Forschungsbericht – Research Report

Dimeric Silsesquioxanes and Metallasilsesquioxanes – En route to large, well-defined Si-O-assemblies

Volker Lorenz and Frank T. Edelmann*
Magdeburg, Chemisches Institut der Otto-von-Guericke-Universität

Received March 9th, 2004.

Dedicated to Professor Reinhard Schmutzler on the Occasion of his 70th Birthday

Abstract. Recent advances in the chemistry of dimeric silsesquioxanes and metallasilsesquioxanes are reviewed. The number of metal-free silsesquioxane dimers is still quite limited, although some promising synthetic routes have already been developed. In contrast, metallasilsesquioxanes containing two silsesquioxane ligands are known with numerous metals, including Li, K, Be, Al, In, Sc, Sm, Yb, U, Ti, Zr, V, Ta, Cr, and Cu. A major breakthrough in this chemistry was the successful synthesis of fully metalated silsesquioxane precursors such as \((\text{Cy}_7\text{Si}_7\text{O}_{12})_2\text{Li}_6(\text{THF})_2\) (15).

Keywords: Silsesquioxanes; Metallasilsesquioxanes

Dimere Silsesquioxane und Metallasilsesquioxane – Auf dem Weg zu großen, wohldefinierten Si-O-Aggregaten

Inhaltsübersicht. Über jüngste Fortschritte in der Chemie der dimeren Silsesquioxane und Metallasilsesquioxane wird zusammenfassend berichtet. Obwohl bereits einige vielversprechende Syntheseverfahren entwickelt wurden, ist die Zahl der metallfreien Silsesquioxandimere noch sehr begrenzt. Metallasilsesquioxane mit zwei Silsesquioxanliganden sind dagegen von zahlreichen Metallen bekannt, einschließlich Li, K, Be, Al, In, Sc, Sm, Yb, U, Ti, Zr, V, Ta, Cr und Cu. Einen wesentlichen Durchbruch in dieser Chemie brachte die erfolgreiche Synthese von vollständig metallierten Silsesquioxanvorstufen wie \((\text{Cy}_7\text{Si}_7\text{O}_{12})_2\text{Li}_6(\text{THF})_2\) (15).

Introduction

Polyhedral oligosilsesquioxanes having the general formula \((\text{RSiO}_{1.5})_n\) form an unusual and interesting class of organosilicon compounds which currently have a tremendous impact on both catalysis research [1, 2] and materials science [3]. Due to their chemical composition they can be viewed as intermediates between silica, \((\text{SiO}_2)\), on one side and the silicones, \((\text{R}_2\text{SiO})_n\), on the other side. In accordance with several unique properties the polyhedral silsesquioxanes have been termed the “smallest particles of silica possible” [4] or “small soluble chunks of silica” [2]. Of special interest for various promising applications are incompletely condensed silsesquioxanes retaining reactive Si-OH functional groups. The fact that silsesquioxane molecules like 1a–d contain covalently bonded reactive functionalities make them also promising monomers for polymerization reactions or for grafting these monomers to polymer chains. In recent years this has been the basis for the development of novel “nanostructured” hybrid materials which offer a variety of useful properties [3, 4]. This area of applied silsesquioxane chemistry has been largely developed by Lichtenhan et al. [4]. With respect to catalysis research the chemistry of metallasilsesquioxanes also receives considerable current interest [1, 2, 5, 6]. Incompletely condensed silsesquioxanes such as \(\text{R}_7\text{Si}_7\text{O}_9(\text{OH})_3\) (1a–d, Scheme 1)
Frank T. Edelmann was born in Hamburg, Germany, in 1954. He studied chemistry at the University of Hamburg, where he obtained his diploma in 1979 and PhD in 1983 with Ulrich Behrens. After 2 years of postdoctoral research in Canada and the USA (with Josef Takats, John W. Gilje and Tristram Chivers) he finished his habilitation at the University of Göttingen in 1991 (in the group of Herbert W. Roesky). In 1995 he was appointed Full Professor at the Otto-von-Guericke-University in Magdeburg. His main research interests are in silicon chemistry (silsesquioxanes and metallasilsesquioxanes), organolanthanide and -actinide chemistry, and fluorine chemistry.

Volker Lorenz was born in Remda, Germany, in 1963. He obtained his diploma from the TH Merseburg and his PhD from the University of Halle-Wittenberg in 1994 (with Karl-Heinz Thiele). This was followed by postdoctoral work with John J. Eisch at Binghamton University (USA) in 1994/95 (titanocene and zirconocene compounds). He is currently Senior Researcher in the Edelmann group. His research interests include silsesquioxane and metallasilsesquioxane chemistry as well as alkaline earth metal and lanthanide compounds for catalytic applications and materials science.

Dimeric silsesquioxanes

Only a small number of bis(silsesquioxanes) molecules have been reported so far. As shown by Duchateau et al., intermolecular dehydroxylation of \((c-C_5H_9)_7Si_7H_9(OSiMePh_2)_3(O_2Si(OH))_3\) (3) yielded the unprecedented siloxy-bridged dimeric bis(silanol) \((\mu-O)[(c-C_5H_9)_7Si_7O_9(OSiMePh_2)-O_2Si(OH))]_2\) (4) (Scheme 2) [12].

Two different synthetic routes have been developed to prepare the sterically encumbered bis(silsesquioxy)ether \((\mu-O)(Cy_7Si_7O_12)_2\) (5). Compound 5 was first obtained in 56 % yield during the carefully controlled hydrolysis of the chlorosilsesquioxane precursor \(Cy_7Si_7O_12Cl\) (6) in the presence of triethylamine and moisture [13]. A recently developed, more rational synthesis (69 % yield) involves the reac-

share astonishing structural similarities with \(\beta\)-cristobalite and \(\beta\)-tridymite and are thus quite realistic models for the silanol sites on silica surfaces [7–11]. Metal complexes derived from 1 are therefore commonly regarded as “realistic” models for industrially important metal catalysts immobilized on silica surfaces [2, 8]. Preparation and derivative chemistry of 1b have been mainly developed by Feher and co-workers [6], although the first reports on this derivative date back until 1965, when Brown and Vogt first described the polycondensation of cyclohexyltrichlorosilane, \(CySiCl_3\) (2, \(Cy = cyclo-C_6H_{11}\)), in acetone/water mixtures [9]. The improved preparation of the cyclohexyl-substituted derivative 1b published by Feher et al. is simple and straightforward, though time-consuming. The synthetic procedure also involves the controlled hydrolysis of 2 in an acetone/water mixture. Separation of 1b from two other silsesquioxane derivatives (a fully condensed prismatic hexamer and a disilanol tetramer) formed in this reaction can be accomplished by a simple extraction procedure. A certain disadvantage of this synthesis is that the kinetically controlled formation of the incompletely condensed silsesquioxane cage by condensation of the \(in situ\) formed cyclohexylsilanetriol, \(CySi(OH)_3\) (3), requires reaction times of up to 3 years (!) to proceed to completion. This process cannot be accelerated significantly by means of stirring, heating, ultrasound etc. [6]. However, synthetically useful quantities of 1 can be “harvested” already after a few months. We started making this useful precursor already in 1992 in the labs of H. W. Roesky at Göttingen, and since then we produced several kilograms of 1b following the procedure given by Feher et al. [6].

This research report summarizes our findings on larger aggregates containing two silsesquioxane cages in one molecule. Such compounds are stepping stones on the way toward higher silsesquioxide oligomers and finally polymers. While the latter have already found practical uses, current knowledge about oligomeric molecules containing 3-6 silsesquioxane is scarce. Thus this article is intended to stimulate further work in that direction.
formation of hexachlorodisiloxane with two equivalents of 1b in the presence of pyridine (Scheme 3) [14].

A similar reaction with hexachlorodisilane afforded (Cy7Si8O12)2 (7) as the first bis(silsesquioxane) derivative containing a Si-Si bond. It is interesting to note that the reactions outlined in Scheme 3 can also be carried out in a 1:1 molar ratio, thereby making the novel silyl-functional silsesquioxanes Cy7Si8O12OSiCl3 (8) and Cy7Si8O12SiCl3 (9) readily available [14].

Two silanol groups in 1b can be bridged by a SiMe₂ unit upon treatment of 1b with one equivalent of Me₂SiCl₂ in the presence of triethylamine to give Cy7Si7O9(O2SiMe₂)-(OH) (10) in 62% yield [14]. The reaction takes a different course when the starting materials are employed in a molar ratio of 2:3 according to Scheme 4. Under these conditions the SiMe₂-bridged bis(silsesquioxane) Me2Si[Cy7Si7O10-(O2SiMe₂)]₂ (11) can be isolated in 76% yield in the form of colorless crystals [15].

Very little developed is the chemistry of silsesquioxanes containing amino and other nitrogen-based functional groups. Recently the synthesis of the first bis(silsesquioxanyl)amine has been described, which has the potential of becoming a useful precursor for further derivative chemistry. The preparation of (µ-NH)(Cy7Si8O12)2 (12) involves reacting the two closo-silsesquioxanes Cy7Si8O12Cl (13) and Cy7Si8O12NH₂ (14) in the presence of triethylamine to eliminate HCl (Scheme 5) [16].

Colorless crystals of 12 were isolated in 88% yield. Future investigations will reveal if the central secondary amino group in 12 can be metalated and used for further reactions.

**Dimeric metallasislesquioxanes**

In contrast to the limited data on dimeric silesquioxanes, the chemistry of metallasislesquioxanes is already quite well developed, and a number of metal complexes containing...
two silsesquioxanes ligands have been reported [1, 2, 5, 6]. Such compounds are of fundamental interest as “realistic” models for silica-supported heterogeneous catalysts. It has been demonstrated that various metals can be placed on the “model silica surface” formed by two formally trianionic \([\text{Cy}_7\text{Si}_7\text{O}_{12}]^{3-}\) moieties in a face-to-face arrangement. Different synthetic routes leading to such complex metallasilsesquioxanes have been developed. While in some cases simple salt-elimination reactions may be successful, most syntheses requires more elaborate routes using reactive metal alkyls, amides or other organometallic precursors. A major breakthrough came from the finding, that well-defined, crystalline alkali metal derivatives of \(1b\) are readily available in synthetic quantities. Previously, there had been contradictory reports in the literature concerning the metalation of \(1b\) by alkali metal reagents. It was reported by
Feher et al. that treatment of 1b with three equivalents of NaOEtBu resulted in complete breakdown of the silsesquioxane cage [17]. In contrast, Aspinall et al. more recently succeeded in synthesizing Cy7Si7O9(OLi)3 by the reaction of 1b with n-butyllithium [18]. Cy7Si7O9(OLi)3 was isolated in virtually quantitative yield as an amorphous, air-stable (!) solid of unknown structure. We found that with the proper choice of deprotonating agents well-characterized, crystalline alkali metal silsesquioxanes are easily accessible. These have been established to represent excellent precursors for the preparation of unprecedented catalyst model compounds.

We found that alkali metal bis(trimethylsilylamides) are the reagents of choice for achieving smooth and high-yield deprotonation of the incompletely condensed silsesquioxane 1b. Treatment of 1b with LiN(SiMe3)2 in diethyl ether/THF according to Scheme 6 afforded the crystalline lithium silsesquioxane dimer (Cy7Si7O12)2Li6(THF)2 (15) in 93% yield. This reaction is not limited to the THF-adduct 15. The corresponding acetone solvate (Cy7Si7O12)2Li6(Me2CO)3 (15b) has been isolated in a similar manner [1, 19]. Both lithium derivatives can be isolated in large quantities in the form of colorless, crystalline materials which are soluble in polar organic solvents such as diethyl ether and THF.

An X-ray diffraction study of 15 revealed the dimeric molecular structure as shown in Scheme 6. The central structural unit of 15 consists of a box-shaped Li6O6 polyhedron. THF ligands are coordinated to two lithium ions while the other four interact with framework oxygen atoms of the silsesquioxane cages. This bonding situation results in tetra-coordination around each Li. Structurally related box-shaped Li5O6 or Li6S6 polyhedra have previously been reported for some hexameric lithium phenoxides or arenethiolates [20], but are unprecedented in silsesquioxane chemistry. With the lithiated silsesquioxane 15 now being readily available in large quantities, we began exploring its derivative chemistry with the aim of synthesizing novel molecular model systems for silica-supported heterogeneous catalysts.

For this purpose isolated 15 can be employed as starting material, but it has been found that the use of in situ prepared Cy7Si7O9(OLi)3 in further reactions also gives excellent results. For example, subsequent reaction with anhydrous BeCl2 according to Scheme 6 afforded the novel heterobimetallic beryllium silsesquioxane 16 in 81% isolated yield. In a similar manner, the reaction of Cy7Si7O9(OLi)3 with ZrCl4 in THF/acetone followed by crystallization from acetone afforded the novel heterobimetallic metallasilsesquioxane [Cy7Si7O12Li(OCMe2)]2Zr (17) as a colorless, crystalline material (Scheme 6). According to a single-crystal X-ray analysis of 17, the central Zr atom is encapsulated by two silsesquioxane cages resulting in an approximate octahedral coordination environment. Two [Li(OCMe2)] units are attached to this formally dianionic [Zr{Cy7Si7O12}2]2/moity. Tetracoordination around each Li ion is achieved through coordinative interaction with three cage oxygen atoms. Certainly the most unusual heterometallasilsesquioxane made from 15 thus far is the ytterbium bis(trimethylsilylamide) derivative [{Cy7Si7O12}2Li4YbN(SiMe3)2] (18) which was prepared by reacting in situ prepared 15 with anhydrous Ybc1 according to Scheme 6 (51% yield). The structurally characterized ytterbium(III) complex 18 represents a novel type of heterobimetallic metallasilsesquiox-
anes, as it contains an additional functional group at the metal center. The ytterbium atom is coordinated via oxygen atoms to a lithium silsesquioxane framework made up of two Cy7Si7O12Li2 units. Due to the involvement of cage oxygen atoms in the coordination to Li there are no additional ligands such as Et2O or THF present in this molecule. The overall structure with a reactive YbN(SiMe3)2 unit residing on a model silica surface resembles that of typical catalytically active lanthanide metallocenes such as (C5Me5)2LnN(SiMe3)2 [21–25]. In 18 two bulky silsesquioxane cages play the role of the pentamethylcyclopentadienyl ligands in the bent metallocene unit. Most notably, however, the molecular compound 18 represents the first “realistic” model for a reactive lanthanide silylamide species bound to a silica surface. Such lanthanide silylamides grafted on silica or the mesoporous silicate MCM-41 are interesting catalysts which have been investigated in detail by Anwander et al. [26–28]. The synthetic route to complex heterobimetallic metalla-bis(silsesquioxanes) as outlined in Scheme 6 appears to be quite general, as shown by the recent synthesis of the lithium/chromium species 19. These examples show that the two silsesquioxane cages in a face-to-face arrangement form an ideal platform for modeling silica-supported heterogeneous catalysts.

Straightforward and complete deprotonation of 1b can also be achieved with other alkali metal bis(trimethylsilylamides). A structurally characterized example is the potassium derivative 20, which was prepared in high yield (77 %) according to Scheme 7. Once again the molecular structure consists of dimeric molecules containing the characteristic box-shaped K6O6 central unit [19].

Among the Group 13 elements, silsesquioxane derivatives have been reported for boron [29–32], aluminum [33–39], indium [40], gallium [32, 41, 42] and thallium [43, 44]. Our contribution to Group 13 metallasilsesquioxanes comprises two bis(silsesquioxane) derivatives of Al and In. An anionic aluminum species, [Et3NH][Al(Cy7Si7O11(OSiMe3))2] (22), was made according to Scheme 8 by reacting the monosilylated precursor 21 with anhydrous AlCl3 (molar ratio 2:1) and the required amounts of triethylamine. Compound 21 also proved to be a very useful starting material in the preparation of the first copper silsesquioxane as an example of
Dimeric Silsesquioxanes and Metallasilsesquioxanes

Scheme 9 Preparation of 
\[[\text{Cy}_7\text{Si}_{12}\text{InMe(OH)}]_2\, (24)\]

Scheme 10 Preparation of the dimeric titanasilsesquioxanes 25–27.

a late transition metal derivative. Tetrameric copper(I) t-butoxide reacted with 21 to afford the tetranuclear complex 23 in which the central eight-membered Cu₄O₄ ring system is retained. Once again an impressive example demonstrating the high versatility of the bis(silsesquioxane) platform!

The compound \([\text{Cy}_7\text{Si}_{12}\text{InMe(OH)}]_2\, (24)\) was prepared in high yield (84%) by reacting 1b with trimethylindium in toluene solution at 20 °C (Scheme 9). The molecular structure of 24 has been determined by X-ray diffraction. In the solid state, self-assembly leads to the formation of a dimeric indasilsesquioxane molecule which is stabilized by two intramolecular hydrogen bonds.

Group 4 silsesquioxanes complexes have been intensively investigated, especially in view of their potential catalytic
applications. Their chemistry has been compiled in several recent review articles \[1, 2b, 45\]. Group 4 (Ti, Zr, Hf) derivatives also form the largest group of dimeric metallasilsesquioxanes. The first compounds of this type were reported by Crocker et al. \[46\] and Johnson et al. \[47\] in 1997. These groups reported that \(1\) reacts with titanium tetraalkoxides to give alkoxide-bridged titanasilsesquioxane dimers. Related reactions investigated in our laboratory are summarized in Scheme 10. The alkoxide-bridged species \(25\) and \(26\) are very similar to those reported earlier \[46, 47\], while \(27\) represents the first compound of this type containing a siloxanediolate bridge. All titanasilsesquioxanes shown in Scheme 10 were isolated in the form of colorless, moisture-sensitive crystals. The ethoxide derivative \(25\) was structurally characterized by a single-crystal X-ray diffraction study \[48\].

With the use of the monosilylated precursor \(21\) as starting material, a series of more unusual titanium bis(silsesquioxane) complexes have become accessible. These reactions are summarized in Scheme 11. The only easily predictable product in this series is the homoleptic complex \(28\), which was prepared in up to 97% yield from \(21\) and titanium tetraethoxide according to Scheme 10. The molecular structure of \(28\) was determined by X-ray diffraction \[48\].

Quite in contrast, seemingly simple reactions between \(1\) and titanocene dichlorides in the presence of triethylamine

\[
\begin{align*}
\text{Scheme 11} & \quad \text{Dimeric titanasilsesquioxanes (28–31).}
\end{align*}
\]
Scheme 12 Preparation of tantalum(V) silsesquioxane complexes (carborane hydrogen atoms in 33 omitted for clarity).

Scheme 13 Synthesis of 36 and 37.
turned out to be somewhat messy and accompanied by side reactions. Despite the use of carefully dried solvents, the formal hydrolysis products 29 and 30 were among the isolated and fully characterized (including X-ray structure analyses) products [48]. It remains speculative whether or not the bridging oxygen atoms might originate from degradation of the silsesquioxane cages. Perhaps the most "realistic" catalyst model to date is the unprecedented mono(pentamethylcyclopentadienyl) titanium(IV) complex 31 [49]. This compound was synthesized by the "fulvene route" according to Scheme 11. Treatment of the "tucked-in" fulvene complex (C₅Me₅)Ti(C₅Me₅CH₂) with 2 equivalents of 1b resulted in elimination of pentamethylcyclopentadiene and formation of the yellow titanium(IV) bis(silsesquioxane) complex 31. A free silanol group, though "tamed" through intramolecular hydrogen bonding, in close proximity to the titanium center makes 31 a truly advanced model system for a silica immobilized titanium catalyst [49].

Vanadium complexes containing two silsesquioxane ligands have already been described in 1990 by Feher et al. [50–52]. The catalytic activity of vanadium(V) silsesquioxanes as well as that of microporous vanadium silicates derived therefrom [53, 54] has been studied in detail. More recently an anionic tantalum(V) complex of the bis(silsesquioxane) type has been reported [54]. A straightforward "amide route" as illustrated in Scheme 12 was employed to prepare the anionic tantalum(V) bis(silsesquioxane) complex 32 in 89 % yield [55]. Compound 33 was made analogously by treatment of the amido tantalacarborane complex (C₂B₁₁H₁₁)Ta(NMe₂)$_₂$ with 1b and isolated in the form of orange crystals in 82 % yield. Although it is not a compound of the bis(silsesquioxane) type, it is mentioned here as a remarkable first representative of a novel class of "inorganic sandwich complexes" combining silsesquioxane and carborane cage compounds in one molecule.

The closo-silsesquioxanesilanol 34 [56] and its lithium derivative 35 (Scheme 13) have rarely been used as building blocks in metallasilsesquioxane chemistry. Recently we reported their use as precursors for the synthesis of two bis(silsesquioxane) complexes of scandium and samarium [57]. The reaction of (C₅Me₅)Sc(acac)$_₂$ with two equivalents of 34 resulted in protolytic elimination of the pentamethylcyclopentadienyl ligand and formation (61 % yield) of the dinuclear scandium complex 36 in which the scandium atoms are bridged by two silsesquioxanesilanolate ligands (Scheme 13). Similar bridging of samarium and lithium occurs in the samarium complex 37, which was prepared by the reaction of the "ate"-complex (C₅Me₅)₂Sm(µ-Cl)Li(THF)$_₂$ with 35 in a molar ratio of 1:2. The air-sensitive yellow crystals of 37 were isolated in 68 % yield. Both complexes were structurally characterized by X-ray diffraction studies [57].

In 1998 Smet et al. reported the formation and structural characterization of the neutral tungsten(VI) bis(silsesquioxane) complex W(Cy₇Si₇O₁₂)$_₂$ (38) [58]. In this remarkable molecule a single W atom is encapsulated between two silsesquioxane cages. It was later found that the analogous uranium(VI) complex U(Cy₇Si₇O₁₂)$_₂$ (39) is readily formed upon treatment of different uranium(IV) precursors with 1b. The use of uranocene as starting material as depicted in Scheme 14 provides a particular clean and salt-free access to 39 [1].

**Conclusions and future outlook**

This short Research Report summarizes our findings in the field of dimeric silsesquioxanes and silsesquioxanes. As no larger oligomers containing 3-6 silsesquioxane units are known until now, this is only the first step towards such large Si-O aggregates. Especially the chemistry of metal-free oligosilsesquioxanes is virtually an open field where numerous classes of novel functional silsesquioxanes remain to be uncovered. The disilazane derivative (µ-NH)(Cy₇Si₇O₁₂)$_₂$ (12) is only the first representative of a bis(silsesquioxane) containing a reactive functional group. Related compounds containing e.g. phosphorus, arsenic, sulfur or selenium functional groups are completely unknown. More complex though well-defined molecules containing more than two silsesquioxane "substituents" are easily imaginable and are currently under investigation in our laboratory. Although metallasilsesquioxane complexes of the bis(silsesquioxane) type have been investigated in greater detail, there are virtually unlimited possibilities for future research in this area as well. Large aggregates based on metal cluster cores surrounded by silsesquioxane ligands have not been explored at all. A particularly intriguing approach is the use of functionally substituted metallasilsesquioxanes in the preparation of novel catalysts. A first promising step in this direction has recently been made by van Santen et al. [59] who reported the cross-linking of vinyl-substituted silsesquioxane titanium complexes with siloxane oligomers. This
method afforded novel highly active and selective catalysts for the epoxidation of alkenes using H₂O₂ as cheap oxidizing agent. Clearly the chemistry of oligomeric silsesquioxanes and metallasilsesquioxanes will remain a hot topic in silicon chemistry for years to come.

References


