_7$Si$_7$O$_5$(OH)O$_2$Sn(acac)$_2$ (4) appeared to be extremely stable. Extensive heating (boiling in toluene) or addition of another donating group (CH$_3$CN) had no effect on the complex. This proved that forcing the remaining silanol to react with Sn and form a closed caged -SiO$_3$Sn-X moiety (X = donating atom) in which one of the acetylacetonate ligands are removed is not possible. Apparently, coordination of Sn to the acetylacetonate ligands in a stable 6-coordinate fashion is much stronger than coordination to the silanol and much stronger than the often observed tendency of silsesquioxanes to form closed caged complexes.
Another way to prepare stable tetra-siloxy tin species is to react an incompletely condensed silsesquioxane to trichlorotin-alkoxide. Therefore $[\text{Cl}_3\text{SnOE}_2\text{EtOH}]_2$ was reacted with two equivalents of $(\text{c-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9\text{Sn}(\text{OEt})_2\text{EtOH}$. NMR spectroscopy provided some evidence for the straightforward formation of the product $(\text{c-C}_5\text{H}_9)_7\text{Si}_7\text{O}_9\text{Sn}(\text{OEt})_2\text{EtOH}$ (Scheme 3). In the $^1\text{H}$-NMR spectrum broad signals were found at positions indicative for both OCH$_2$CH$_3$ and HOCH$_2$CH$_3$ groups and the $^{13}\text{C}$-NMR showed patterns for the CH and CH$_2$ of the cyclopentyl group indicative for a closed caged symmetric compound. However, the resolution of the spectra was too poor to locate the carbon signals of the ethoxy and ethanol groups. Slow crystallization from CHCl$_3$ afforded well-shaped crystals.

Unfortunately, several attempts to solve the crystal structure remained unfruitful; the crystals did not diffract and thus the molecular structure could not be solved. $^1\text{H}$-NMR spectroscopy reveals the presence of exactly 1 equivalent of CH$_3$CH$_2$OH per silsesquioxane cage. Based on the Sn satellites ($\tilde{\Delta}J(\text{Sn}^{'-1}\text{H}) = 10.2 \text{ Hz}$) it could be concluded that the alcohol is coordinated to the Sn atom. Figure 4
indicates that ethoxy groups are no longer present. The $^{13}$C-NMR spectrum reveals that the methine signals of the cyclopentyl groups have become inequivalent, indicating an unsymmetric silsesquioxane complex. From these data was concluded that the most likely formed product is the dimeric \(((c-C_5H_9)_{7}Si_7O_9(O_3SnO).EtOH)_2(\mu O)\) (5) (Scheme 3) with 6-coordinated tin$^{IV}$-atoms octahedrally surrounded.

Scheme 3. Synthesis of \(((c-C_5H_9)_{7}Si_7O_9(O_3Sn).EtOH)_2\) (6) via \(((c-C_5H_9)_{7}Si_7O_9(O_3Sn(OEt)).EtOH)_2\)

**Figure 4.** $^1$H-NMR and $^{13}$C-NMR spectra of 6.
An alternative route towards the desired type of compounds is the reaction of \((c-C_9H_{18})_3Si\_3O_9(OH)\_3\) with SnCl\(_4\) and subsequent hydrolysis in order to form \(-O_2SnOH\) species. Reaction of SnCl\(_4\) with \((c-C_9H_{18})\_3Si\_3O_9(OH)\_3\) in toluene in the presence of NEt\(_3\) afforded the trimeric cluster \([(c-C_9H_{18})\_3Si\_3O_9(O_2Sn)Cl\_3]_{\mu}HClNEt_3\) (7), which could be deduced from the integral values in the \(^1H\)-NMR spectrum. Reaction of SnCl\(_4\) and \((c-C_9H_{18})\_3Si\_3O_9(OH)\_3\) in the presence of the more sterically demanding \(N'(Pr)_2\)Et amine afforded a trimeric cluster as well; \([(c-C_9H_{18})\_3Si\_3O_9(O_2Sn)]_{\mu}(\mu-Cl)_2HN(Pr)_2Et\) (8). Reaction of SnCl\(_4\) and the incompletely condensed \((c-C_9H_{11})\_3Si\_3O_9(OH)\_3\) in the presence of NEt\(_3\) afforded a cluster \([(c-C_9H_{11})\_3Si\_3O_9(O_2Sn)]_{\mu}(\mu-Cl)_2H(NEt)_2\) (9) in which, according to the integrals in the \(^1H\)-NMR spectra, the ratio amine to silsesquioxane cage is 2 to 3 (instead of 1 to 3 for 7 and 8). The di-amine based ammonium salt resembles a proton-sponge that delocalizes one proton over two amines.

Crystallization of 7 in CHCl\(_3\) afforded an inadequately solved crystal structure (R = 20% with the Sn atom being anisotropic), which in spite of the weak data revealed that 7 possesses bridging chlorides. This confirmed the assumption of a trimeric cluster coordinated to a tri-ethylammonium group. In the chloride bridged cluster each tin atom is connected to two different silsesquioxane cages and the chlorides are bridged between the tin atoms in which each tin is 6-coordinate. From \(^{13}\)C-NMR spectroscopy of 7, 8 and 9 can be deduced that the clusters are C\(_{3v}\) symmetric. The signals found at the \(^{29}\)Si-NMR spectrum of 7 also indicates C\(_{3v}\) symmetry and \(^{119}\)Sn shows a signal at \(-614.87\) for 7, indicative for highly coordinated tin. The most plausible structure of 7, 8 and 9 is shown in Scheme 4.

![Scheme 4. Synthesis of the trimeric clusters 7, 8 and 9.](image)

When the colored solids 7, 8 and 9 are dissolved in chloroform, layered with wet aceton and left at ambient temperature the color slowly disappears and white crystals emerge. Unfortunately, the crystals lose solvent easily and were not suitable for X-ray structure determination. The white precipitate can be dissolved in THF and when silver nitrate is added, the solution stays clear, indicating that chloride is no longer present. \(^1H\)-NMR spectroscopy in THF-\(d_8\) shows the presence of an OH signal at 6.17 ppm for the hydrolyzed product from 7 and 8, and at 6.16 ppm for the hydrolyzed product from 9. From \(^{13}\)C-
NMR can be deduced that the hydrolyzed products possess C₃v symmetry since the methyne ratio of the cycloalkyl is 3 to 3 to 1, the spectra of the products of the cyclopentyl substituted 7 and 8 are practically identical. When 7 is dissolved in a solvent with higher boiling point (CHBr₃) slowly crystals suitable for X-ray determination are formed which are pictured in Figure 7. The hydrolyzed product from 7, \([(c-C₅H₅)₂SnO₃(O₂Sn)]⁻\{\mu-\text{OH}\}_2\text{HNEt}_3\) (10) is a cluster similar to the suggested structure of 7. It consists of three silsesquioxane cages linked by three tin atoms which have four bridging hydroxyls. Three OH groups are bridged by two tin atoms and the fourth OH groups is bridged by three tin atoms and pointing outwards (Figure 7A, 7C in Section 6.3). Chloride and hydroxyls can be easily exchanged since the binding properties to tin is almost identical, this exchange ability is utilized in biologic membranes. The structural similarities between bridged chloride and bridged hydroxyls indicate an identical trimeric structure for 7-9 and their hydrolyzed products.

When the hydrolyzed products from 7, 8 and 9 are dissolved in THF-d₆, most likely they push away the amine and coordinate (weakly) to THF instead resulting in a solvent separated ion pair. The ammonium salts can no longer be observed on the NMR time-scale and \([(c-C₅H₅)₂SnO₃(O₂Sn)]⁻\{\mu-\text{OH}\}_2\text{HNEt}_3\) (10) and \([(c-C₅H₅)₂SnO₃(O₂Sn)]₂[\mu-\text{OH}]_3\text{HN(Pr)₂Et}\) (11) (the hydrolyzed products from 8) appear as identical complexes \([(c-C₅H₅)₂SnO₃(O₂Sn)]₂[\mu-\text{OH}]_3\) (10a). A signal at –659.44 ppm was observed in the \(^{119}\text{Sn}\) spectrum of 10a, indicative for highly coordinated tin. For tin incorporated in zeolite framework, Corma observed a band at –444 ppm which was assigned to tetrahedrally coordinated tin (solid state \(^{119}\text{Sn}\)-NMR). \([(c-C₅H₅)₂SnO₃(O₂Sn)]₃[\mu-\text{OH}]_4\text{HN(Pr)₂Et}_2\text{NEt}_3\) (12), the hydrolyzed product of 9, also appears in THF-d₆ as a solvent separated ion pair \([(c-C₅H₅)₂SnO₃(O₂Sn)]₃[\mu-\text{OH}]_4\). The FT-IR spectrum of 10 (Nujol mull) reveals two bands in the hydrogen bond region; a small sharp band at 3591 cm⁻¹ and a broad band at 3134 cm⁻¹ (Figure 5A). The band located at 3591 cm⁻¹ is likely to be the Sn-OH, which is pointed away from the coordinated ammonium (Figure 7), the broad band is assigned to the other bridged hydroxyls pointing towards the ammonium. When D₂O is added to 10 in THF and stirred for a few hours, the infrared spectrum indicates that part of the hydroxyls is exchanged by deuterium (Figure 5B); The broad band at 3134 cm⁻¹ has less intensity than the band observed at that position of the hydroxyl bridged 10 (Figure 5A). A new band, located at 2366 cm⁻¹ has appeared which is assigned to bridging Sn-OD. When D₂O is reacted to the tin-chloride species 7, the chlorides are exchanged by OD groups (Figure 5C). The infrared spectrum shows a broad band at 2366 cm⁻¹ (suggesting Sn-OD species) whereas at 3134 cm⁻¹ (indicative for bridging hydroxyls) no vibration is found. Since the reaction 7 with D₂O was performed in air, hydrogen exchange of the easily accessible outward pointing bridging OD into bridging OH could explain the tiny peak located at 3591 cm⁻¹ (Figure 5C). Vibration bands due to the proton in ammonium salts can usually be found between 2300 and 2700 cm⁻¹. For compound 10 and deuterium exchanged 10 and 7, only resonances of very weak intensities can be found in this region (except for the strong OD band in the case of deuterium exchanged 10 and 7), therefore the NH signals can not be assigned unambiguously.
6.3. Structural characterization

The crystal structure of the dimeric Sn\textsuperscript{II} complex \([\text{c-C}_9\text{H}_8]_2\text{Si}_2\text{O}_7(\text{OSiMe}_3)\text{O}_2\text{Sn}\text{II}_2\) (1), the synthesis of which is described in Section 6.2, is shown in Figure 6. Selected bond distances and angles are given in Table 1. The dimeric structure possesses an inversion center in the middle of the \((\text{SnO})_2\) ring, each Sn\textsuperscript{II} atom is coordinated three oxygens. Both silsesquioxane cages are trans oriented and nearly perpendicular with respect to the oxygen connected to both the \((\text{SnO})_2\) ring and the cage \((\text{O}1-\text{Sn}-\text{O}2 = 92.28(13)\,^\circ, \text{O}1-\text{Sn}-\text{O}2 = 90.23(14)\,^\circ)\), consequently stretching the \text{Sn-O2-Si2} (156.5(2)\,^\circ) and \text{Si2-O6-Si6} (156.3(3)\,^\circ) angles somewhat. The four-membered \((\text{SnO})_2\) ring is planar with a strained geometry at each Sn atom with an O-Sn-O1A angle of 75.39(13)\,^\circ and an Sn-O1-SnA angle of 104.61(13)\,^\circ. A similar trans-dimer has been described for the bulky tin-alkoxide \([\text{Sn}\text{II}(\text{O}t\text{Bu})(\mu-\text{O}t\text{Bu})]_2\).\textsuperscript{47} They reported a slightly larger endocyclic O-Sn-O angle of 76(2)\,^\circ and slightly smaller Sn-O bonds for the \((\text{SnO})_2\) ring \((\text{Sn-O} = 2.16(1)\,\text{Å} \text{ compared to } \text{Sn-O1} = 2.177(3)\,\text{Å} \text{ and } \text{Sn-O1A} = 2.172(3)\,\text{Å for 1). Binuclear tin(II) calixarene, prepared form } [\text{Bucalix}]\text{H}_4 \text{ and Sn(N(SiMe}_3)_2]_2\) possess two 3-coordinate tin atoms as well, with an even more strained \((\text{SnO})_2\) ring \((\text{O-Sn-O angle of 68.2(1) }^\circ)\).\textsuperscript{48} The Sn-O bonds in the \((\text{SnO})_2\) parallelogram are 2.193(2) and 2.169(2)\,Å which are also smaller than observed for 1. The distance of each tin atom to the third oxygen compared to the Sn-O distance within the \((\text{SnO})_2\) ring is smaller in all three described structures; 1.995(3)\,Å for 1 (Sn-O2 in Figure 6), 1.97(2)\,Å for \([\text{Sn}\text{II}(\text{O}t\text{Bu})(\mu-\text{O}t\text{Bu})]_2\) and 2.054(2)\,Å for the Sn\textsuperscript{II}-calix[4]arene.
Figure 6. Crystal structure of \([\text{c-C}_5\text{H}_9]_7\text{Si}_7\text{O}_9(\text{OSiMe}_3)\text{O}_2\text{Sn}^{\text{II}}]_2\ 1\).

Table 1: Selected interatomic distances and angles for 1

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\([\text{c-C}_5\text{H}_9]_7\text{Si}_7\text{O}_9(\text{OSn})_3[\mu-\text{OH}]_3\text{HNEt}_3\ 10\) is a cluster consisting of three silsesquioxane cages held together by three tin atoms with intramolecular bridging hydroxyls. The crystal structure of 10 is depicted in Figure 7, several bond distances and angles are given in Table 2. Three OH groups are each bridged by two tin atoms and a fourth hydroxyl is bridged by three tin atoms and pointing outwards (Figure 7A, 7C). Each silsesquioxane cage is connected to two tin atoms, monodentate to one tin atom and bidentate to the other tin atoms. Each tin atom is six-coordinate and octahedrally surrounded in an almost undistorted manner. In most tin solid-state compounds, the tin atom is six coordinated, the octahedral symmetry of 10 closely resembles the rutile structure of the principal ore of tin, cassiterite (SnO₂).¹ The cluster coordinates to the ammonium via the three bridging hydroxyls Sn–\(\mu^2\)OH–Sn that causes a small distortion of the complex, this is visualized in the side-view of Figure 7B. The three four-membered rings consisting of (Sn–\(\mu^2\)OH)₂ form a portion of an incomplete cube (best seen in Figure 7A and 7C). The Sn–\(\mu^2\)OH distances range from 2.087(5) Å to 2.137(5) Å for the
hydroxyls bridged by two Sn atoms and are slightly elongated for the hydroxyl bridged by three Sn atoms (Sn-μ³OH = 2.261(6) Å, 2.277(6) Å and 2.292(6) Å). The Sn-μ³OH-Sn angles are 111.9(2)°, 112.8(3)° and 112.2(2)° whereas the Sn-μ³OH-Sn angles are slightly smaller (101.9(2)°, 100.8(2)° and 100.1(2)°). The average length of an Sn-O bond connected to the silsesquioxane cages is 1.974(4) Å. The Sn-O-Si angle is around 140° for the monodentate link between tin and the silsesquioxane cage and is around 134° when it comprises the bidentate link between tin and the cage. Multinuclear tin complexes stabilized by intramolecular hydrogen bonding have been observed in which the tin is coordinated to phosphinates or iron in order to fulfill an advantageous octahedral 6-coordinate surrounding. Reaction of n-butylstannoic acid with diphenylphosphoric acid results in the hydroxyl bridged \([\{\text{n-BuSn(μ²OH)O}_2\text{PPh}_2\}_3]\text{Ph}_2\text{PO}_2\] and exhibits just as was observed for \[\text{10}\] three four-membered rings. The symmetric structure has Sn-OH distances of 2.12(8) Å, somewhat longer than observed for \[\text{10}\], and Sn-μ³OH-Sn angles of 100.1(2)° comparable to those observed for \[\text{10}\]. The structurally similar trinuclear cluster \([\{\text{BzSn(μ²OH)(O}_2\text{P(c-C}_6\text{H}_{11})}_2\}_3\text{O}]\text{O}_2\text{P(c-C}_6\text{H}_{11})_2\] possesses an additional capped oxygen in between the three tin atoms just as the fourth hydroxyl in \[\text{10}\] is capped by three tin atoms. For this complex, Sn-μ²OH distances range from 2.05(1) to 2.16(1) Å and Sn-μ²OH-Sn angles from 98.2(6) to 99.8(5)°, this differs slightly from the distances and angles found for \([\{\text{n-BuSn(μ²OH)O}_2\text{PPh}_2\}_3]\text{Ph}_2\text{PO}_2\] and \[\text{10}\]. The average Sn-O-Sn angle at the capped oxygen is about 103.3° which is somewhat larger than the Sn-μ³OH-Sn angles observed in \[\text{10}\] (average 100.9(5)°).
Figure 7. Crystal structure of \( [(c-C_5H_9)_7Si_7O_9(O_3Sn)]_3(\mu-OH)_4 \) HNEt_3 (10); front view (A), side view (B) and selection of the anionic tin-hydroxyl bridged center (C). R groups attached to the the silsesquioxane cages are omitted for clarity.

Table 2: Selected interatomic distances and angles for \( [(c-C_5H_9)_7Si_7O_9(O_3Sn)]_3(\mu-OH)_4 \) HNEt_3 (10)

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6.4. Catalytic oxidation reactions

Screening of the catalytic activity in several oxidation reactions was performed with representative examples of the described silsesquioxane tin-siloxy compounds. Compounds 1 and 2 were excluded from the catalytic oxidation due to their instability when exposed to moisture. When possible, catalytic conditions were the same as used for the catalytic oxidations reactions of tin containing silicates (see Section 6.1 of this Chapter).

A. Baeyer-Villiger oxidation

Baeyer-Villiger oxidation of cyclohexanone by 2 mol% of \[\{((c-C_5H_9)_7Si_7O_9(O_3Sn))_3\{\mu-OH\}_4\}HNEt_3(10)\] or \{((c-C_5H_9)_7Si_7O_9(O_3Sn).EtOH\}_2(\muO) (5) with diluted H_2O_2 as oxidant were tested under different circumstances. Stirring overnight at 70 °C with either acetonitrile or dioxane as a solvent did not result in conversion of cyclohexanone into ε-caprolactam. Characteristic signals of cyclohexanone could still be traced (\(^{13}\)C-NMR and IR-measurements). Acidifying the reaction conditions by adding some HCl, or raising the temperature to 100 °C and thus approaching heterogeneously applied conditions had no effect. Using the more reactive substrate cyclopentanone instead of cyclohexanone or using TBHP (t-butyl-hydroperoxide) as oxidant instead of H_2O_2 was neither of influence. In no circumstance oxidation reactivity could be observed.

B. Meerwein-Ponndorf-Verley-Oppenaer

The Meerwein-Ponndorf-Verley reduction of cyclohexanone by 2-propanol into cyclohexanol was mimicked by \[\{((c-C_5H_9)_7Si_7O_9(O_3Sn))_3\{\mu-OH\}_4\}HNEt_3 (10)\] as catalyst. The reaction performed in THF-d_8 at 60 °C with 10 µmol of catalyst and a catalyst/alcohol/keton ratio of 1/50/200 was followed by NMR. After several days still no formation of cyclohexanol was observed.

C. Epoxidation

The epoxidation of cyclooctene into cyclooctene-oxide with \((c-C_3H_9)_3Si_O_3(O_3SiMe_3)O_2Sn(acac)\_2 (3), (c-C_3H_9)_3SiO_3(Oh)O_2Sn(acac)\_2 (4), ((c-C_3H_9)_3SiO_3(O_3Sn)Cl)_2NEt_3 (7) and \(((c-C_3H_9)_3SiO_3(O_3Sn))_3\{\mu-OH\}_4 (10a)\) was followed by NMR at 60 °C with C_6D_6 as solvent. A ratio of catalyst/substrate/oxidant of 1/50/100 was used with TBHP as oxidant. No epoxidation activity could be observed. A change of polarity of the solvent (THF-d_8 instead of C_6D_6) or higher reaction temperatures (up to 100 °C) was of no influence. When the ethanol coordinated complex \{((c-C_5H_9)_7Si_7O_9(O_3Sn).EtOH)\}_2(\muO) (5) was used as catalyst in the epoxidation of cyclooctene with TBHP as oxidant, some activity could be found. After 2½ hours at 100 °C a conversion of 11% into cyclooctene-oxide could be detected by \(^1\)H-NMR.
Unfortunately these findings neither can confirm the proposed active species in tin-silicates being tin$^\text{IV}$ species tetrahedrally surrounded by alkoxydes nor refute it. The mobility the silsesquioxanes cages due to their homogeneity allows the formation of thermodynamically stable multinuclear tin aggregates where tin is 6-coordinate and satisfactorily octahedrally surrounded. These type of reactions are unlikely to take place in silicates. Moreover, the anionic character of the trimeric hydroxyl bridged species such as complex 10, which is not present in tin-silicate materials, can be the reason that no activity could be observed. The steric crowding around the tin centers and an electronically saturated complex state prevents coordination of the substrate.

6.5. Concluding remarks

Several siloxy tin silsesquioxanes could be prepared in which tin exhibited a 3-, 4-, or 6-coordinate surrounding. The prepared 3- and 4-coordinate tin-siloxy complexes (respectively [(c-C$_5$H$_9$)$_7$Si$_7$O$_9$-(OSiMe$_3$)$_2$O$_2$]Sn$^\text{II}$ and [(c-C$_5$H$_9$)$_7$Si$_7$O$_7$-(OSiMe$_3$)$_2$O$_2$]Sn$^\text{IV}$) were not stable when exposed to protic derivatives. Cleavage of the Sn-O bond unexpectedly induces the formation of condensed R$_6$Si$_6$O$_9$ species. Due to their lability these tin-siloxy complexes were not suitable as possible oxidation catalysts. The 6-coordinate tin silsesquioxanes were of the types R$_7$Si$_7$O$_9$(OR')$_2$Sn(acac)$_2$, {R$_7$Si$_7$O$_9$(O$_3$Sn).EtOH}$_2$ and [[R$_7$Si$_7$O$_9$(O$_3$Sn)]$_3$(µ-OH)]$_3$NR'. The latter were the result of the mobility of silsesquioxide ligands; trimeric clusters could be formed in which the tin atoms possess an octahedrally filled environment and are electronically saturated. Crystal structures turned out to resemble the rutile structure of the octahedrally symmetric SnO$_2$. The prepared 6-coordinate tin silsesquioxanes showed in almost every case no activity as oxidation reaction catalysts. Only [R$_7$Si$_7$O$_9$(O$_3$Sn).EtOH]$_2$(µO) showed some activity in the epoxidation of cyclooctene. The anionic character of the clusters together with steric crowding around the tin centers and an electronically satisfying surrounding prevent coordination of the substrate or hinders the oxidation reaction in an effective manner.
6.6. Experimental section

General Remarks - Reactions were performed under an argon atmosphere using Schlenk techniques when necessary. Solvents were distilled from K (THF), Na/K alloy (hexanes, C₆D₆) and benzophenone (Et₂O) or dried over 4 Å molecular sieves (NEt₃, CDCl₃) and stored under argon. ¹H- and ¹³C-NMR spectra were recorded on Varian Mercury 400 spectrometers (25°C, ¹H NMR: 400 MHz, ¹³C NMR: 100.6 MHz). ²⁹Si- and ¹¹⁹Sn-NMR spectra were recorded on a Varian Indigo 500 spectrometer (25°C, ²⁹Si NMR: 99.3 MHz, ¹¹⁹Sn NMR: 186.4 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (¹H, ¹³C NMR) or external standards (²⁹Si: SiMe₄ = 0 ppm, ¹¹⁹Sn: SnMe₄ = 0 ppm). In some cases, the ¹¹⁹Sn-NMR signals were fairly broad due to partially relaxed ¹¹⁹Sn-Cl coupling, therefore short acquisition times (< 0.3 s) were used in those cases. Fourier Transformed Infrared spectra were recorded at room temperature on a Nicolet Avatar™ 360 spectrophotometer. Solid-state samples were recorded as Nujol-mulls (prepared under inert atmosphere, glovebox). Elemental analyses were carried out at the Mikroanalytic Laboratory H. Kolbe in Mülheim an der Ruhr, Germany; quoted data are the average of at least two independent measurements. Silsesquioxane starting materials (c-C₇H₅SiO₃(OH)₃ and (c-C₆H₅)₃SiO₃(OSiMe₃)₂(OH)₂ were prepared following referred literature procedures (see previous chapters of this thesis). Most tin starting materials were purchased from Merck or Gelest and used as received, Sn(N(SiMe₃))₂ and [Cl₂SnOEt₂EtOH]₂⁵⁵,⁵⁴ were prepared following referred literature procedures.

\[
[(c-C₇H₅)₃SiO₃(OSiMe₃)₂Sn]²⁺ (1). (c-C₇H₅)₃SiO₃(OSiMe₃)(OH)₂ (1.00 g, 1.06 mmol) and Sn(N(SiMe₃))₂ (0.46 g, 1.06 mmol) were weighed in a schlenk and cooled to -40 °C. Subsequently 30 mL of hexanes was added and the mixture was stirred and allowed to warm up to room temperature. The reaction was completed after another three hours of stirring at room temperature. The hexanes-solution was concentrated and stored at -4 °C which afforded crystals suitable for X-ray determination. Evaporation of the remaining solution and thorough drying was supposed to result in elementally pure 1 but the product appeared not stable and by NMR only the closed caged determination product (c-C₇H₅)₃SiO₃Sn₂ could be detected. Yield 56% (0.43g, 0.59 mmol). ¹H NMR of (c-C₇H₅)₃SiO₃Sn₂ (400 MHz, CDCl₃, 25 °C): δ = 1.20 (m, CH-C₇H₅, 6H), 1.51 (m, CH₂-C₇H₅, 12H), 1.72 (m, CH₂-C₆H₅, 24H), 1.92 (m, CH₂-C₆H₅, 12H). ¹³C NMR (100.6 MHz, C₆D₆, 25 °C): δ = 22.76 (CH-C₇H₅), 27.46; 27.84 (CH₂-C₇H₅). ²⁹Si NMR (99.8 MHz, C₆D₆, 25 °C): δ = -0.65.54.

\[
[(c-C₆H₅)₃SiO₃(OSiMe₃)₂Sn]²⁺ (2). To a cooled solution (0 °C) of (c-C₆H₅)₃SiO₃(OSiMe₃)(OH)₂ (3.00 g, 3.17 mmol) in 30 mL of hexanes, ¼ an equivalent of SnCl₄ (0.41 g, 1.58 mmol) diluted in 20 mL of hexanes was added slowly. While keeping the mixture at 0 °C, 4 equivalents of NEt₃ (1.8 mL, 0.13 mol) diluted in 20 mL of hexanes were added dropwise. The reaction mixture was allowed to warm up to ambient temperature and stirred overnight. Et₃N(H)Cl was removed by filtration and the hexanes were removed under reduced pressure until 2 remained as a white powder. Yield 76% (2.41 g, 2.28 mmol). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 0.17 (s, OSi(CH₃)₃, 9H), 0.99 (m, CH-C₆H₅, 7H), 1.52 (br s, CH₂-C₆H₅, 28H), 1.62 (br s, CH₂-C₆H₅, 14H), 1.78 (br s, CH₂-C₆H₅, 14H). ¹³C NMR (100.6 MHz, CDCl₃, 25 °C): δ = 1.86 (OSi(CH₃)₃), 22.24; 22.33; 23.08; 23.49; 23.55; 23.99; 24.20 (7-CH-C₆H₅), 26.84 – 27.78 (CH₂-C₆H₅).
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(c-C₄H₉)₃SiO₃(OSiMe₃)O₂Sn(acac)₂ (3). To a mixture of the solids (c-C₄H₉)₃SiO₃(OSiMe₃)(OH)₂ (1.50 g, 1.58 mmol) and 1 equivalent of C₅H₅Sn(acac)₂ (0.61 g, 1.57 mmol) was added 50 mL of toluene. Subsequently an excess of NEt₃ was added (about 2 mL) and the whole was stirred at 80 °C overnight. The next day Et₂N(H)Cl was removed by filtration and the toluene was removed under reduced pressure. Hexanes (50 mL) was added and thorough evaporation removed the last traces of toluene together with the hexanes and a white powder remained. Yield 88% (1.09 g, 1.38 mmol). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 0.99 (m, CH₃,C₆H₅, 7H), 1.54 (br s, CH₂-C₆H₅, 42H), 1.76 (br s, CH₂-C₆H₅, 14H), 2.06; 2.09; 2.15; 2.24 (4·s, 12H, CH₃,OSiMe₃), 5.60; 5.62 (2·s, CH₃,OSiMe₃). ¹³C NMR (100.6 MHz, CDCl₃, 25 °C): δ = 22.40; 22.44; 22.72; 22.77; 22.94; 23.99; 24.26 (7·CH₂,C₆H₅), 27.00 – 28.03 (CH₂-C₆H₅, CH₃,OSiMe₃), 101.96; 102.30 (2·CH₃,OSiMe₃), 194.50; 195.00; 195.05; 196.11 (4·CO,OSiMe₃). ²⁹Si NMR (99.8 MHz, C₅D₅, 25 °C): δ = -68.58; -67.27; -65.77; -65.25; -64.79; -64.19; -63.39 (7·OSiMe₃, ratio 1:1:1:1:1:1:1), 9.12 (OSiMe₃). ¹¹⁷Sn NMR (186.4 MHz, C₅D₅, 25 °C): δ = -739.68. Elemental analysis calc (%) for C₅H₅O₃SiSnC₆H₅: C 48.09, H 7.47; found C 48.15, H 7.10.

(c-C₄H₉)₃SiO₃(OSiMe₃)O₂Sn(acac)₂ (4). Compound 4 was prepared starting from (c-C₄H₉)₃SiO₃(OH)₂ and C₅H₅Sn(acac)₂ in a similar manner as described for compound 3 and isolated as a white powder. Yield 91%. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 0.18 (s, OSi(CH₃)₅, 9H), 0.96 (m, CH₃,C₆H₅, 7H), 1.55 (br s, CH₂-C₆H₅, 42H), 1.76 (br s, CH₂-C₆H₅, 14H), 2.04; 2.05; 2.13; 2.21 (4·s, CH₃,OSiMe₃, 12H), 4.91 (s, Si-CH₂, 1H), 5.56; 5.57 (2·s, CH₃,OSiMe₃, 2H). ¹³C NMR (100.6 MHz, CDCl₃, 25 °C): δ = 1.96 (OSi(CH₃)₅), 22.56; 22.64; 23.39; 24.15; 24.41; 24.58; 24.64 (7·CH₂-C₆H₅). 194.50 – 29.06 (CH₂-C₆H₅, CH₃,OSiMe₃), 101.83; 102.04 (2·CH₃,OSiMe₃), 194.65; 195.24; 196.27 (3·CO,OSiMe₃). ²⁹Si NMR (99.8 MHz, C₅D₅, 25 °C): δ = -68.05; -66.04; -65.47; -64.42; -63.49; -62.04 (6·OSiC₆H₅, ratio 1:1:1:1:1:1), -55.87 (Si-OSi). ¹¹⁷Sn NMR (186.4 MHz, C₅D₅, 25 °C): δ = -731.82. Elemental analysis calc (%) for C₅H₅O₃SiSnC₆H₅: C 44.50, H 6.60; found C 44.65, H 6.60.

(c-C₄H₉)₃SiO₂(OSiMe₃)O₂SnMe₂ (5). To a solution of (c-C₄H₉)₃SiO₃(OH)₂ (1.70 g, 1.94 mmol) and an excess of NEt₃ (2 mL) in 30 mL of toluene was added 0.43 g of C₅H₅SnMe₂ (1.94 mmol) in a 10 mL toluene solution. Filtration of the Et₂N(H)Cl salt, removal of the toluene under reduced pressure, adding hexanes (10 mL) with subsequent thorough evaporation to remove all traces of toluene, afforded the white powder 5. Yield 90% (1.75 g, 1.73 mmol). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 0.82 (s, SN-CH₂, 3H), 0.86 (s, SN-CH₂, 3H), 1.01 (m, SN-CH₂, 7H), 1.53 (br s, SN-CH₂, 28H), 1.62 (br s, SN-CH₂, 14H), 1.78 (br s, SN-CH₂, 14H), 5.16 (s, Si-CH₂, 1H). ¹³C NMR (100.6 MHz, CDCl₃, 25 °C): δ = 0.09 (SN-CH₂), 1.30 (SN-CH₂), 22.18; 22.26; 22.66; 22.69; 23.88 (7·SN-CH₂, ratio 1:1:1:2:2), 26.99 – 27.92 (SN-CH₂), 29Si NMR (99.8 MHz, CDCl₃, 25 °C): δ = -66.57; -65.47; -64.56; -60.42 (7·SN=Si) = 21.5 Hz); -54.86 (6·OSiC₆H₅, ratio 2:1:1:2:1). -21.38 (Si-OSi). ¹¹⁷Sn NMR (186.4 MHz, C₅D₅, 25 °C): δ = 3.74. Elemental analysis calc (%) for C₅H₅O₂Si₂SN (99.25): C 44.88, H 7.31; found C 44.84, H 7.25 (incl. toluene).

[(c-C₄H₉)₃SiO₂(OSiSn)·EtOH]₂(MO) (6). An excess of NEt₃ (1.5 mL) was added to a solution of (c-C₄H₉)₃SiO₃(OH)₂ (2.00 g, 2.28 mmol) in 50 mL of toluene. To this mixture a solution of [C₅H₅SnOEt₂OH] (0.72 g, 1.14 mmol) in toluene (20 mL) was added dropwise. Stirring overnight at room temperature afforded not much visible Et₂N(H)Cl and decided was to heat the mixture to 60 °C and stir for another three hours. The mixture was then filtered and the toluene was removed under reduced pressure. Hexanes (20 mL) was added and thorough evaporation removed the last traces of toluene together with the hexanes and a white powder remained. Crystallization from CHCl₃ afforded the stable product [(c-C₄H₉)₃SiO₂Sn(OEt)₃] (6). Yield 41% (0.95 g, 0.93 mmol when n=2, 27% when n=3, 20% when n=4, etc.). ¹H NMR (400 MHz, THF-d₈, 25 °C): δ = 0.92 (m, CH₃-C₆H₅, 7H), 1.33 (t, CH₃-CH₂OH, 3H), 1.49 (m, CH₂-C₆H₅, 56H), 3.27 (q, CH₃-CH₂OH, 2H), 5.62 (s, EIOH, 1H, 2·SN=Sn⁻¹ = 10.2 Hz). ¹³C NMR (100.6 MHz, THF-d₈): δ = 9.78 (CH₃-CH₂OH), 24.14; 24.58; 24.76; 25.14; 25.22; 25.93; 27.28 (7·CH₂-C₆H₅), 28.31 – 29.83 (c-C₄H₉), 48.40 (CH₃-CH₂OH). ²⁹Si NMR (99.8 MHz, THF-d₈): δ = -70.00; -66.79; -66.65; -66.33; -66.09; -63.97; -58.82 (7·OSiC₆H₅), 9.12 (OSiMe₃). Elemental analysis calc (%) for C₇H₁₂O₂Sn₂Si₂Sn: C 42.07, H 6.36; found C 42.49, H 6.56 (loss of EtOH).

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\[([c-C_8H_8]_3SiO_3Sn)\_2[\mu-Cl]_3HNEtb] (7). An excess of NEtb (3.5 mL) was added to a suspension of (c-C_8H_8)SiO_3(OH)_2 (5.00 g, 5.71 mmol) in toluene (100 mL). The mixture was cooled to 0 °C and 1 equivalent of SnCl_2 (1.49 g, 5.71 mmol) diluted with 20 mL of toluene was added slowly. The whole was allowed to warm up to room temperature and stirred overnight. The pinkish suspension was filtered and the toluene was removed under reduced pressure. Hexanes (20 mL) was added and thorough evaporation removed the last traces of toluene together with the hexanes and a pale pink solid remained. Yield 85% (3.89 g, 1.21 mmol).

\[SNMR (186.4 MHz, THF-\_d_8): \delta = -65.94, -65.22, -64.79, -62.52, -65.22 (7·O)]

Recrystallization from CHBr_3 afforded white crystals which were structurally identified. Yield 94% (5.73 g, 1.80 mmol). ^1H NMR (400 MHz, CDCl_3, 25 °C): \(\delta = 0.90\) (t, N(CH_2CH_2)_b, 9H), 1.21 (m, CH_2-CH_2-b, 18H), 1.82 (m, CH_2-CH_2-b, 168H), 2.65 (q, N(CH_2CH_2)_b, 6H). ^13C NMR (100.6 MHz, CDCl_3, 25 °C): \(\delta = 8.84\) (N(CH_2CH_2)_b), 23.00; 23.58; 25.11 (7·CH_2-b, ratio 3:3:1), 27.64 - 28.72 (CH_2-b, CH_2), 46.35 (N(CH_2CH_2)_b). ^29Si NMR (99.8 MHz, THF-d_8, 25 °C): \(\delta = -66.50, -65.10\) (7·O, SiC, ratio 4:3).

\[^{119}Sn NMR (186.4 MHz, CDCl_3, 25 °C): \delta = -614.87.\]

\[([c-C_8H_8]_3SiO_3Sn)\_2[\mu-Cl]_3H N(Pr)_2Et] (8). To (c-C_8H_8)SiO_3(OH)_2 (4.00 g, 4.57 mmol) suspended in 50 mL of toluene were added 4 equivalents of N(Pr)_2Et (3.11 mL, 18.3 mmol, predried over molsieves). The mixture was cooled to 0 °C and 1 equivalent of SnCl_2 (4.57 mmol, 11.9 g of a 0.1 g / g solution in toluene) was added dropwise. The whole was allowed to warm up to room temperature and stirred overnight. The yellowish suspension was filtered and the toluene was removed under reduced pressure. Hexanes (20 mL) was added and thorough evaporation removed the last traces of toluene together with the hexanes and a yellow solid remained. Yield 85% (3.89 g, 1.21 mmol). ^1H NMR (400 MHz, CDCl_3, 25 °C): \(\delta = 0.97\) (m, CH_2-CH_2-b, 12H), 1.52 (m, CH_2-CH_2-b, 126H), 1.75 (br s, CH_2-CH_2-b, 42H), 3.17 (m, N(Pr)_2-b(CH_2CH_2), 2H), 3.70 (m, N(Pr)_2-b(CH_2CH_2), 2H). ^13C NMR (100.6 MHz, CDCl_3, 25 °C): \(\delta = 12.27\) (N(Pr)_2-b(CH_2CH_2), 17.35; 18.65 (N(CH_2CH_2-b)Et), 21.99 - 22.62 (7·CH-CH_2-b), 26.82 - 27.87 (CH_2-CH_2-b), 42.37 (N(Pr)_2-b(CH_2CH_2), 54.10 (N(CH_2CH_2-b)Et).

\[([c-C_8H_8]_3SiO_3Sn)\_2[\mu-Cl]_3H(NEtb)_b] (9). Compound 9 was prepared in a similar manner as described for compound 7 from (c-C_8H_8)SiO_3(OH)_2 and SnCl_2 and isolated as a pale pink solid. Yield 94% (5.73 g, 1.80 mmol). ^1H NMR (400 MHz, CDCl_3, 25 °C): \(\delta = 0.75\) (m, CH-CH-b, 21H), 1.27 (m, CH_2-CH-b, 105H), 1.43 (t, N(CH_2CH_2)_b, 18H), 1.76 (m, CH_2-CH-b, 105H), 3.25 (q, N(CH_2CH_2)_b, 12H). ^13C NMR (100.6 MHz, CDCl_3, 25 °C): \(\delta = 8.85\) (N(CH_2CH_2)_b), 23.37; 23.85; 25.00 (7·CH-CH-b, ratio 1:3:3), 26.65 - 28.02 (CH-CH-b), 46.15 (N(CH_2CH_2)_b).

\[([c-C_8H_8]_3SiO_3Sn)\_2[\mu-OH]_3HNEtb] (10). A solution of 2.74 g of 7 in 20 mL of CHCl_3 (0.86 mmol), was layered with 20 ml of aceton. After five days at ambient temperature the pink colour had disappeared and 10 could be isolated as white crystals. Recrystallization from CHBr_3 afforded white crystals which were structurally identified. Yield 38% (1.03 g, 0.33 mmol). IR (Nujol Mull, cm\(^{-1}\)): 3591 (w), 3134 (br s), 1135 (vs), 930 (s) 725 (s). Spectroscopic analysis of solvent separated \([([c-C_8H_8]_3SiO_3Sn)\_2[\mu-OH]_3]) (10a). ^1H NMR (400 MHz, THF-d_8, 25 °C): \(\delta = 0.97\) (m, CH-CH-b, 21H), 1.50 (m, CH_2-CH-b, 126H), 1.76 (m, CH_2-CH-b, 42H), 6.17 (s, \(\mu\-OH\)), ^13C NMR (100.6 MHz, THF-d_8, 25 °C): \(\delta = 23.78, 24.22, 24.55\) (7·CH-CH-b, ratio 3:3:1), 28.30; 28.67; 28.80; 28.83 (CH_2-CH-b). ^29Si NMR (99.8 MHz, THF-d_8, 25 °C): \(\delta = -67.22, -65.69, -57.81\) (7·O, SiC, ratio 1:3:3).

\[^{119}Sn NMR (186.4 MHz, THF-d_8, 25°C): \delta = -659.44.\]

\[([c-C_8H_8]_3SiO_3Sn)\_2[\mu-OH]_3HN(Pr)_2Et] (11). In a similar manner of the hydrolysis of 7 in to 10, complex 8 could be hydrolyzed into white crystalline 11. Yield 43%. When dissolved in THF-d_8, trimeric 10a coordinated to THF instead of amine is formed.
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\[
[[\text{c-C}_6\text{H}_{11}]\text{SiO}_3\text{OSn}_2][\mu-\text{OH}]_3 \text{HNEt}_3] \quad (12)
\]

In a similar manner of the hydrolysis of 7 in to 10, complex 9 could be hydrolyzed into white crystalline 12. Yield 46%. When dissolved in THF-\(d_8\), 12 is a solvent separated ion pair and ammonium nor amine could be detected. \(^1\)H NMR (400 MHz, THF-\(d_8\), 25 °C): δ = 0.76 (m, \text{CH}_3-\text{C}_5\text{H}_{9}, 21H), 1.25 (m, \text{CH}_2-\text{C}_5\text{H}_{9}, 105H), 1.80 (m, \text{CH}_2-\text{C}_5\text{H}_{9}, 105H), 6.16 (s, \mu-\text{OH}). \(^{13}\)C NMR (100.6 MHz, THF-\(d_8\), 25 °C): δ = 25.17, 25.46 (6·\text{C}_5\text{H}-\text{C}_5\text{H}_{9}, \text{ratio 3:3, 7}^{th}\text{C}_5\text{H}-\text{C}_5\text{H}_{9} \text{underneath THF-}d_8\text{signals}), 28.24; 28.36; 28.83; 28.89; 28.95 \text{(CH}_2-\text{C}_5\text{H}_{9}). \(^{29}\)Si NMR (99.8 MHz, THF-\(d_8\), 25 °C): δ = -69.54; -68.20; -67.05 \text{(7-O}_3\text{SiC, ratio 3:3:1)}. \(^{119}\)Sn NMR (186.4 MHz, THF-\(d_8\), 25°C): δ = -650.01. Elemental analysis calcd (%) for \text{C}_{138}\text{H}_{267}\text{N}_2\text{O}_{40}\text{Si}_{21}\text{Sn}_3(3437.29) + 4 eq toluene: C 51.01, H 7.71, N 0.72; found C 51.35, H 7.74, N 0.76.

**Table 5.** Crystal data and details of the structure determination of 1 and 10.

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<td>Triclinic, P-1</td>
</tr>
</tbody>
</table>
| Unit cell dimensions | \begin{tabular}{ll}
Å & Å & Å \\
11.0773(9) & 14.6916(12) & 16.5481(14) \\
14.584(3) & 20.826(4) & 27.208(5) \\
93.022(3) & 90.817(3) & 94.583(3) \\
\end{tabular} | \begin{tabular}{ll}
Å & Å & Å \\
14.584(3) & 20.826(4) & 27.208(5) \\
93.022(3) & 90.817(3) & 94.583(3) \\
\end{tabular} |
| Volume, Å\(^3\) | 2578.0(4) | 8224(2) |
| Z | 1 | 2 |
| \(T, K\) | 203(2) | 203(2) |
| \(\rho_{calc}, \text{g cm}^{-3}\) | 1.371 | 1.372 |
| Crystal size, mm | 0.20 x 0.10 x 0.10 | 0.30 x 0.30 x 0.10 |
| Final R indices \([I >2\sigma(I)]\) | \begin{tabular}{ll}
R1 = 0.0539 & R2 = 0.1455 \\
R1 = 0.0793 & wR2 = 0.1940 \\
\end{tabular} | \begin{tabular}{ll}
R1 = 0.081 & R2 = 0.1470 \\
wR2 = 0.1647 & wR2 = 0.2200 \\
\end{tabular} |
| Goodness-of-fit on \(F^2\) | 1.012 | 1.114 |

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References and notes

Summary

The focus of this thesis is on the synthesis and characterization of homogeneous model systems of various silica surface silanols. Silsesquioxanes are considered to be one of the most realistic homogeneous models for silica surface properties and help to unravel some of the complexity of heterogeneous or homogeneous supported catalysts. The model systems offer a unique opportunity for detailed studying of silica surface properties independently while remaining their accuracy.

Molecular properties of silicas are strongly affected by the nature of their surface sites. The unsaturated surface valencies are satisfied by surface hydroxyl functionalities, which exist as vicinal (hydrogen bonded silanols), geminal (two silanol groups attached to the same silicon atom), or isolated (no hydrogen bonds possible) silanol sites. Silsesquioxane model systems for vicinal and isolated silanols were already available. In Chapter 2 silsesquioxane geminal silanols have been described. These systems were obtained from reaction of silylether substituted vicinal disilanol silsesquioxanes with tetrachlorosilane and subsequent hydrolysis. It was found that the two silanols of the geminal silsesquioxanes are different in nature. In solution one of the silanols is intramolecularly hydrogen bonded while the other is isolated. In the solid state both silanols are hydrogen bonded, one intramolecularly and the other intermolecularly. Depending on the steric and electronic properties of the silylether substituent, geminal silsesquioxanes appeared to undergo intramolecular condensation or intermolecular dehydroxylation. Relative Brønsted acidities of the geminal silanols have been determined using $pK_a$ measurements in tetrahydrofuran. Silsesquioxane geminal disilanols with less effective intramolecular hydrogen bonding due to the character of the silylether substituent, showed a slightly higher Brønsted acidity.

Model systems for partly silylated silica surfaces in the presence of silanols have been presented in Chapter 3. Reaction of tri-silanol silsesquioxanes with several $\alpha,\omega$-dichlorosil(ox)anes resulted in intramolecular disilylated products. The products possess one remaining silanol with a neighboring siloxane ring; the disilylated part of the complex that mimicks partly silylated surfaces. NMR and FT-IR studies indicated that one or more siloxy units of the siloxane ring interact with the mono-silanol via intramolecular hydrogen bonding since the acidity of the silanol is considerably lowered. An optimum in siloxane ring-size, i.e. effective intramolecular hydrogen bonding and low Brønsted acidity, was found for compounds with two or three -OSiMe$_2$O- units. To diminish mobility of the silsesquioxane ligands and inhibit formation of aggregates (thus closer mimicking zeolite pores), several approaches were tested to force intermolecular silylation of R$_7$Si$_7$O$_9$(OH)$_3$ with difunctional reactants. Entropically beneficial intramolecular ring formation appeared to be preferred in most approaches except in the case of hydrosilylation catalyzed by platinum catalysts where intramolecular reaction is impossible.
With the availability of these novel types of silsesquioxane silanol models, the most important silica surface silanols have now been mimicked (Scheme 1 on page 128). In Chapter 4 an overview is given of the (individual) features of the four types of silanols: geminal silanols, perturbed mono-silanols, vicinal silanols and isolated silanols. The characteristics of silsesquioxane silanols were compared to the (indirect) knowledge of the corresponding silica surface silanol groups and evaluated. Solid state characteristics most pronouncely showed the mobility of silsesquioxane ligands to form aggregates by intermolecular hydrogen bonds. This behavior made comparison with the corresponding rigid silica surface silanols sometimes inaccurate. When intermolecular interactions became sterically hampered, which was shown to be more effective in solution, the silsesquioxane cages tend to be monomeric and excellent analogies were found with corresponding silica surface silanols. Even the order in acidity of the various silanols of the modelsystems agreed well with the predicted order in acidity of silica surface silanols. For different types of silanols the order in diminishing acidity proved to be: vicinal tetra- and tri-silanols >>> isolated silanols > vicinal di-silanols ~ geminal silanols ~ perturbed silanols.

Protonolysis reactions of perturbed mono-silanol silsesquioxanes with gallium and titanium precursors have been explored in Chapter 5. The Lewis acidity of OGaMe$_2$ and its tendency to form stable tetrahedrally surrounded gallium complexes was found to be stronger than the weak donating abilities of the siloxane ring. The monomeric titanium complexes provided soluble models for silica-grafted catalysts with neighboring silica surface siloxy oxygens. To probe the effect of the siloxane ring, the catalytic activity of these complexes in 1-hexene and 4-metyl-1-pentene polymerization reactions was tested. The catalysts were activated by fluoroaryl based complexes and formation and stability of the activated species was followed by $^{19}$F-NMR spectroscopy. The presence of an adjacent siloxane ring resulted in a lower initial polymerization activity when compared to the analogue without an additional siloxane ring. Conversely, the stability of the cationic species was considerably improved. Phenyl substituents at the intramolecular siloxane ring facilitated the formation of the active species.

Tin incorporated in zeolite frameworks show excellent chemoselective catalytic activity in oxidation reactions with hydrogen peroxide. The proposed active tin species in these processes are isolated tetra-siloxy tin species embedded in the zeolite. In Chapter 6 these proposed species have been mimicked by reacting silsesquioxanes with several tin-precurors. A series of siloxy tin silsesquioxanes have been prepared in which tin exhibited a 3-, 4-, or 6-coordinate surrounding. The prepared 3- and 4-coordinate tin-siloxy complexes were not stable when exposed to any protic derivative. In these complexes, cleavage of Sn-O unexpectedly induced the formation of condensed R$_6$Si$_6$O$_9$. Therefore these tin-siloxy complexes were not suitable as possible oxidation catalysts. The 6-coordinate tin silsesquioxanes were the result of the mobility of silsesquioxane ligands; trimeric clusters were formed in which the tin atoms have an octahedral coordination and are electronically saturated. Crystal structures turned out to resemble the rutile structure of the octahedrally symmetric SnO$_2$. The anionic character of the clusters together with steric crowding around the tin centers and an electronically satisfied surrounding probbaly prevent coordination of a substrate and low or no catalytic activity in several oxidation reactions have been found.
**Samenvatting**

De nadruk van het onderzoek beschreven in dit proefschrift ligt op de synthese en karakterisatie van homogene modelsystemen voor diverse silanolen aanwezig op een silica-oppervlak. Silsesquioxanen werden beschouwd als een van de meest realistische homogene modellen voor de eigenschappen van een silica-oppervlak. Onderzoek heeft aangetoond dat silsesquioxanen toepasbaar zijn als veelzijdige homogene modelsystemen voor het ontravelen van (een deel van) de complexiteit van heterogene of homogene geïmmobiliseerde katalysatoren. De modelsystemen maken het mogelijk om eigenschappen van silica-oppervlakken apart van elkaar in detail te bestuderen terwijl de nauwkeurigheid van het model behouden blijft.


In Hoofdstuk 3 worden modellen bekeken van mono-silanolen in de invloedssfeer van gedeeltelijk gesilyleerde silica-oppervlakken. Reactie van niet volledig gecondenseerde trisilanol silsesquioxanen met diverse α,ω-dichlorosil(ox)anen bleek te resulteren in intramoleculaire gesilyleerde produkten. Deze producten bezitten één overgebleven silanol in de directe aanwezigheid van een siloxaan ring; het gesilyleerde deel wat een deels gesilyleerd silica-oppervlak naboost. De interactie van deze siloxaanring met de overbleven silanolgroep werd onderzocht. NMR en FT-IR studies wezen uit dat intramoleculaire waterstofbruggen tussen de silanol en een of meerdere –OSiMe₃O- siloxy eenheden van de siloxaanring de zuursterkte van het complex aanzienlijk verlagen. Verbindingen met twee of
Drie siloxy eenheden bleken de meest optimale siloxaanring grootte te hebben (met de meest effective intramoleculaire waterstofbruggen en laagste zuursterkte). Om mobiliteit van silsesquioxanen te verminderen en daarmee de vorming van aggregaten te voorkomen (en een stap dichter te zijn bij een zeolietporie-model) werden verschillende methodes getest die intermoleculaire silylering van R₇Si₉O₉(OH)₃ met bifunctionele reactanten zouden kunnen forceren. In de meeste gevallen bleken echter entropisch voordelige intramoleculaire reacties de voorkeur te hebben behalve in het geval van hydrostyrlering gekatalyseerd door platinum katalysatoren.

Met de beschikking over deze nieuwe types silsesquioxaan silanol modellen zijn er nu modelsystemen voor de meest belangrijke silica oppervlakte silanolen (zie Schema 1 op pagina 128). In Hoofdstuk 4 werd een uitgebreid overzicht gegeven van de (individuele) kenmerken van vier silanol types: geminale silanolen, mono-silanolen met naburige interactie mogelijkheden, vicinale silanolen en geïsoleerde silanolen. De eigenschappen van silsesquioxaan silanol modellen werden vergeleken met silica-oppervlakte silanolen en geëvalueerd. Vaste-stof eigenschappen laten het meest duidelijk de mobiliteit zien van silsesquioxanen liganden. In deze toestand bleken makkelijk aggregaten verbonden door sterke intermoleculaire waterstofbruggen te worden gevormd. Door dit gedrag was een goede vergelijking van silsesquioxaan silanol modellen met de overeenkomende silica silanol modellen niet altijd mogelijk. In oplossing is het vormen van intermoleculaire interacties moeilijker. Silsesquioxanen komen dan vaker voor als monomeren en eigenschappen bleken veel beter overeen te komen met die van de corresponderende silica silanol. Opvallend was dat zelfs de ordening in zuursterkte van de verschillende types silanol gevonden voor de modelsystemen overeenkwam met de gevonden volgorde voor silica silanol. Voor silanol modellen geldt de volgende reeks in afnemende zuursterkte: vicinale tetra- en tri-silanolen >> geïsoleerde silanol > vicinale disilanolen ~ geminale silanol ~ beïnvloedde mono-silanolen.

Protonolysereacties van monosilanolen onder invloed van een nabijgelegen siloxaan ring met gallium en titaan uitgangsstoffen werden onderzocht in Hoofdstuk 5. De Lewis zuursterkte van OGaMe₂ en de neiging om tetraëdisch omringde galliumcomplexen te vormen bleek sterker dan het gebruik maken van de zwak donerende kwaliteiten van de naburige siloxaanring. Stabiele dimere galliumsystemen werden gevormd zonder aanwijsbare interactie met de nabijgelegen siloxaanring. De monomere titaancomplexen leverden oplosbare modellen voor silica-gegrafte katalysatoren met naburige silica-oppervlakte siloxyl groepen. Een mogelijke invloed van de nabijgelegen siloxaanring werd onderzocht door de katalytische activiteit te testen van het geactiveerde complex tijdens de polymerisatie van 1-hexeen en 4-methyl-1-penteen, met en zonder de aanwezigheid van extra siloxyl groepen. De katalysatoren werden geactiveerd met boorfluoroaryl complexen en de vorming en stabiliteit van de geactiveerde species werd gevolgd met ¹⁹F-NMR spectroscopie. De aanwezigheid van een nabijgelegen siloxaanring resulteerde in een lagere initiële polymerisatie activiteit vergeleken met de soortgelijke katalysator zonder siloxaan ring. Aan de andere kant werd de stabiliteit van het kationische deel in aanwezigheid van een siloxaan ring aanzienlijk verhoogd. Wanneer de siloxaanring gesubsitueerd werd met phenyl groepen in plaats van methyl groepen, dan werd de vorming van het actieve deeltje versneld.
Tin atomen ingebed in een zeoliet zorgen voor een uitstekende chemoselectieve katalytische activiteit tijdens oxidatieraties met waterstofperoxide als oxidant. De veronderstelde actieve tin centra in deze processen zijn geïsoleerde tetra-siloxy tin species ingebouwd in een zeolietrooster. In Hoofdstuk 6 werden deze voorgestelde actieve centra gemodelleerd door tin-silsesquioxanen vanuit diverse tin uitgangsstoffen te synthetiseren. Een serie siloxy tin-silsesquioxanen werd verkregen waarbij tin een 3-, 4- of 6- gecoördineerde omgeving aannam. De verkregen 3- en 4- gecoördineerde tin-siloxy complexen bleken niet stabiel te zijn wanneer ze blootgesteld werden aan protische verbindingen. De Sn-O binding werd hierbij verbroken wat de onverwachte vorming van gecondenseerde R₆Sn₆O₉ deeltjes induceerde. Om deze reden waren deze tin-siloxy verbindingen niet geschikt als oxidatiekatalysatoren. De 6-gecoördineerde tin-silsesquioxanen konden gevormd worden dankzij de mobiliteit van de silsesquioxaan liganden; trimere clusters werden gevormd waarbij de tinatomen een octaëdrische omringing aannamen met een elektronisch verzadigde omgeving. Opheldering van de kristalstructuur wees uit dat deze octaëdrische omringing sterk bleek te lijken op de rutiel structuur van octaëdrisch symmetrisch SnO₂. Het anionische karakter van de clusters in combinatie met weinig ruimte voor reactie rond het tin centrum en een elektronisch verzadigde omgeving voorkwam de coordinatie van een inkomend substaraat tijdens katalyse en lage of helemaal geen katalytische activiteit van de tin-silsesquioxanen werd gevonden tijdens oxidatieraties.
Scheme 1. Overview of the most important silanols occurring on silica surfaces and their corresponding silsesquioxane silanol model systems: A – vicinal silanols, B – geminal silanols, C - isolated silanols and D – perturbed mono-silanols.

Schema 1. Overzicht van de belangrijkste silanolen die voorkomen op silica oppervlaktes en de daarbij korresponderende silsesquioxaan silanol model systemen: A – vicinale silanolen, B – geminale silanolen, C – geisoleerde silanolen and D – mono-silanols beïnvloed door hun omgeving.
Publikatielijst


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