Metallasilsesquioxanes

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Dedicated to Professor Karl-Heinz Thiele on the occasion of his 75th birthday

I

## INTRODUCTION

Polyhedral oligosilsesquioxanes having the general formula $(RSiO_{1.5})_n$ 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, (SiO_2), on one side and the silicones, $(R_2SiO)_n$, on the other (the Latin word *sesqui* translates as one and a half). 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] In general, one can distinguish between completely condensed polyhedral silsesquioxanes and incompletely condensed molecules.

The first report on silsesquioxanes ever in the literature was published in 1946 by Scott.[5] Thermal rearrangement of the cohydrolysis product of dichlorodimethylsilane and trichloromethylsilane afforded six different methypolysiloxanes. One of them was a sublimable material, which was assigned the formula $[CH_3SiO_{3/2}]_{2n}$. The first structural investigations on crystalline organosilsesquioxanes were carried out by Barry and co-workers in 1955.[6] These authors prepared a series of organo-silsesquioxanes and were the first to demonstrate that these materials have cage-like oligomeric structures. Crystalline cubic octamers were isolated in the case of the methyl, ethyl, *n*-propyl, *n*-butyl and cyclohexyl derivatives, while in the case of methyl substituents a hexagonal prismatic dodecamer was also obtained and characterized. A trigonal prismatic structure was proposed for a phenylsilsesquioxane derivative. The polycondensation of phenylsilanetriol leading to 8- to 12-unit cage-like oligophenylsilsesquioxanes was later investigated in detail by Brown.[7] Among the

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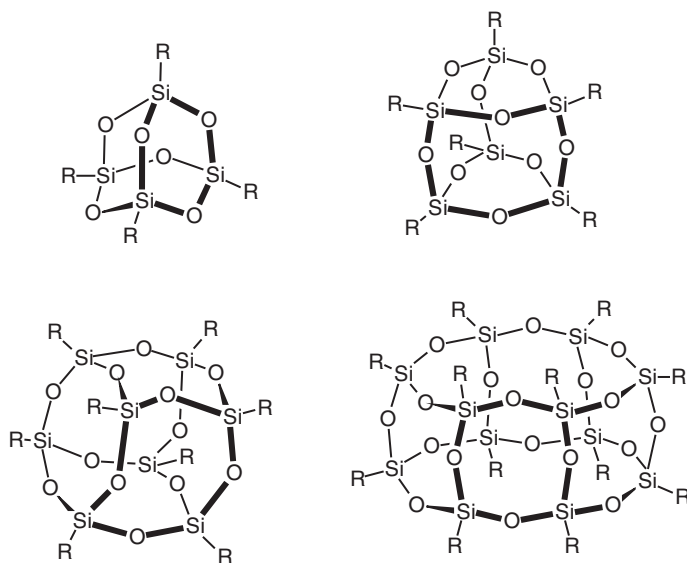
SCHEME 1. Completely condensed oligomeric silsesquioxanes (R = H, alkyl, cycloalkyl, aryl).

simplest members of this class, the silsesquioxane cage molecules $(HSiO_{3/2})_n$ with $n = 8, 10, 12, 14$ and 16 have been reported.[8,9] Scheme 1 gives an overview of such *closo*-silsesquioxane cages known to date.

Much more interesting with respect to various promising applications are incompletely condensed silsesquioxanes retaining reactive Si–OH functional groups. Compounds of this type range from simple disiloxanediols, $[RSi(OH)_2]_2O$, to 12-membered-ring tetrasilanols and incompletely condensed cubic cage compounds. Scheme 2 depicts the most prominent examples of incompletely condensed silsesquioxanes. Among these, the cage-like derivatives can be regarded as small, soluble, three-dimensional fragments of certain silica structures such as β-tridymite and β-crystobalite. Feher and co-workers[10] were the first to point out this structural relationship. This important finding was the starting point for numerous studies in the area of incompletely condensed silsesquioxanes and metallasilsesquioxanes derived from them.

The first report on such compounds dates back to 1965, when Brown and Vogt first described the polycondensation of trichlorocyclohexylsilane, $CySiCl_3$ (**1**, Cy = *cyclo*-C_6H_{11}), in acetone/water mixtures.[11] Thus given the right reaction conditions, incompletely condensed silsesquioxanes can be isolated from the same reaction mixtures as their *closo*-counterparts. Until now the main synthetic access to incompletely condensed polyhedral silsesquioxanes involves hydrolysis of organo-trichlorosilanes followed by polycondensation. In recent years several synthetic methods have also been developed to open the closed-cage structures depicted in Scheme 1 in order to convert these rather unreactive materials into synthetically more useful oligosilanol derivatives.[12–17]
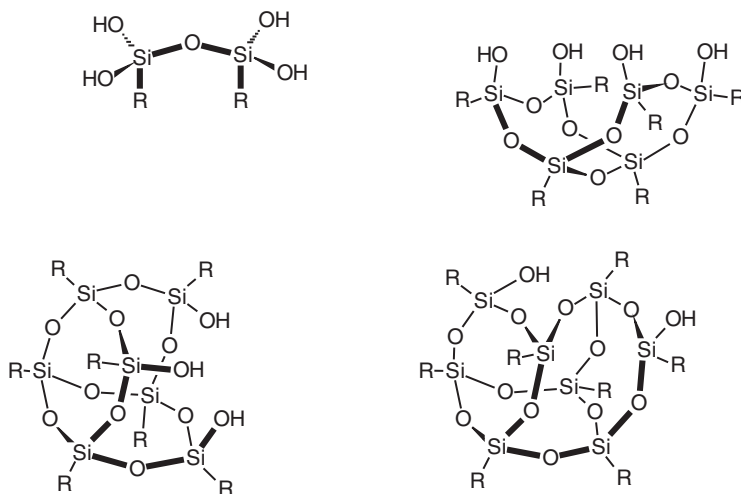
SCHEME 2. Incompletely condensed oligomeric silsesquioxanes (R = alkyl, cycloalkyl, aryl).

The formation of incompletely condensed polyhedral silsesquioxanes involves hydrolysis of the starting monoorganosilanes $RSiX_3$ (X = Cl, OR) followed by a multistep hydrolysis process as illustrated in Scheme 3. In the first step the organo-trichlorosilane (or organotrialkoxysilane) is attacked by water to form an organo silanetriol intermediate, which under these conditions is generally unstable with respect to subsequent condensation reactions. Among open-chain condensation products which can be found in these reaction mixtures are tetraorganodisiloxanediols and hexaorganotrisiloxanetriols. Other intermediates can be cyclic oligosilanols. Finally, completely and incompletely condensed oligomeric silsesquioxanes are formed. The relative amounts of individual compounds in the resulting reaction mixtures depend on several factors such as the nature of the R group, the pH as well as the concentration of water and solvents.[18–20]

By far the most important and most thoroughly investigated representatives among the incompletely condensed polyhedral silsesquioxanes are the heptameric trisilanols $R_7Si_7O_9(OH)_3$ (Scheme 4).

The fact that silsesquioxane molecules like 2–7 contain covalently bonded reactive functionalities make them 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 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 metal-lasilsesquioxanes also receives considerable current interest.[1,2,10,21] As mentioned above, incompletely condensed silsesquioxanes of the type $R_7Si_7O_9(OH)_3$ (2–7, Scheme 4) share astonishing structural similarities with β-tridymite and β-cristobalite and are thus quite realistic models for the silanol sites on silica surfaces.[1,2,21–26] Metal complexes derived from 2–7 are therefore commonly regarded as "realistic" models for industrially important metal catalysts immobilized on silica surfaces.[1,2,22] It is
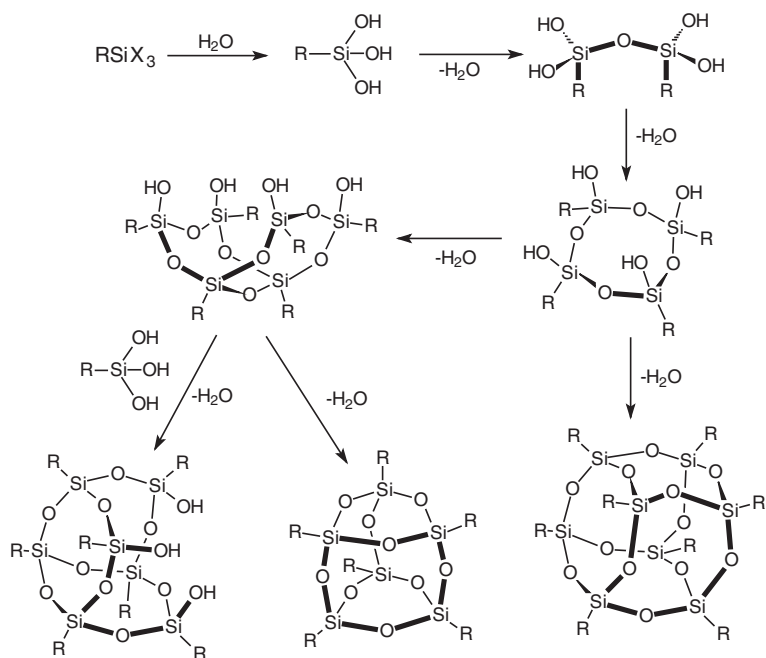
SCHEME 3. Formation of completely and incompletely condensed silsesquioxanes upon hydrolysis of $RSiX_3$ (X = Cl, OR) followed by condensation steps.
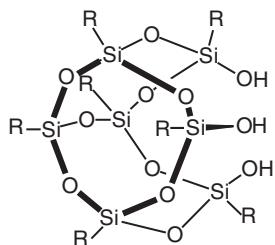
2: R = *cyclo*-C_5H_9

3: R = *cyclo*-C_6H_{11}

4: R = *cyclo*-C_7H_{13}

5: R = norbornyl

6: R = *i*-butyl

7: R = *i*-octyl

SCHEME 4. Schematic representation of heptameric trisilanols $R_7Si_7O_9(OH)_3$.
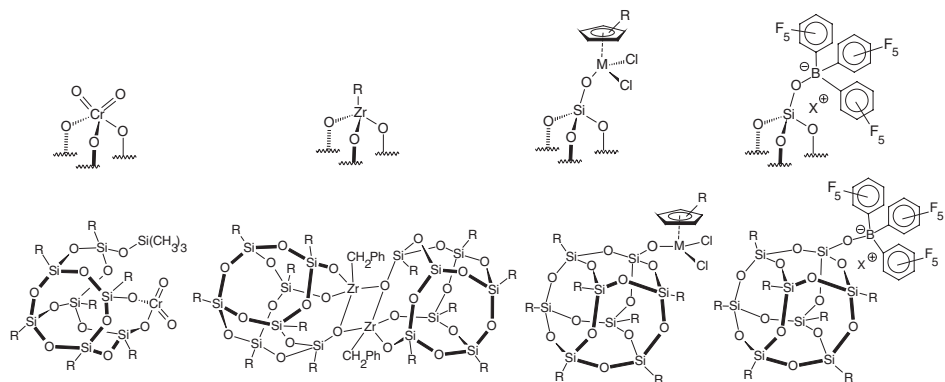
SCHEME 5. Silica-supported species, which have been successfully modeled with the use of silsesquioxanes.

mainly the latter aspect, i.e. the mimicking of heterogeneous metal catalysts with the use of soluble compounds, that currently attracts various research groups to the chemistry of incompletely condensed silsesquioxanes. Examples of silica-supported species, which have been successfully modeled with the use of silsesquioxanes are e.g., Phillips- and Ziegler-Natta-type olefin polymerization catalysts as well as silica-supported perfluoroborato co-catalysts (Scheme 5).[27]

II

SILSESQUIOXANE PRECURSORS

Preparation and derivative chemistry of **3** have been mainly developed by Feher and co-workers.[10] The preparation of the cyclohexyl-substituted derivative **3** is simple and straightforward, though time-consuming. The synthetic procedure involves the controlled hydrolysis of **1** in an acetone/water mixture. Separation of **3** from two other silsesquioxane derivatives (the 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, $CySi(OH)_3$ (**8**), requires reaction times of up to 3 years (!) to proceed to completion. In the case of R = cyclohexyl, the process cannot be accelerated significantly by means of stirring, heating, ultrasound etc.[10] However, synthetically useful quantities of **3** can be "harvested" already after a few months.

The hydrolysis/condensation process takes a somewhat different course when cyclopentyl and cycloheptyl substituents are employed instead of cyclohexyl. In 1991 Feher *et al.*[28] reported the preparation of **2** and **4** *via* hydrolytic condensation reactions of c-$C_5H_9SiCl_3$ (**9**) and c-$C_7H_{13}SiCl_3$ (**10**), respectively. It was reported that these straightforward syntheses produce multigram quantities of incompletely condensed silsesquioxanes within a few days. In these two cases no completely condensed silsesquioxane derivatives were formed. While **2** was obtained as the sole

product, a mixture of **4** and the tetrasilanol $(c\text{-}C_7H_{13})_6Si_6O_7(OH)_4$ (**11**) was obtained with R = cycloheptyl. The cyclopentyl derivative **2** has been frequently employed in the synthesis of metallasilsesquioxanes, whereas **4** did not receive much attention as a possible starting material. Thus far, the majority of metallasilsesquioxanes have been synthesized starting with the cyclohexyl-substituted species **3**. In our laboratory, we found over the years that crystallinity and/or solubility of metallasilsesquioxanes are generally most favorable when **3** is used as starting material. These practical reasons justify the greater efforts put into the time-consuming and more tedious preparation of **3** as compared to **2** and **4**.

The preparation of the heptanorbornyl silsesquioxane trisilanol **5** has been reported by Maschmeyer et al.[29] It is formed in admixture with the corresponding tetrasilanol. The norbornyl-substituted species still await further exploration as precursors in metallasilsesquioxane chemistry. The same applies for the isobutyl and isooctyl derivatives **6** and **7**, respectively, which have been propagated in the patent literature by Lichtenhan and Abbenhuis.[1] The application of high-speed experimentation techniques to optimize the preparation of silsesquioxanes as precursors for Ti catalysts has been reported by Maschmeyer et al.[30]

Various synthetic routes are available to introduce metal atoms into the cage systems of **2**–**7**. The most straightforward route involves protonation of suitable metal precursors such as alkoxides, amides or organometallic compounds by the free trisilanols **2**–**7**.[1–3] For example, as shown by Feher et al., the reactivity of **3** can be modified and tuned by silylation of the Si–OH functions using Me_3SiCl/NEt_3 in different stoichiometric amounts.[10,31] This way the silylated derivatives $Cy_7Si_7O_9(OH)_2(OSiMe_3)$ (**12**), $Cy_7Si_7O_9(OH)(OSiMe_3)_2$ (**13**) and $Cy_7Si_7O_9(OSiMe_3)_3$ (**14**) can be selectively prepared starting from **3**. Another possibility of modifying the reactivity of **3**, **12** and **14** is to prepare the corresponding thallium silanolates by treatment of the free silanols with thallium ethoxide (vide infra).[32] Both the silyl derivatives and the thallium salts have been successfully employed in the preparation of metallasilsesquioxanes, especially via reactions with high-oxidation state transition metal halides.[1–3]

III

METALLASILSESQUIOXANES

A. Metallasilsesquioxanes of Main-Group Metals

1. Group 1 Metal Derivatives (Li, Na, K): Useful Starting Materials

Fully metalated silsesquioxane derivatives of the type $Cy_7Si_7O_9(OM)_3$ (M = Li, Na, K) would constitute highly desirable precursors for the construction of "realistic" catalyst model compounds, including novel heterobimetallic species. However, such alkali metal derivatives of **2**–**7** were unknown until recently, and structural information on such materials was lacking. There have also been contrasting reports in the literature concerning the metalation of **3** by alkali metal
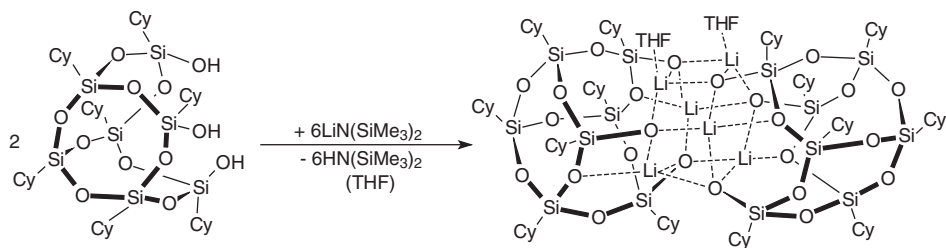
Scheme 6. Synthesis of [(Cy$_7$Si$_7$O$_{12}$)$_2$Li$_6$(THF)$_2$] THF (**16**).

reagents. It was reported by Feher *et al.* that treatment of **3** with three equivalents of NaO*t*Bu resulted in complete breakdown of the silsesquioxane cage.[23] In contrast, Aspinall *et al.* more recently succeeded in synthesizing Cy$_7$Si$_7$O$_9$(OLi)$_3$ (**15**) by the reaction of **3** with *n*-butyllithium.[33] Cy$_7$Si$_7$O$_9$(OLi)$_3$ (**15**) was isolated in virtually quantitative yield as an amorphous, air-stable (!) solid of unknown structure. We found in our laboratory that with the proper choice of deprotonating agents well-defined, crystalline alkali metal silsesquioxanes are readily available. These are excellent precursors for the preparation of unprecedented catalyst model compounds.

Alkali metal bis(trimethylsilyl)amides are the reagents of choice for achieving smooth and high-yield deprotonation of the incompletely condensed silsesquioxane **3**.[34] Treatment of **3** with LiN(SiMe$_3$)$_2$ in diethyl ether/THF (tetrahydrofuran) according to Scheme 6 afforded the crystalline lithium silsesquioxane dimer [(Cy$_7$Si$_7$O$_{12}$)$_2$Li$_6$(THF)$_2$] · THF (**16**) in 93% yield. This reaction is not limited to the THF-adduct **16**. The corresponding acetone solvate [(Cy$_7$Si$_7$O$_{12}$)$_2$Li$_6$(Me$_2$CO)$_3$] (**17**) as well as the dimeric potassium derivative [(Cy$_7$Si$_7$O$_{12}$)$_2$K$_6$(DME)$_4$] (**18**) have been isolated in a similar manner.[34,35]

An X-ray diffraction study revealed a dimeric molecular structure of **16** (Scheme 6). The central structural unit of **16** consists of a box-shaped Li$_6$O$_6$ 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 tetracoordination around each lithium. Structurally related box-shaped Li$_6$O$_6$ or Li$_6$S$_6$ polyhedra have previously been reported for some hexameric lithium phenoxides or arenethiolates,[36] but are unprecedented in silsesquioxane chemistry. The same structural motif has been established for the closely related molecular structure of [(Cy$_7$Si$_7$O$_{12}$)$_2$Li$_6$(Me$_2$CO)$_3$] (**17**).[34,35]

The use of KN(SiMe$_3$)$_2$ as metalating reagent enabled us to prepare the dimeric potassium derivative [(Cy$_7$Si$_7$O$_{12}$)$_2$K$_6$(DME)$_4$] (**18**) as a crystalline solid, which was structurally characterized by X-ray diffraction (Scheme 7). Here again a box-shaped K$_6$O$_6$ polyhedron forms the central structural unit. Four potassium ions are coordinated by DME (1,2-dimethoxyethane) ligands.[35]

The lithiated species **15** and **16** represent highly valuable intermediates in the synthesis of novel metallasilsesquioxanes. For this purpose it is not essential to isolate these lithium derivatives as crystalline solids. It has been found a convenient synthetic route to prepare **15** *in situ* by metalation of **3** with three equivalents of LiN(SiMe$_3$)$_2$
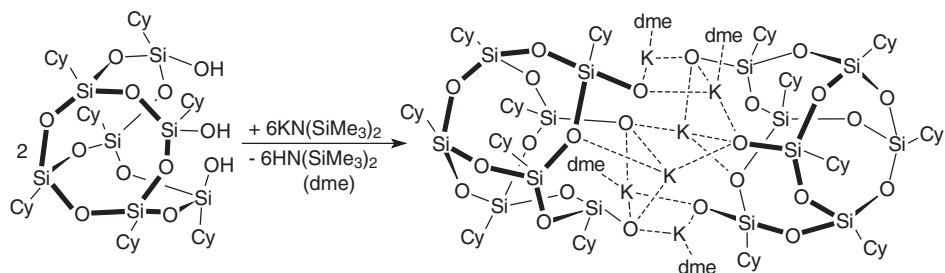
SCHEME 7. Synthesis of [(Cy$_7$Si$_7$O$_{12}$)$_2$K$_6$(DME)$_4$] (**18**).

and to use the resulting solution for subsequent reactions. *In situ* prepared **15** has already been successfully employed for the synthesis of novel heterobimetallic metallasilsesquioxanes containing lithium and beryllium,[37] boron,[38] zirconium,[34] lanthanide elements[33,34] and chromium.[35] They can be expected to play an increasing role as highly useful building blocks in metallasilsesquioxane chemistry.

2. Group 2 Metal Derivatives (Be, Mg)

Metallasilsesquioxanes containing alkaline earth elements remain a little investigated class of compounds. Until now, beryllium and magnesium are the only elements of Group 2 which have been successfully incorporated into silsesquioxane cages. The compound [Cy$_7$Si$_7$O$_{12}$BeLi]$_2$ · 2THF (**19**) was prepared in high yield by reacting *in situ* prepared Cy$_7$Si$_7$O$_9$(OLi)$_3$ (**15**) with anhydrous BeCl$_2$ in THF at 20 °C (Scheme 8).[37] The molecular structure of **19** has been determined by X-ray diffraction and was the first structurally characterized silsesquioxane derivative of beryllium. Self-assembly under formation of a dimer occurs in a rather unsymmetrical manner. Two lithium and two beryllium ions are bridged by the deprotonated silsesquioxane ligands in such a way that a different coordination environment results for each metal ion. THF ligands are coordinated to one lithium and one beryllium, while the other two metal ions are connected only to siloxide oxygens. Both Li ions are tetracoordinate. In contrast, the coordination geometry around one beryllium is distorted tetrahedral, while its counterpart is coordinated in an exactly trigonal planar fashion (angle sum 359.8°).

The only other alkaline earth metal for which metallasilsesquioxanes have been reported is magnesium. The first magnesium derivative was reported by Liu in 1996.[39,40] Butylethylmagnesium reacts with **3** to give [Cy$_7$Si$_7$O$_9$(OH)O$_2$Mg]$_n$ (**20**, $n = 1, 2$). Treatment of **20** with TiCl$_4$ afforded the novel heterobimetallic Mg/Ti metallasilsesquioxane [Cy$_7$Si$_7$O$_{12}$MgTiCl$_3$]$_n$ (**21**, $n = 1, 2$), which shows a high catalytic activity for ethylene polymerization. A polymeric magnesasilsesquioxane material was made by Lichtenhan *et al.* from a silsesquioxane disilanol and dialkyl-magnesium,[41] and another magnesium silsesquioxane has been used as an intermediate in reactions with epoxides.[42] The reaction of **2** with methylmagnesium chloride leads to the unprecedented tetranuclear magnesium silsesquioxane complex **22** in high yield (87%) as large, colorless, cube-like crystals (Scheme 9).[43] The crystal structure shows an unusually short Mg–Cl bond (2.255 Å), indicative of an
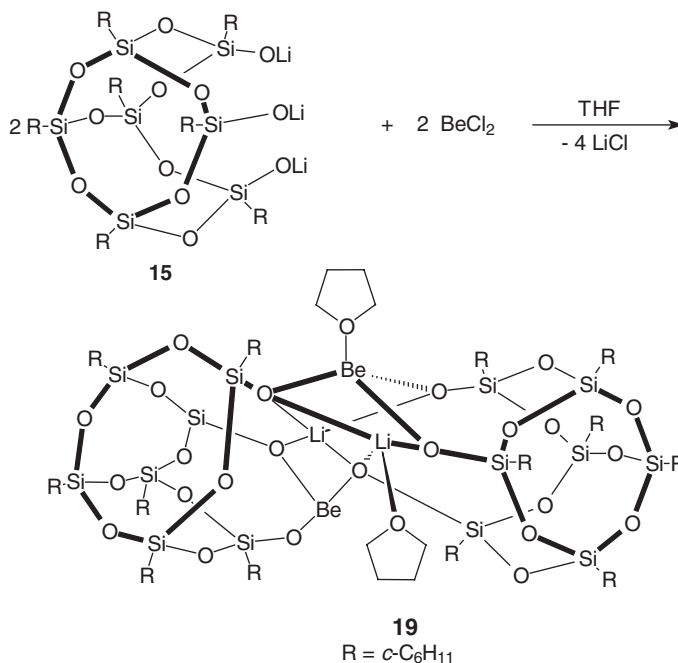
SCHEME 8. Synthesis of $[Cy_7Si_7O_{12}BeLi]_2 \cdot 2THF$ (**19**).
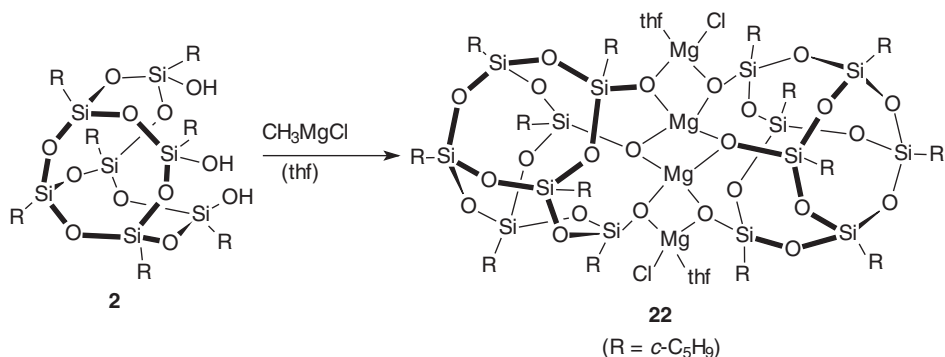
SCHEME 9. Synthesis of $[(c\text{-}C_5H_9)_7Si_7O_{12}]_2Mg_4Cl_2(THF)_2$ (**22**).

electron-deficient magnesium atom. Compound **22** has been used as transmetalation reagent for the synthesis of other metallasilsesquioxanes (Si, Ti), but transmetalation activity was found to be low.

Microporous, amorphous Mg–Si–O metallosilicates with a very narrow pore size distribution around 6 Å diameter and a typical surface area of ca 350 m^2/g were obtained from the controlled calcination of compound **22**.[44] The resulting Mg–Si–O material was found to be very active in 1-butanol conversion even at 200 °C giving both dehydrogenation and dehydration.

## 3. Group 13 Metal Derivatives (B, Al, Ga, In, Tl)

Group 13 metallasilsesquioxane chemistry is well developed. All elements from boron to thallium have been successfully incorporated into silsesquioxane cages. The first boron-containing silsesquioxane species, $[Cy_7Si_7O_{12}B]_2$ (**23**), was reported by Feher *et al.* in 1992.[45] The analogous cyclopentyl-substituted derivative was described by Duchateau *et al.*[38] Dimeric **24** was prepared as colorless crystals in 64% yield upon treatment of **2** with BI_3 in the presence of triethylamine according to Scheme 10. Compound **24** was also obtained when **2** was reacted with $LiBH_4$, eliminating LiH.[38]

When the monosilylated precursor **26** was reacted in a similar manner with $LiBH_4$ according to Scheme 11, the resulting product was the solvent-free lithium borate salt **27** (74% yield). This compound could be recrystallized from *n*-hexane.

In addition, several silsesquioxane–borato complexes have been described and their reactivity investigated.[46] Treatment of $B(C_6F_5)_3$ with the *closo*-silsesquioxane monosilanol $(c\text{-}C_5H_9)_7Si_8O_{12}(OH)$ (**28**) or **2** in the presence of a Brønsted base afforded the silsesquioxane–borates $X^+[(c\text{-}C_5H_9)_7Si_8O_{13}B(C_6F_5)_3]^-$ (**29**, $X^+ = PhN(H)Me_2^+$; **30**, $X^+ = Et_3NH^+$) and $X^+[(c\text{-}C_5H_9)_7Si_7(OH)_2O_{10}B(C_6F_5)_3]^-$ (**31**, $X^+ = PhN(H)Me_2^+$; **32**, $X^+ = Et_3NH^+$), respectively (cf. Scheme 5). When the stronger nucleophilic base pyridine is used, only $(C_6F_5)_3B \cdot (NC_5H_5)$ is formed instead, demonstrating the competition between $B(C_6F_5)_3$ and H^+ to react with the
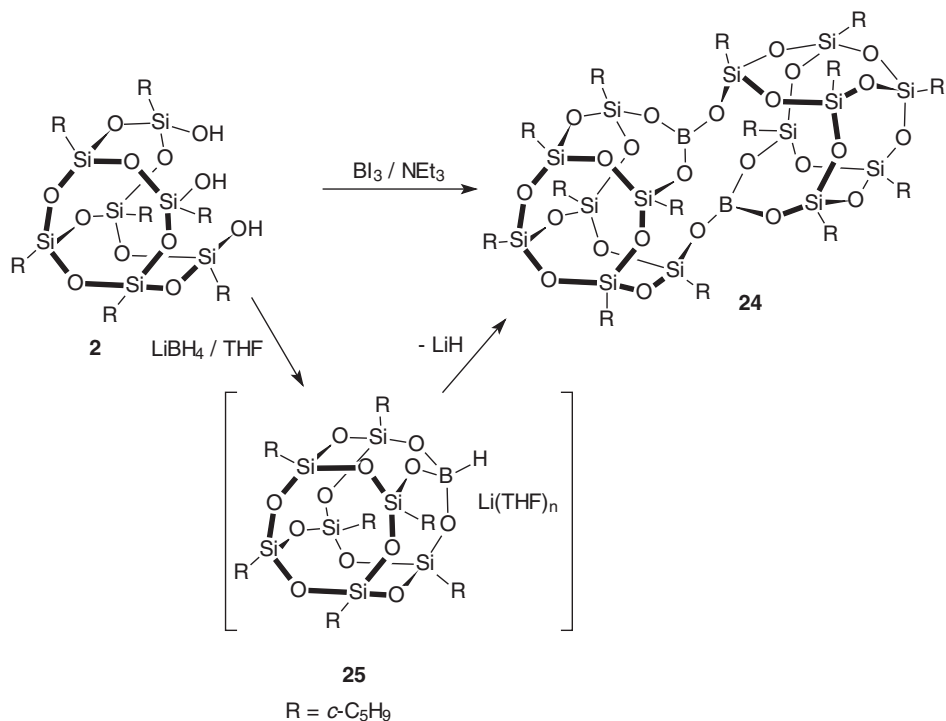

SCHEME 10. Alternative preparations of the dimeric boron silsesquioxane **24**.
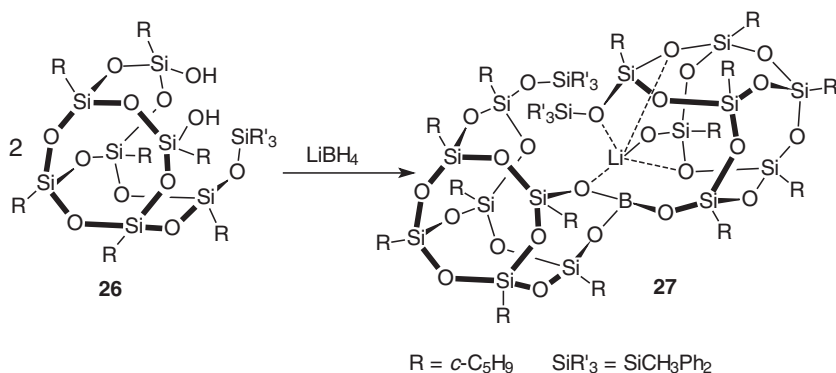
SCHEME 11. Synthesis of Li[B{(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSiMePh$_2$)}$_2$] (**27**).

added amine. The dimethylaniline in **29** and **31** is readily exchanged by NEt$_3$ to form **30** and **32**. With the more nucleophilic base pyridine the B–O bond in **29** and **30** is split, yielding (C$_6$F$_5$)$_3$B · (NC$_5$H$_5$) and the free silsesquioxane silanol **28**. Initial reactivity studies showed that complexes **29**–**32** readily undergo hydrolysis under formation of the hydroxyborato complexes X$^+$[(C$_6$F$_5$)$_3$BOH]$^-$ (X$^+$ = PhN(H)Me$_2^+$, Et$_3$NH$^+$), while alcoholysis of **29** and **31** with i-PrOH gave the alkoxide [PhN(H)Me$_2$]$^+$[(C$_6$F$_5$)$_3$BOiPr]$^-$.[46]
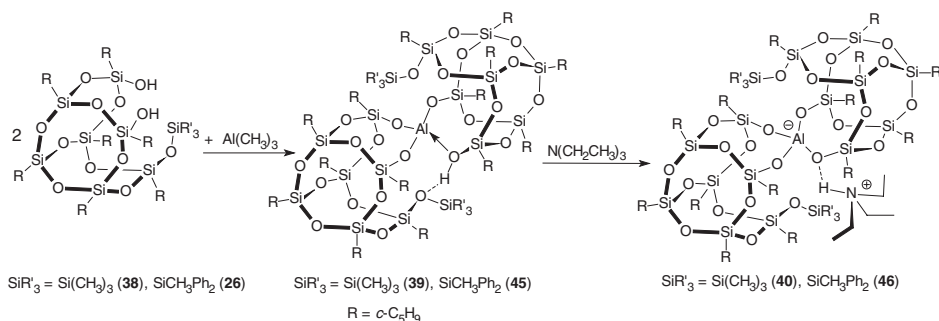
The first aluminasilsesquioxane derivative was made by Feher and co-workers in 1989.[47] The reaction of a benzene solution of **3** with AlMe$_3$ afforded in virtually quantitative yield the dimeric aluminasilsesquioxane [Cy$_7$Si$_7$O$_{12}$Al]$_2$ (**33**), i.e. the aluminum analog of [Cy$_7$Si$_7$O$_{12}$B]$_2$ (**23**). A similar reaction of **3** with (i-PrO)$_3$Al also produced **33** in nearly quantitative yield, although only after prolonged heating to 65–110 °C. No monomeric intermediates could be observed in these reactions. However, the monomeric adducts Cy$_7$Si$_7$O$_{12}$Al(ONMe$_3$) (**34**) and Cy$_7$Si$_7$O$_{12}$Al(OPPh$_3$) (**35**) were readily obtained by cleavage of the dimer in the presence of Me$_3$NO or Ph$_3$PO, respectively.[47] The triphenylphosphine oxide adduct **35** was structurally characterized by X-ray diffraction.

In striking contrast to the formation of dimeric **33** from **3** and AlMe$_3$ as reported by Feher et al.,[47] the analogous reaction between the cyclopentyl-substituted silsesquioxane precursor **2** and AlEt$_3$ according to Scheme 12 afforded polymeric [(c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$Al]$_n$ (**36**), which was found to be insoluble in most common organic solvents (hexane, toluene, THF).[48] Monomeric [(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSiMe$_3$)]AlEt · NEt$_3$ (**37**) was obtained when the monosilylated precursor (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiMe$_3$)(OH)$_2$ (**38**) was treated with one equivalent of AlEt$_3$ in the presence of triethylamine. By allowing AlEt$_3$ to react with two equivalents of **38**, the Brønsted acidic aluminasilsesquioxane [(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSiMe$_3$)]Al[(c-C$_5$H$_9$)$_7$Si$_7$O$_{10}$(OSiMe$_3$)(OH)] (**39**) was selectively formed, which contains a strong intramolecular hydrogen bond. Although the high strength of this hydrogen bond reduces the Brønsted acidity of **39** substantially, the compound can be easily deprotonated by amines to yield the corresponding ammonium salts X$^+$[{(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSiMe$_3$)}$_2$Al]$^-$ (**40**–**42**, X$^+$ = Et$_3$NH$^+$, PhN(H)Me$_2^+$, C$_5$H$_5$NH$^+$).
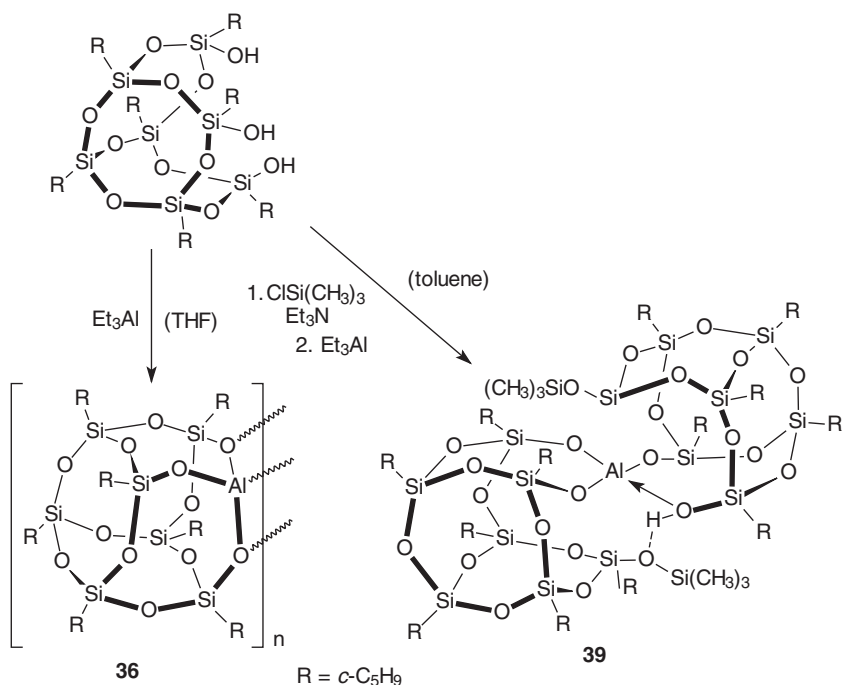
SCHEME 12. Synthesis of the aluminasilsesquioxanes **36** and **39**.
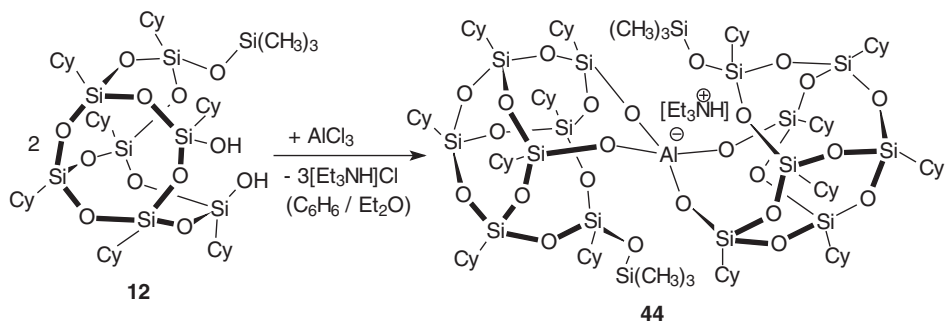
SCHEME 13. Synthesis of $[Et_3NH]^+[\{Cy_7Si_7O_{11}(OSiMe_3)\}_2Al]^-$ (**44**).

An X-ray crystal structure of **40** revealed that the ammonium cation is bonded to the aluminasilsesquioxane anion by a hydrogen bond. The corresponding lithium salt $[Li(THF)_2]^+[\{(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)\}_2Al]^-$ (**43**) could best be prepared by protonolysis of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMe_3)(OH)_2$ (**38**) with half an equivalent of LiAlH$_4$.[48]

The cyclohexyl-substituted analog of **40**, $[Et_3NH]^+[\{(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}_2Al]^-$ (**44**), was synthesized independently in our laboratory by dehydrochlorination of the monosilylated precursor **12** with anhydrous AlCl$_3$ in the presence of triethylamine (Scheme 13).[49] A comparison of the X-ray crystal structures of

SiR'$_3$ = Si(CH$_3$)$_3$ (**38**), SiCH$_3$Ph$_2$ (**26**)   SiR'$_3$ = Si(CH$_3$)$_3$ (**39**), SiCH$_3$Ph$_2$ (**45**)   SiR'$_3$ = Si(CH$_3$)$_3$ (**40**), SiCH$_3$Ph$_2$ (**46**)

R = c-C$_5$H$_9$

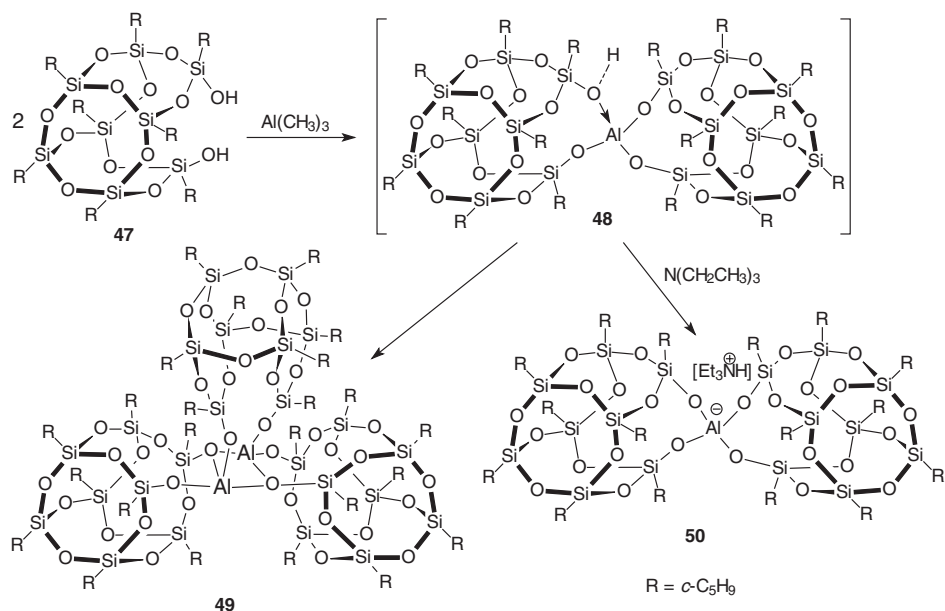SCHEME 14. Formation of aluminasilicates **40** and **46**.

40 and **44** clearly revealed the difference in steric congestion between cyclopentyl and cyclohexyl-substituted aluminasilsesquioxanes. Whereas in the latter structure the aluminasilicate anion and the triethylammonium cation form a separated ion pair,[49] less steric crowding in **40** allows the formation of a contact ion pair in which the ammonium proton forms a hydrogen bond with one of the Al–O–Si oxygen atoms in the aluminasilicate anion.[48]

The steric factors affecting the Brønsted acidity of these aluminasilsesquioxanes have been studied in great detail by Duchateau *et al.* (Scheme 14).[50] By reacting AlMe$_3$ with two equivalents of the monosilylated precursors **38** and **26**, the corresponding Brønsted acidic aluminasilsesquioxanes **39** and **45** were prepared. These complexes react readily with triethylamine to yield the corresponding triethylammonium salts **40** and **46**. Hydrogen bonding between the acidic SiO(H)→Al proton and the pendant silylether function is effectively reduced by increasing the steric bulk of the silyl ether substituents, resulting in a higher acidity for **45** compared to that of **39**.[50]

With the rarely used octameric silsesquioxane ligand (c-C$_5$H$_9$)$_8$Si$_8$O$_{11}$(OH)$_2$ (**47**), which lacks pendant silylether functions, the acidic proton cannot satisfactorily be stabilized. This renders the putative Brønsted acid [(c-C$_5$H$_9$)$_8$Si$_8$O$_{13}$]Al[(c-C$_5$H$_9$)$_8$Si$_8$O$_{12}$(OH)] (**48**) unstable. In the absence of proton acceptors, the disproportionation product [(c-C$_5$H$_9$)$_8$Si$_8$O$_{13}$]$_3$Al$_2$ (**49**) is formed instead of **48**. However, in the presence of triethylamine the initially formed Brønsted acid **48** readily transfers its proton to the amine, affording the triethylammonium salt **50** (Scheme 15).[50]

Several other aluminasilsesquioxanes have been studied in detail by Duchateau *et al.* as model supports for silica-grafted aluminum alkyl species.[51] Upon treatment with AlMe$_3$ the *closo*-silsesquioxane monosilanol (c-C$_5$H$_9$)$_7$Si$_8$O$_{12}$(OH) (**28**) afforded polymeric [{(c-C$_5$H$_9$)$_7$Si$_8$O$_{13}$}AlMe$_2$]$_n$ (**51**), which is readily transformed into the corresponding monomeric pyridine adduct, [(c-C$_5$H$_9$)$_7$Si$_8$O$_{13}$]AlMe$_2$(py) (**52**) (Scheme 16).

When the monosilylated precursor (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiMePh$_2$)(OH)$_2$ (**26**) was analogously reacted with AlMe$_3$, noticeable amounts of the 1:2 product [{(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSiMePh$_2$)}(AlMe$_2$)$_2$]$_2$ (**53**) and the Brønsted acidic 2:1 product **45** were formed besides the main product of the reaction, [{(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSi-MePh$_2$)}AlMe]$_2$ (**54**) (Scheme 17). The latter is a mixture of three dimeric

SCHEME 15. Formation of aluminasilsesquioxanes **49** and **50**.
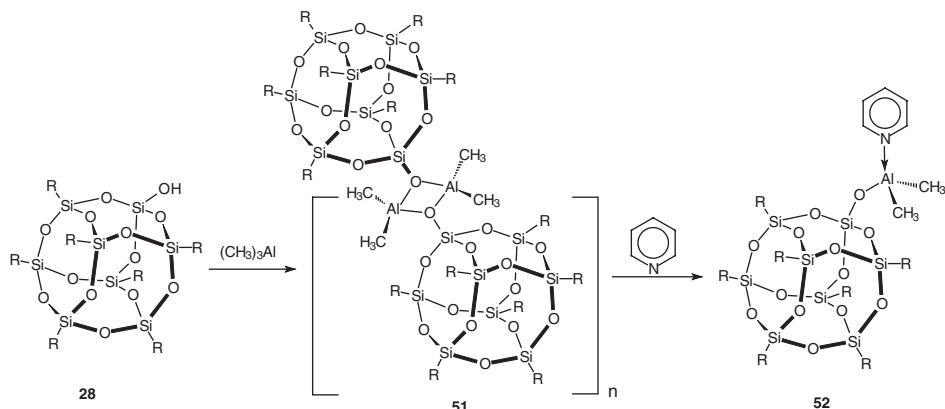
SCHEME 16. Synthesis of aluminasilsesquioxanes **51** and **52**.

conformational isomers, all with the aluminum methyls *trans* to each other. The difference of the conformers originates from the different orientation of the silsesquioxane ligands.[51]

The first and thus far only indasilsesquioxane derivative was synthesized in our laboratory. The compound $[Cy_7Si_7O_{12}InMe(OH)]_2$ (**55**) was prepared in high yield (84%) by reacting trisilanol **3** with trimethylindium in toluene solution at 20 °C (Scheme 18). The molecular structure of **55** has been determined by X-ray diffraction. Self-assembly under formation of a centrosymmetric dimer occurs through
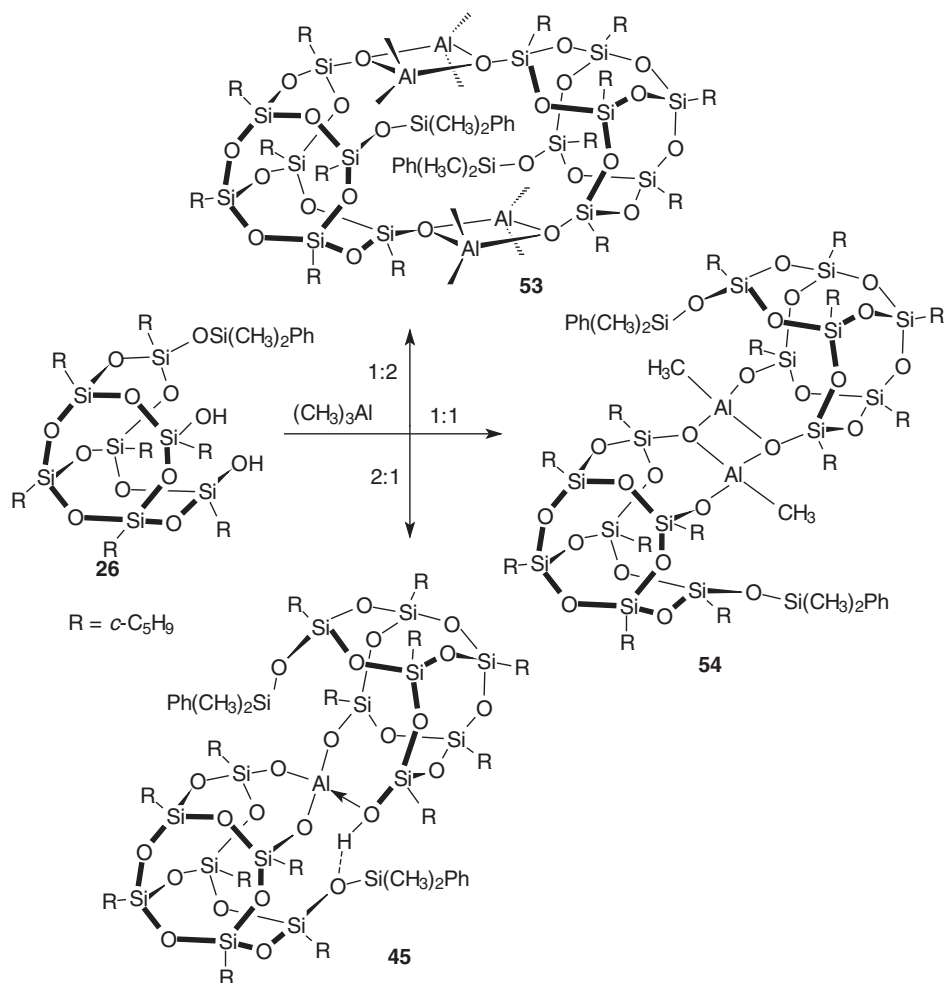
SCHEME 17. Reactions of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMePh_2)(OH)_2$ (**26**) with $AlMe_3$.

cage oxygen atoms, which act as bridging ligands between the two indium atoms. The central four-membered In_2O_2 ring forms a rectangular plane with In–O–In and O–In–O bond angles of 101.0(1) and 79.0(1), respectively, and an average In–O distance of 2.123 Å. Certainly, the most striking structural feature of **55** is the presence of two Si–OH groups in close proximity to the methylindium centers. However, no further protonation of the methyl groups at indium can occur, because the silanol functions are both engaged in hydrogen bonding to oxygen atoms of the silsesquioxane cages.[52]

Several gallium-containing metallasilsesquioxanes have been reported, although their chemistry is still less developed than that of their aluminum congeners. According to a report by Feher et al., **3** reacts with $GaCl_3$ in the presence of "proton sponge" to form the ionic complex $[C_{14}H_{19}N_2]^+[Cy_7Si_7O_{12}GaCl]^-$ (**56**)
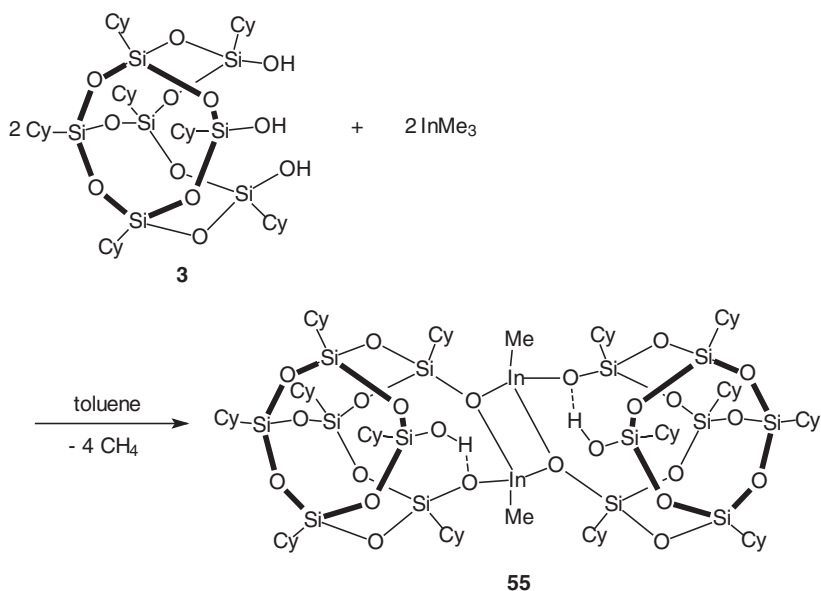
SCHEME 18. Synthesis of $[Cy_7Si_7O_{12}InMe(OH)]_2$ (**55**).

56   (R = c-C_6H_{11})
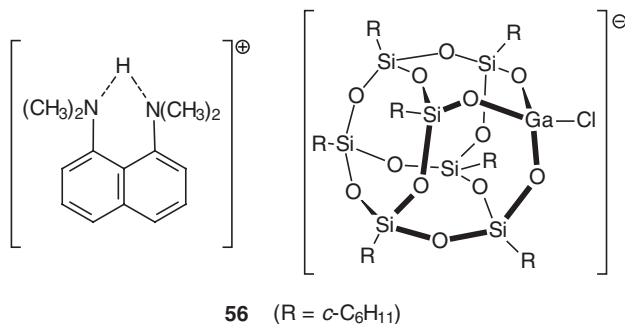
SCHEME 19. Structure of $[C_{14}H_{19}N_2]^+[Cy_7Si_7O_{12}GaCl]^-$ (**56**).

(Scheme 19).[53] Refluxing of **56** in THF led to the formation of dimeric $[Cy_7Si_7O_{12}Ga]_2$ (**57**) as a structural analog of the corresponding boron and aluminum dimers **23** and **33**, respectively. The reactivity of **58** also resembles that of the aluminum species **33** in that the dimeric structure could readily be split by triphenylphosphine oxide to form the neutral Lewis base adduct $Cy_7Si_7O_{12}Ga(OPPh_3)$ (**58**).

More recently the chemistry of gallium-containing metallasilsesquioxanes has been studied in greater detail by Duchateau and co-workers (Scheme 20).[38] Using similar conditions Feher *et al*. reported for the synthesis of **56** and the dimer $[Cy_7Si_7O_{12}Ga]_2$ (**57**),[53] the reaction of **3** with $GaCl_3$ in the presence of triethylamine gave moderate yields (38%) of the monomeric gallasilsesquioxane **59**. The bulky
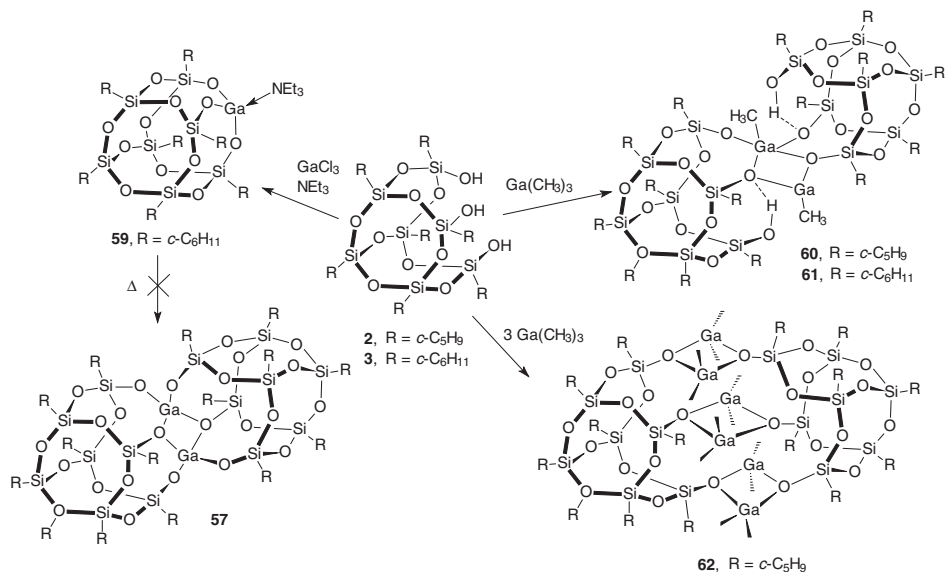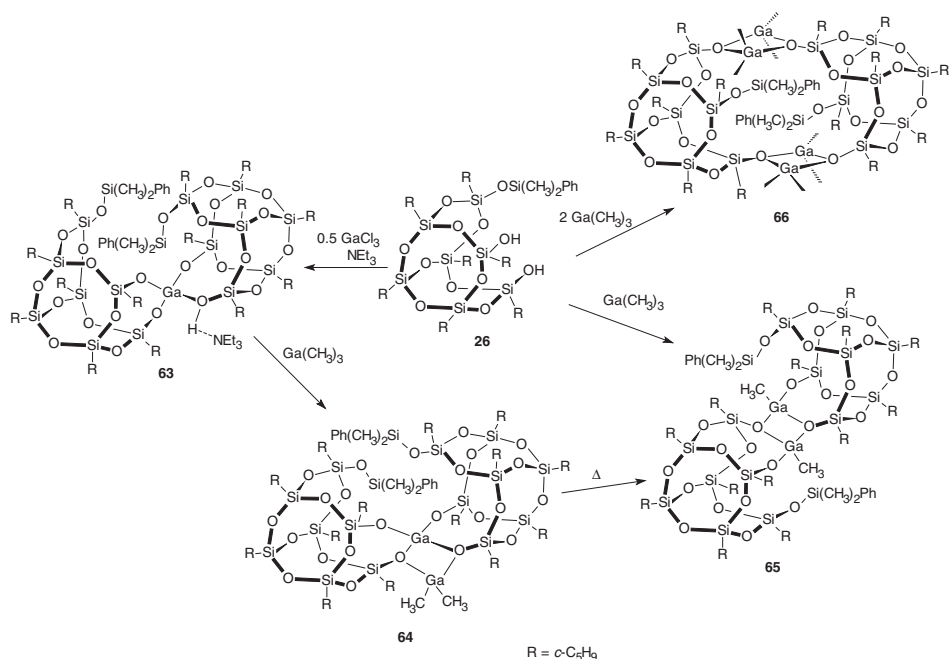
SCHEME 20. Synthesis of gallasilsesquioxanes derived from **2** and **3**.

triethylamine in **59** binds surprisingly strongly to the gallium center, as attempts to form $[Cy_7Si_7O_{12}Ga]_2$ (**57**) by heating **59** in toluene failed.

A second series of gallasilsesquioxanes was prepared using the monosilylated derivative **26** as precursor.[38] Salt metathesis between **26** and 0.5 equivalents of gallium trichloride in the presence of triethylamine yielded the triethylammonium gallate $[Et_3NH]^+[\{(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)\}_2Ga]^-$ (**63**), similar to the aluminate complex $[Et_3NH]^+[\{(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMePh_2)\}_2Al]^-$ (**46**), which was obtained when **26** was reacted with $AlCl_3$ in the presence of NEt_3. An X-ray crystal structure determination of **63** revealed a contact ion pair in the solid state in which the ammonium ion is hydrogen bonded to one of the Ga–O–Si oxygens.

Upon treatment with another equivalent of trimethylgallium, **63** is readily deprotonated with liberation of triethylamine and formation of the dimethylgallium gallate **64**. When, instead of **2**, the monosilylated disilanol **26** was treated with an equimolar amount of GaMe₃, the dimeric monomethylgallium silsesquioxane complex **65** was formed. A similar reaction with two equivalents of trimethylgallium afforded the tetranuclear gallium complex **66** in good yields (72%) in the form of an air-stable white solid (Scheme 21).[38] Controlled calcination of certain gallium silsesquioxane precursors has been shown by Wada *et al.*[54] to afford microporous gallium silicate materials.

Several thallium silsesquioxane complexes have been reported by Feher *et al.*[23,32] These include the compounds $R_7Si_7O_9(OTl)_3$ (**67**, R = $c\text{-}C_5H_9$; **68**, R = $c\text{-}C_6H_{11}$), $R_7Si_7O_9(OSiMe_3)(OTl)_2$ (**69**, R = $c\text{-}C_5H_9$; **70**, R = $c\text{-}C_6H_{11}$) and $R_7Si_7O_9(OSiMe_3)_2(OTl)$ (**71**, R = $c\text{-}C_5H_9$; **72**, R = $c\text{-}C_6H_{11}$). These thallasilsesquioxanes are not prone to cycloelimination reactions or the formation of "ate" complexes. Thus they are versatile anionic equivalents of the incompletely condensed silsesquioxane

SCHEME 21. Synthesis of gallasilsesquioxanes derived from **26**.

systems, which react with a variety of metal and non-metal halides to afford high yields of the corresponding metallasilsesquioxanes. They are especially useful for reactions with high-valent transition metal halides where dehydration reactions of the silsesquioxane framework is a frequently encountered problem. However, their overall synthetic value is limited due to the high toxicity of thallium reagents.

4. Group 14 Metal Derivatives (Ge, Sn)

Silylated derivatives of incompletely condensed silsesquioxanes are often used as starting materials for the synthesis of metallasilsesquioxanes. However, their chemistry is not considered to fall within the scope of this review article. Thus, only germanium and tin derivatives will be mentioned. Apparently, lead-containing metallasilsesquioxanes have not yet been reported in the literature. The first report on a germanium silsesquioxane complex dates back to 1989, when Feher *et al.*[10] described the synthesis of $Cy_7Si_7O_{12}GeMe$ (**73**) from **3** and methyl trichlorogermane in the presence of triethylamine. Colorless crystals of **73** were isolated in 92% yield. In the same paper, the synthesis of the first tin(IV) silsesquioxane derivative was reported. Treatment of **3** with $MeSnCl_3/NEt_3$ afforded $Cy_7Si_7O_{12}SnMe$ (**74**) in 96% yield. A series of di- and triorganotin(IV) silsesquioxane complexes has been prepared in our laboratory in 1999.[55] These include the diorganotin(IV)-capped silsesquioxanes $Cy_7Si_7O_9(OSiMe_3)(O_2SnR_2)$ (**75**, R = Me; **76**, R = *n*-Bu) and the triorganotin(IV) derivatives $Cy_7Si_7O_9(OSiMe_3)_2(OSnR_3)$ (**77**, R = Me; **78**,
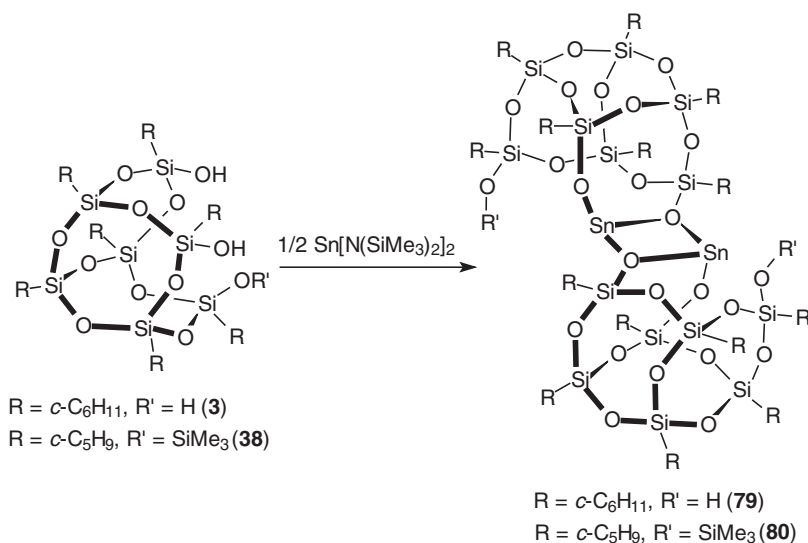
SCHEME 22. Preparation of stannasilsesquioxanes **79** and **80**.

R = CH$_2$Ph). All these compounds have been made by reacting **3** with the corresponding organotin(IV) chlorides in the presence of appropriate amounts of triethylamine. Recently various other stannasilsesquioxanes have been reported, including the first tin(II) species.[56] Protonolysis of tin(II) amides was found to be an effective route to prepare tin(II) silsesquioxanes. For example, the reaction of Sn[N(SiMe$_3$)$_2$]$_2$ with trisilanol **3** or disilanol **38** afforded the stannasilsesquioxanes [Cy$_7$Si$_7$O$_{11}$(OH)Sn^{II}]$_2$ (**79**) and [(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSiMe$_3$)Sn^{II}]$_2$ (**80**) (Scheme 22). Both are dimers with three-coordinated tin centers. Taking the lone pair into account, the tin atoms are distorted-tetrahedrally surrounded. The central four-membered Sn$_2$O$_2$ ring is planar.

Similar to the longer known diorganotin(IV)-capped silsesquioxanes Cy$_7$Si$_7$ O$_9$(OSiMe$_3$)(O$_2$SnR$_2$) (**75**, R = Me; **76**, R = n-Bu), two stannasilsesquioxanes have been prepared in which two silanol oxygens are bridged by a Sn(acac)$_2$ moiety. The compounds **81** and **82** were made in good yields according to Scheme 23 by reaction of the precursors **2** and **38**, respectively, with Cl$_2$Sn(acac)$_2$ in the presence of NEt$_3$.[56]

Unexpectedly, the reaction of SnCl$_4$ with **38** was sluggish and produced ill-defined products.[56] Treatment of **2** with an equimolar amount of SnCl$_4$ in toluene in the presence of NEt$_3$ afforded the ionic trimer **83** instead of the expected mono-meric (c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$SnCl (Scheme 24). In this chloride-bridged cluster each tin atom is connected to two different silsesquioxane cages. Three chlorides are μ$_2$-bridging, while one is μ$_3$-bridging between all three tin centers. The chloro complex **83** is moisture sensitive and gradually hydrolyses to the corresponding hydroxide species **84**. When for example, a bromoform solution of **83** was layered with water and left at ambient temperature, large colorless crystals of **84** suitable for X-ray analysis formed overnight. Complex **84** is isostructural to **83** and consists of an
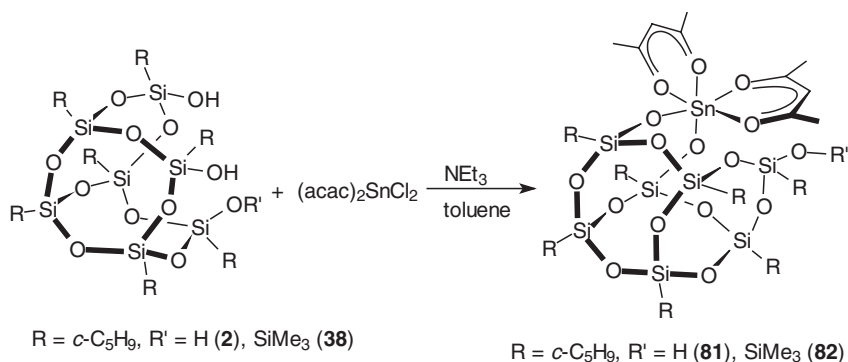
SCHEME 23. Preparation of stannasilsesquioxanes **81** and **82**.
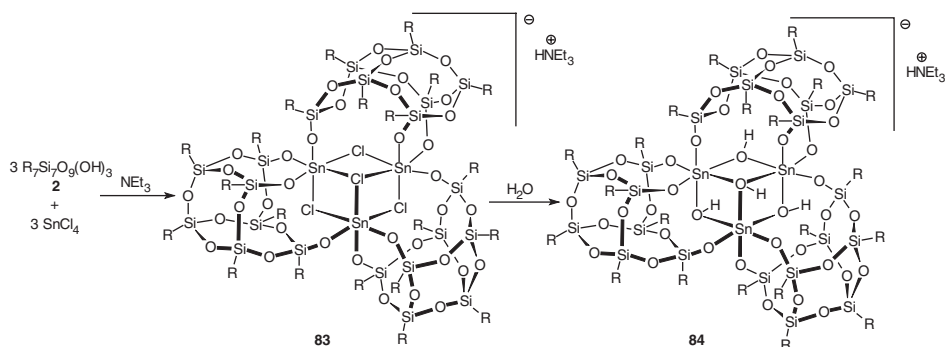
SCHEME 24. Preparation of the trinuclear tin silsesquioxane clusters **83** and **84**.

anionic cluster in which three silsesquioxane cages are held together by three tin atoms with bridging hydroxyl groups.

B. *Metallasilsesquioxanes of the Early Transition Metals*

1. Group 3 Metal Derivatives (Sc, Y, La, and the Lanthanides and Actinides)

Metallasilsesquioxanes of rare earth metals could be very important as homogeneous analogs of rare earth metal silica-supported catalysts and rare earth silicates, which are potential materials for optoelectronics. Thus this area of research is of considerable interest for several fields of chemistry including catalysis and materials science. However, investigations in the area of metallasilsesquioxanes of rare earth metals are often hampered by difficulties with crystallization and characterization of these compounds. The first metallasilsesquioxanes incorporating lanthanide elements have been described in 1994 by Herrmann *et al.*[57] These materials were obtained by reacting **3** with the tris(silylamides) Ln[N(SiMe₃)₂]₃ of Y and Nd. Due to their very high solubility no structural characterization of the initially formed products was possible. However, with the use of triphenylphosphine oxide
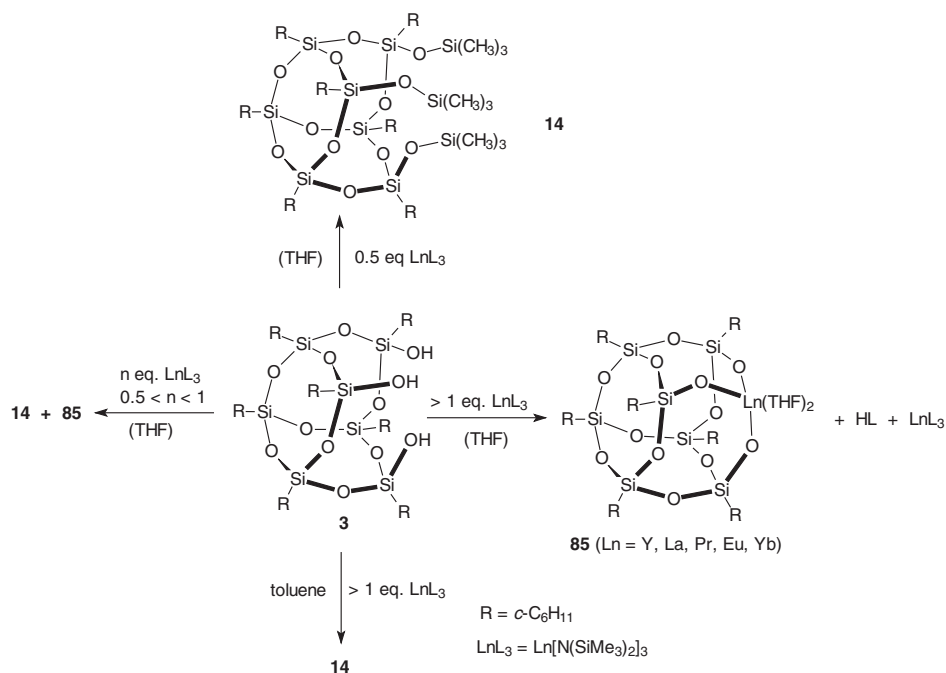
SCHEME 25. Reactions of **3** with Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Y, La, Pr, Eu, Yb).

as supporting ligand X-ray quality single crystals could be obtained, and a dimeric structure was established for the Y and Nd silsesquioxane complexes.

More recently, Aspinall *et al.* reported the synthesis of a series of lanthanide silsesquioxanes resulting from reactions of **3** with lanthanide tris(silylamides) Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Y, La, Pr, Eu, Yb).[58] However, single crystals of these materials suitable for X-ray diffraction could not be obtained. The somewhat complicated situation is illustrated in Scheme 25. The lanthanide tris(silylamides) reacted with two-third equivalents of the trisilanol **3** in THF to give the lanthanide silsesquioxanes **85**, which are dimeric in solution at 233 K. Reaction of Ln[N(SiMe$_3$)$_2$]$_3$ with one equivalent of **3** in THF resulted in complete conversion of **3** to the trisilylated compound **14**, as did the reaction of Ln[N(SiMe$_3$)$_2$]$_3$ with two-third equivalents of **3** in toluene.

Variable temperature ^{13}C NMR data of the Y derivative were consistent with a monomer/dimer equilibrium for compounds **85** in solution as depicted in Scheme 26.[58]

The chloro-functionalized lanthanide silsesquioxane complexes **86** (Ln = Y, La) are accessible by the reaction of **85** with one equivalent of Me$_3$SiCl according to Scheme 27.[58]

Well-defined monomeric derivatives could be obtained by reacting **85** (Ln = Y, La, Yb) with (Me$_2$NCH$_2$CH$_2$)$_2$NMe (PMDTA) (PMDTA = N,N,N′,N″,N″-pentamethyldiethylenetriamine) in a 1:1 molar ratio in THF solution. The products
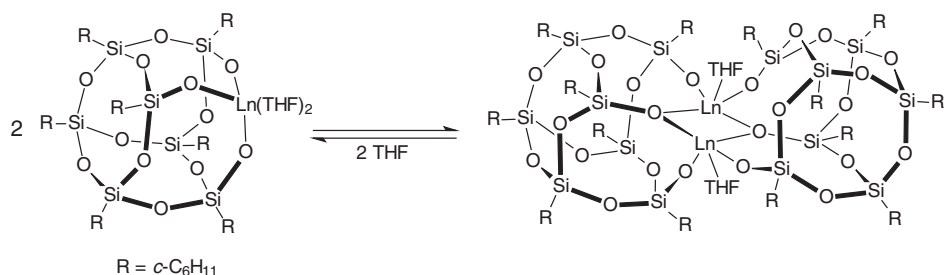
SCHEME 26. Proposed monomer/dimer equilibrium for compounds **85**.
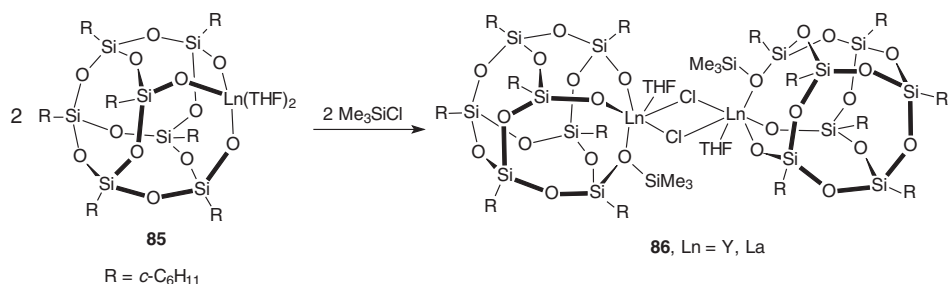
SCHEME 27. Preparation of functionalized lanthanide silsesquioxanes **86**.
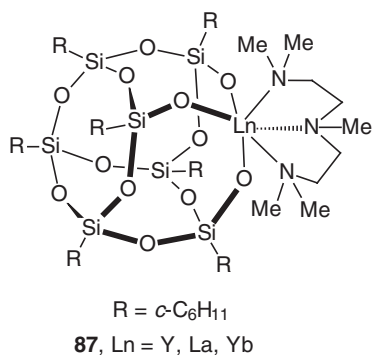
SCHEME 28. Structure of $Cy_7Si_7O_{12}Ln(PMDTA)$ (**87**, Ln = Y, La, Yb).

$Cy_7Si_7O_{12}Ln(PMDTA)$ (**87**, Ln = Y, La, Yb) are depicted in Scheme 28. In all these cases severe disorder problems prevented a structural characterization of the lanthanide silsesquioxanes by X-ray diffraction.[58]

The ytterbium derivative $Cy_7Si_7O_{12}Yb(PMDTA)$ (**87**, Ln = Yb) was also obtained directly by reacting $Yb[N(SiMe_3)_2]_3$ with the trisilanol **3** in the presence of PMDTA.[59] Attempts to grow single crystals of $Cy_7Si_7O_{12}Yb(PMDTA)$ resulted in a small number of good-quality prisms, which were shown by X-ray diffraction to be the heterobimetallic Li/Yb silsesquioxane complex $[(Cy_7Si_7O_{12})\{Cy_7Si_7O_{11}$

2 R$_7$Si$_7$O$_9$(OSiMe$_2$^{t}Bu)(OLi)$_2$
91

$\xrightarrow[\substack{-2\ \text{LiOAr} \\ \text{(toluene)} \\ \text{reflux}}]{\text{Sm(OAr)}_3}$

R = c-C$_5$H$_9$ Ar = C$_6$H$_3$-2,6-^{t}Bu$_2$

92
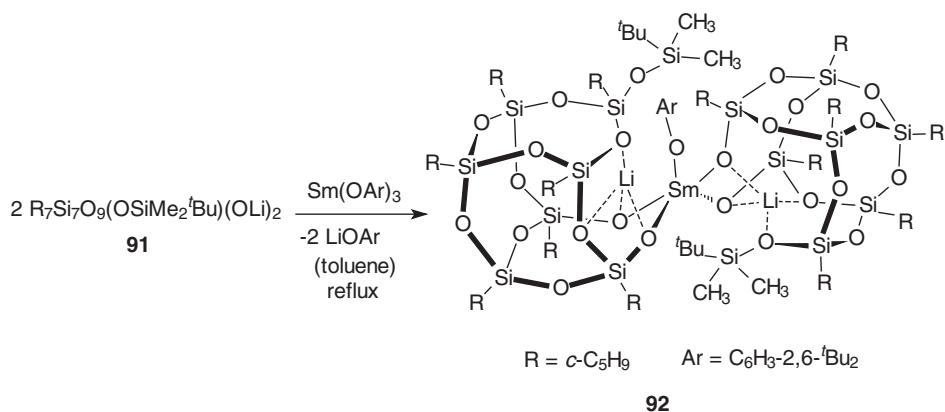
SCHEME 29. Synthesis of the heterobimetallic Li/Sm silsesquioxane complex **92**.

(OSiMe$_3$)}YbLi$_2$(THF)$_2$(MeCN)] · 2.5THF (**88**). Its formation can be ascribed to the presence of a very small impurity of LiN(SiMe$_3$)$_2$ in the Yb[N(SiMe$_3$)$_2$]$_3$ starting material. Although HN(SiMe$_3$)$_2$ does not react directly with **3** on standing at room temperature overnight, small quantities of Cy$_7$Si$_7$O$_9$(OH)$_2$(OSiMe$_3$) (**12**) were probably formed under the catalytic influence of a Lewis acidic lanthanide species, thus accounting for the monosilylated silsesquioxane ligand in **88**. Compound **88** could be more rationally prepared by lithiation of **12** with *n*-BuLi and reaction of the resulting Cy$_7$Si$_7$O$_9$(OLi)$_2$(OSiMe$_3$) (**89**) with Cy$_7$Si$_7$O$_{12}$Yb(THF)$_2$ (**85**, Ln = Yb). The yttrium analog of **88** was prepared in a similar manner.

Arnold *et al.*[60] reported the synthesis and structural characterization of an aryl-oxide-functionalized samarium silsesquioxane complex. Steric protection of **2** by one SiMe$_2$*t*Bu group generated a new disilanol ligand, (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)$_2$(OSiMe$_2$*t*Bu) (**90**), that allows only restricted access to a coordinated metal. Lithiation of **90** with *t*BuLi afforded the stable dilithium intermediate (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OLi)$_2$(OSiMe$_2$*t*Bu) (**91**). Subsequent reaction of **91** with the homoleptic samarium aryloxide Sm(OC$_6$H$_3$*t*Bu$_2$-2,6)$_3$ according to Scheme 29 gave the novel heterobimetallic Li/Sm silsesquioxane complex **92**, which was structurally characterized by X-ray diffraction.

Our own efforts in this field resulted in the isolation of an unprecedented cerium(IV) silsesquioxane complex[61] as well as the structural characterization of a bimetallic ytterbium derivative.[34] Treatment of Ce[N(SiMe$_3$)$_2$]$_3$ with two equivalents of the disilanol Cy$_8$Si$_8$O$_{11}$(OH)$_2$ (**93**) (the cyclohexyl-substituted analog of **47**) in diethyl ether in the presence of an excess of pyridine exclusively afforded the diamagnetic complex (Cy$_8$Si$_8$O$_{13}$)$_2$Ce(py)$_3$ (**94**). The same compound **94**, albeit in somewhat lower yield, could also be prepared by direct reaction of anhydrous CeCl$_3$ with two equivalents of **93** in THF/pyridine mixture (Scheme 30). Quite surprisingly in both cases cerium was oxidized to the tetravalent oxidation state. The compound gave satisfactory C-, H-, N-analysis and was fully characterized by IR and ^{1}H, ^{13}C and ^{29}Si NMR spectra as well as X-ray single crystal diffraction.
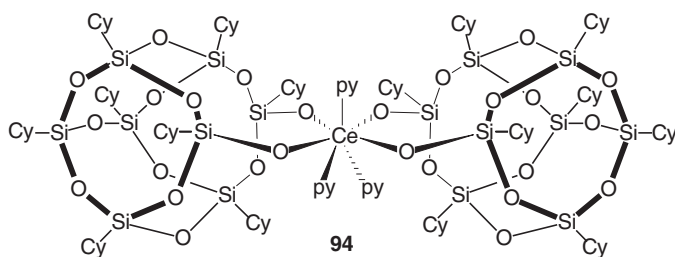
SCHEME 30. Schematic representation of the cerium(IV) silsesquioxane **94**.
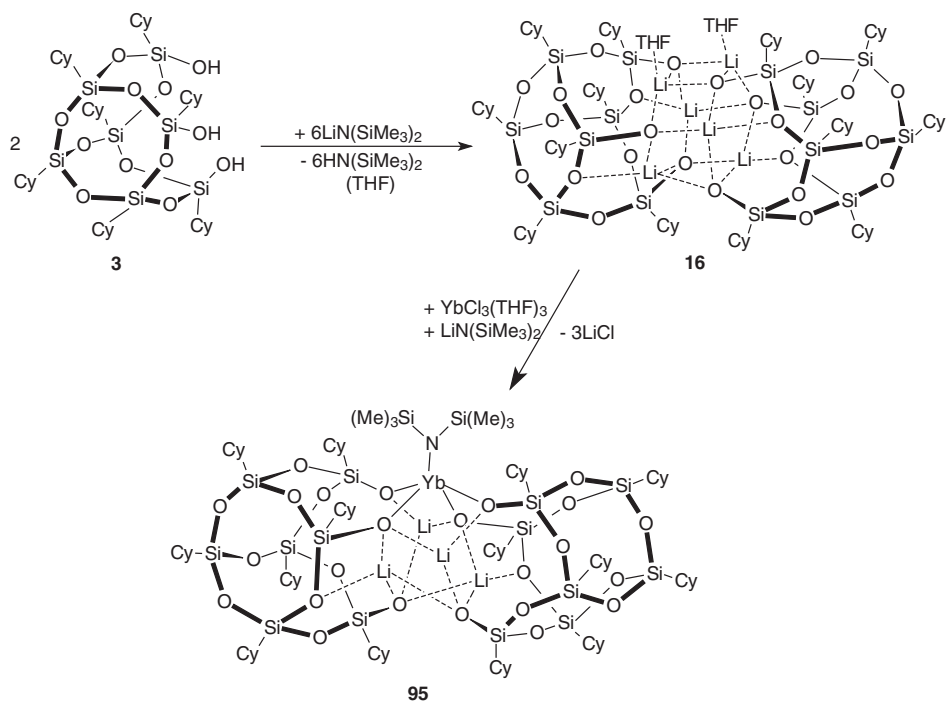
SCHEME 31. Preparation of the amidoytterbium silsesquioxane **95**.

Compound **94** represents the first example of a metallasilsesquioxane derived from the octameric disilanol ligand $[(c\text{-}C_6H_{11})_8Si_8O_{13}]^{2-}$.[14,17,62] The central Ce atom is coordinated by four oxygen atoms of two siloxane ligands and three nitrogens of three pyridine molecules resulting in a distorted pentagonal bipyramidal arrangement.

Finally, an unprecedented functionalized ytterbium silsesquioxane was obtained as outlined in Scheme 31. Trisilanol **3** was lithiated *in situ* using an excess of LiN(SiMe₃)₂, followed by treatment of the reaction mixture with anhydrous ytterbium trichloride.[34] The resulting colorless crystals of **95** were fully characterized by spectroscopic and analytical methods as well as an X-ray crystal structure

determination. In this molecule a reactive ytterbium bis(trimethylsilyl)amide unit resides on a model silica surface formed by two lithium-linked silsesquioxane cages. Thus **95** represents the first example of a monofunctional lanthanide silsesquioxane, which could be of interest for catalytic applications (Scheme 31).[34]

Two novel complexes of samarium and scandium containing silsesquioxane silanolate ligands have been synthesized with the use of the *closo*-silsesquioxane silanolate ligand $Cy_7Si_8O_{12}O^-$ and structurally characterized by X-ray diffraction.[63] Yellow $(C_5Me_5)_2Sm[\mu-Cy_7Si_8O_{12}O]_2Li(THF)$ (**98**), the first *organo*lanthanide silsesquioxane complex reported in the literature, has been obtained by treatment of the ''ate''-complex $(C_5Me_5)_2Sm(\mu-Cl)_2Li(THF)_2$ with $Cy_7Si_8O_{12}OLi$ (**97**) in a molar ratio 1:2 (Scheme 32). The starting material $Cy_7Si_8O_{12}OH$ (**96**) was prepared in close analogy to a published procedure[64] in two steps by treatment of $Cy_7Si_7O_9(OH)_3$ (**3**) with $SiCl_4$ in the presence of triethylamine, followed by hydrolysis of the intermediate chlorosilane $Cy_7Si_7O_{12}Cl$. Metalation of $Cy_7Si_8O_{12}OH$ with methyllithium in diethylether proceeded smoothly at room temperature to afford $Cy_7Si_8O_{12}OLi$ (**97**), which was used *in situ* for further reactions. The ^{29}Si NMR spectrum of **98** shows eight resonances of the same intensity, indicating that all silicon atoms of the $Cy_7Si_8O_{12}$ cages are chemically non-equivalent despite the C_{3v} symmetry of the ligand. This was confirmed by an X-ray diffraction study, which revealed the presence of a heterobimetallic complex in which samarium and lithium are bridged by two silsesquioxane silanolate ligands.

A different synthetic approach was chosen to synthesize a related scandium silsesquioxane complex.[63] Treatment of $(C_5Me_5)Sc(acac)_2$[65] with the free silanol $Cy_7Si_8O_{12}OH$ (**96**) in refluxing toluene (molar ratio 1:1) resulted in elimination of pentamethylcyclopentadiene and formation of the novel binuclear scandium complex $[Sc(acac)_2(\mu-Cy_7Si_8O_{12}O)]_2$ (**99**) (Scheme 32). Colorless single crystals of **99** suitable for X-ray diffraction were obtained by fractional crystallization from pentane. The crystal structure consists of dimeric molecules in which two $Sc(acac)_2$ units are symmetrically bridged by the monoanionic silsesquioxane silanolate ligands. Compound **99** represents the first example of a scandium complex containing silsesquioxane derivatives as ligands. The only closely related compound is the trinuclear scandium disiloxanediolate complex $[(Ph_2Si_2O)_2O]_2Sc_3(acac)_5$, which has been prepared in a similar manner by treatment of $(C_5Me_5)Sc(acac)_2$ with 1,1,3,3-tetraphenyldisiloxanediol.[66]

The first and thus far only silsesquioxane complex of an actinide element is $[Cy_7Si_7O_{12}]_2U$ (**100**).[35] This colorless, nicely crystalline uranium(VI) compound is formed upon reaction of **3** with any uranium precursor, e.g., UCl_4 in the presence of NEt_3. In all cases oxidation of uranium to the hexavalent oxidation state is observed. The best synthetic route leading to **100** in ca. 80% yield is the reaction of **3** with uranocene as outlined in Scheme 33.

2. Group 4 Metal Derivatives (Ti, Zr, Hf)

Apparently, the most thoroughly investigated class of complexes in this area are Ti complexes because of their promising catalytic applications.[1–3] The first Ti derivatives were made by Feher *et al.* and include Ti(III)[67,68] and Ti(IV) silsesquioxanes.[69,70] The former have been prepared by reacting **3** with either
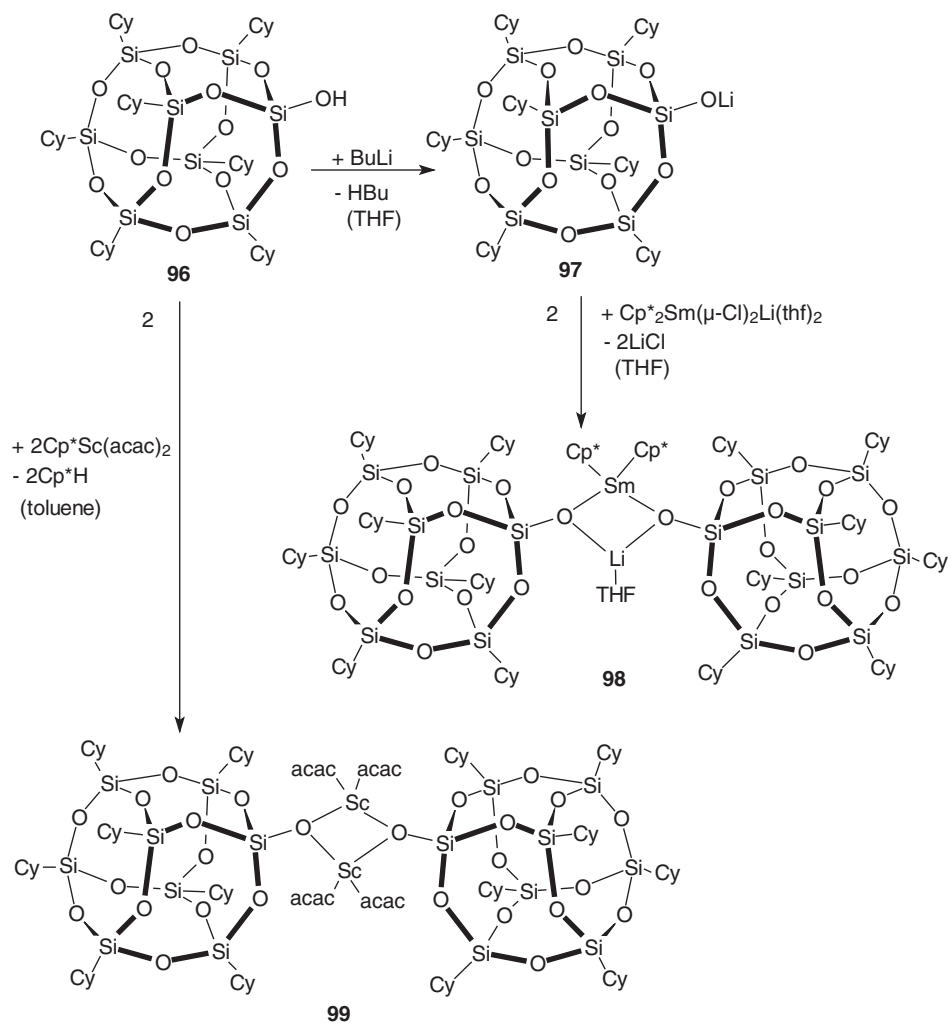
SCHEME 32. Synthesis of the Sm and Sc silsesquioxane complexes **98** and **99**.
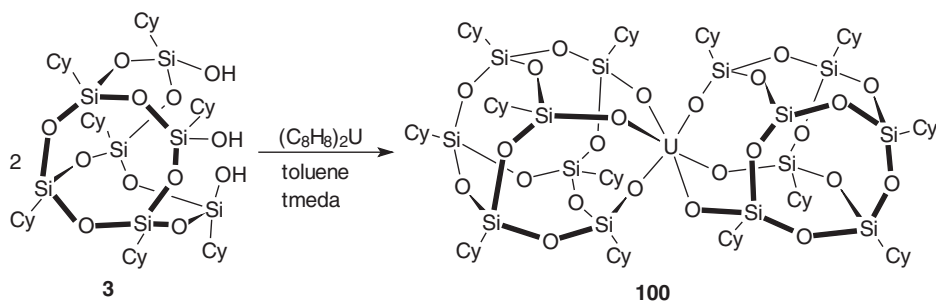
SCHEME 33. Preparation of the uranium(VI) silsesquioxane complex **100**.

Ti[N(SiMe$_3$)$_2$]$_3$ or TiCl$_3$(NMe$_3$)$_2$. Blue dimeric [Cy$_7$Si$_7$O$_{12}$Ti]$_2$ (**101**) is the initial product in these reactions. Treatment of **101** with pyridine affords the bis-adduct [Cy$_7$Si$_7$O$_{12}$Ti(py)]$_2$ (**102**).[67,68] Corner-capping of the silsesquoxane framework with a TiCp unit is also readily achieved yielding monomeric Cy$_7$Si$_7$O$_{12}$TiCp (**103**).[69,70] Other titanasilsesquioxanes have been designed as model compounds for titano-silicates, which are industrially important as oxidation catalysts.[71] Examples of such realistic models include (MeC$_5$H$_4$)$_4$Ti$_4$(SitBu)$_4$O$_{12}$ (**104**),[72] [2,6-iPr$_2$C$_6$H$_3$NH$_3$][(R-SiO$_3$)$_3$Ti$_4$Cl$_4$(μ_3-O)] [**105**, R = 2, 6-iPr$_2$C$_6$H$_3$N(SiMe$_3$)],[73] [Cy$_7$Si$_7$O$_{12}$MgTiCl$_3$]$_n$ (**21**, $n = 1, 2$),[39,40] [(c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$(SiMe$_2$R)]$_2$Ti (**106**, R = vinyl, allyl) and [R$_7$Si$_7$O$_{12}$TiOiPr]$_n$ (**107**, R = c-C$_5$H$_9$; **108**, c-C$_6$H$_{11}$; $n = 1, 2$).[74] It is widely accepted that various titanasilsesquioxanes are versatile catalysts themselves, e.g., in olefin polymerizations and epoxidation reactions.[1–3]

A series of titanasilsesquioxane alkoxides, including [R$_7$Si$_7$O$_{12}$TiOiPr]$_n$ (**107**, R = c-C$_5$H$_9$; **108**, c-C$_6$H$_{11}$; $n = 1, 2$) and [Cy$_7$Si$_7$O$_{12}$Ti(μ-OMe)(MeOH)]$_2$ (**109**) were published by Crocker and co-workers.[74,75] Treatment of Cy$_7$Si$_7$O$_{12}$Ti(O^{i}Pr) (**108**) with methanol affords the six-coordinate titanasilsesquioxane dimer [Cy$_7$Si$_7$O$_{12}$Ti(μ-OMe)(MeOH)]$_2$ (**109**), which was structurally characterized. The monomer/dimer equilibrium of **108** and the formation of **109** are depicted in Scheme 34.[74–77]

The dimeric ethoxide derivative **113** was prepared in our laboratory according to Scheme 35 directly by treatment of **3** with an equimolar amount of titanium tetra-ethoxide.[78] In this case the formation of a monomeric intermediate was not observed. Related complexes, although monomeric, have also been isolated from reactions of **3** with Ti(CH$_2$Ph)$_4$, Ti(NMe$_2$)$_4$ or Ti(OSiMe$_3$)$_4$ yielding Cy$_7$Si$_7$O$_{12}$TiCH$_2$Ph (**110**), Cy$_7$Si$_7$O$_{12}$TiNMe$_2$ (**111**) and Cy$_7$Si$_7$O$_{12}$TiOSiMe$_3$ (**112**), respectively.[74,75]

Compound **113** was isolated in 81% yield as a moisture-sensitive, colorless crystalline solid, which is thermally quite robust (m.p. 263–265 °C). High-thermal stability is quite characteristic for the majority of the metallasilsesquioxanes reported so far. An X-ray crystal structure determination revealed the presence of a dimeric compound with bridging alkoxide ligands and coordinated ethanol molecules in analogy with the structure of the corresponding methoxide derivative [Cy$_7$Si$_7$O$_{12}$Ti(μ-OMe)(MeOH)]$_2$ (**109**).[76] In dimeric **113** the Ti atoms are hexacoordinated with the silsesquioxane cages acting as tridentate ligands. The complex comprises two bridging ethoxide ligands as well as two terminal ethanol molecules coordinated to titanium. Hydrogen bridges connect the OH group of each ethanol ligand with a silsesquioxane oxygen, which is coordinated to the opposite titanium center.[78]

Crocker and co-workers[77] reported the use of **108** as starting material in the preparation of monomeric titanasilsesquioxane phenoxide derivatives. Heating of the isopropoxide precursor with phenols resulted in elimination of i-PrOH and formation of the corresponding titanium phenoxide complexes (Scheme 36).

It was also shown by Crocker et al.[77] that treatment of the monosilylated precursor Cy$_7$Si$_7$O$_9$(OH)$_2$(OSiMe$_3$) (**12**) with one equivalent of Ti(OiPr)$_4$ produced monomeric [Cy$_7$Si$_7$O$_{11}$(OSiMe$_3$)]Ti(OiPr)$_2$ (**117**) as the sole product. A homoleptic bis(silsesquioxane) titanium complex, [Cy$_7$Si$_7$O$_{11}$(OSiMe$_3$)]$_2$Ti (**118**), was prepared by reacting **12** with tetrabenzyltitanium, Ti(CH$_2$Ph)$_4$. Independently it was found in our laboratory that compound **118** is also readily accessible by reacting Ti(OEt)$_4$ or
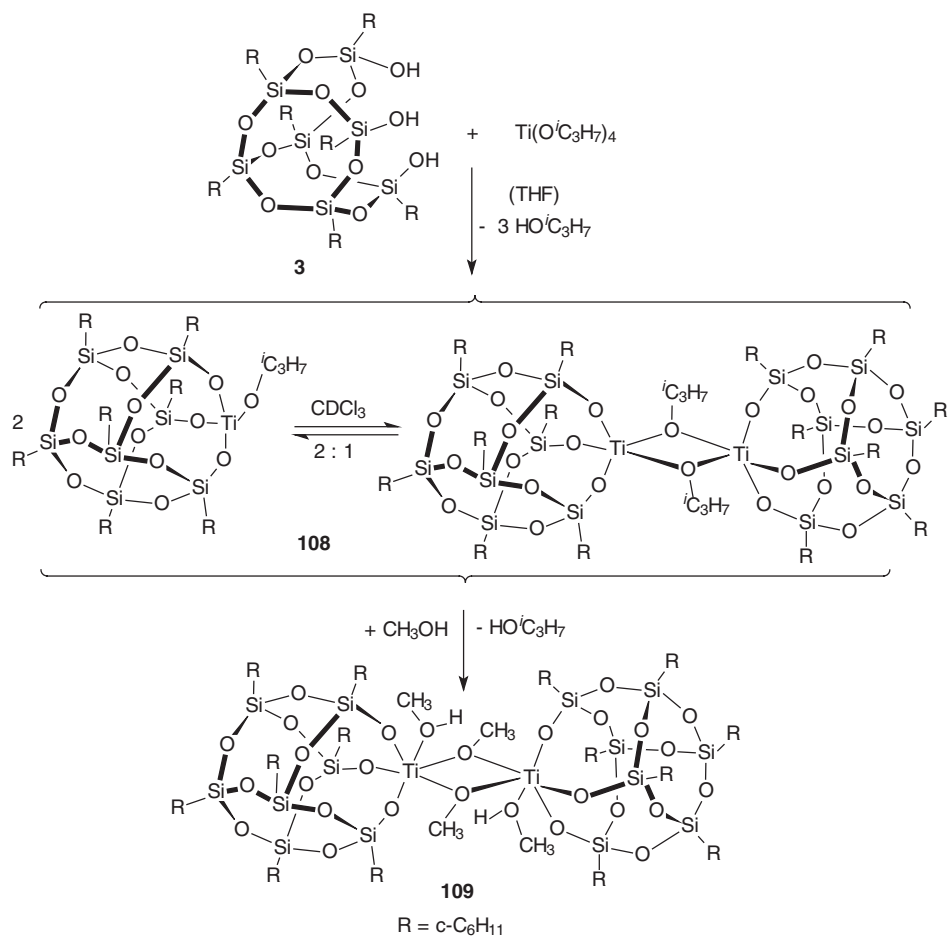
SCHEME 34. Monomer/dimer equilibrium of **108** and formation of **109**.

Ti(O*i*Pr)$_4$ with **12** according to Scheme 37.[78] Both reactions afford white crystalline **118** in almost quantitative yield (96–97%) while employing commercially available reagents. An X-ray diffraction study published by Crocker *et al.*,[77] revealed that the central Ti atom in **118** is tetrahedrally coordinated by the two dianionic sil-sesquioxane cages.

The preparation and characterization of analogous homoleptic titana-silsesquioxane complexes containing vinylic substituents was reported by Wada *et al.* (Scheme 38).[75]

Several titanocene derivatives containing silsesquioxane ligands have also been prepared and characterized.[78] It soon turned out that reactions of **3** or its mono-silylated derivative **12** with titanocene dihalides are not straightforward and usually lead to the formation of product mixtures. A common feature appears to be the formation of μ-oxo species despite the use of carefully dried solvents. Although at this stage the occurrence of partial hydrolysis cannot completely be ruled out, we

3   +   2 Ti(OEt)$_4$ $\xrightarrow{\text{Et}_2\text{O}}$

113

R = *c*-C$_6$H$_{11}$
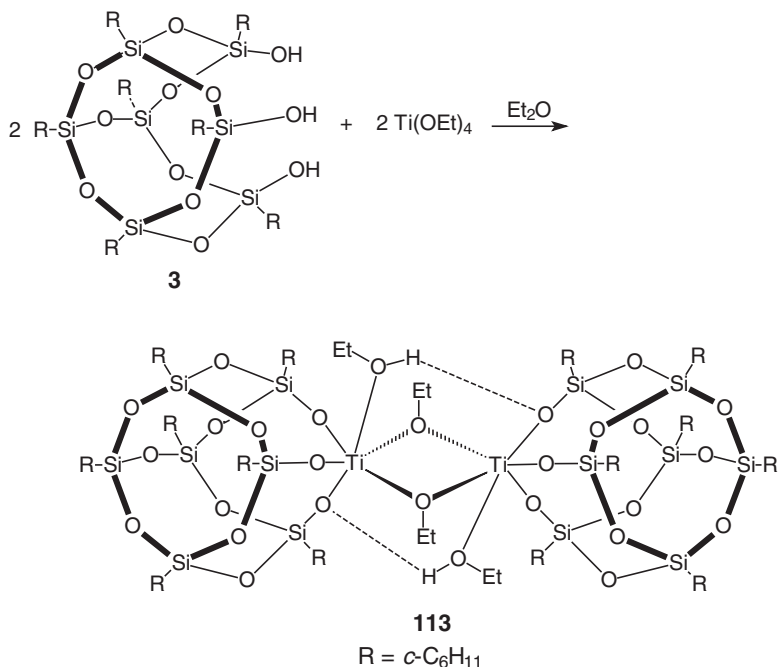
SCHEME 35. Preparation of [Cy$_7$Si$_7$O$_{12}$Ti(μ-OEt)(EtOH)]$_2$ (**113**).
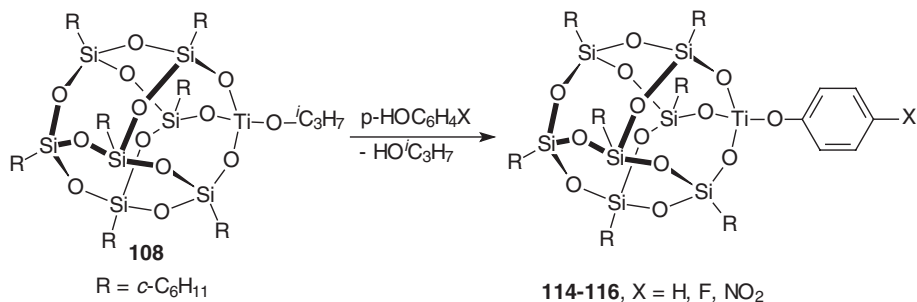
SCHEME 36. Formation of titanasilsesquioxane phenoxides **114**–**116**.

assume that the oxygen bridges in these complexes result from degradation of the silsesquioxane frameworks. A typical example is the reaction of **12** with Cp$_2$TiCl$_2$ in toluene solution in the presence of triethylamine. In this case the μ-oxo-dititanium complex (μ-O)[Cy$_7$Si$_7$O$_{11}$(OSiMe$_3$)Ti]$_2$ (**123**) has been isolated in ca. 70% yield in the form of orange crystals (Scheme 39).

The molecular structure of **123** has been established by an X-ray diffraction analysis, which revealed the presence of a dinuclear metallasilsesquioxane with a central Ti–O–Ti unit. During the course of the reaction one Cp ligand per Ti atom is eliminated upon protonolysis to give the observed mono(cyclopentadienyl) titanium(IV) derivative.
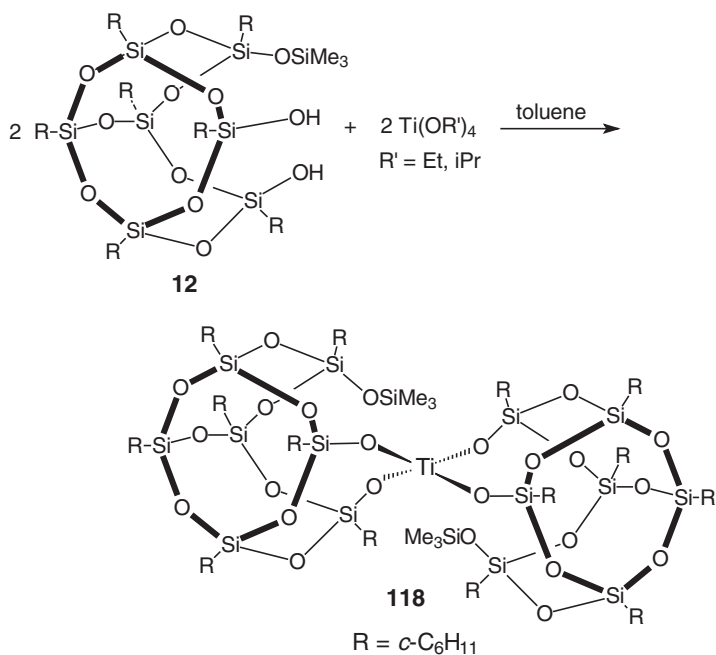
SCHEME 37. Preparation of [Cy$_7$Si$_7$O$_{11}$(OSiMe$_3$)]$_2$Ti (**118**).
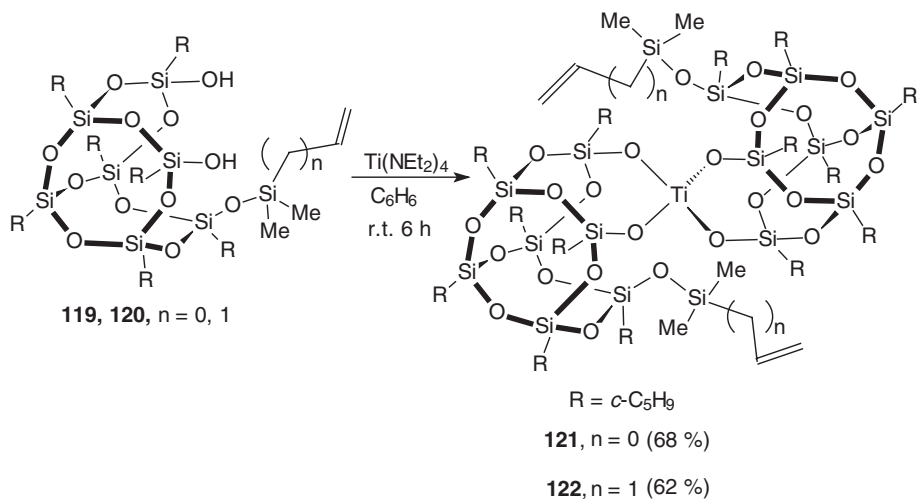
SCHEME 38. Preparation of vinylic titanasilsesquioxanes **121** and **122**.

Apparently, at least two different products are formed when **12** is reacted with the corresponding pentamethylcyclopentadienyl complex Cp$^*_2$TiCl$_2$ in the presence of triethylamine.[78] While a yellow component has not yet been identified, it was possible to isolate and fully characterize the red crystalline trinuclear 1,3,5-trititana-2,4,6-trioxane derivative Cp$^*_2$Ti$_3$O$_3$[Cy$_7$Si$_7$O$_{11}$(OSiMe$_3$)]$_2$ (**124**) (Scheme 40).
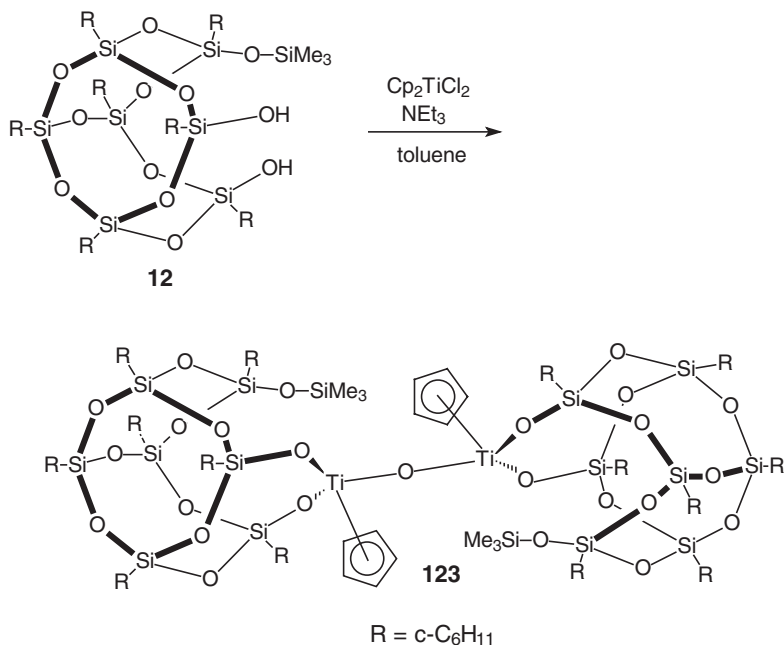
SCHEME 39. Formation of (μ-O)[$Cy_7Si_7O_{11}(OSiMe_3)Ti]_2$ (**123**).

The molecular structure of **124** has been elucidated by an X-ray structural analysis. The central structural motif of **124** is an unsymmetrically substituted six-membered Ti_3O_3 ring. Two pentamethylcyclopentadienyl ligands are coordinated to one titanium atom, while the other two are free of Cp*. They are both part of eight-membered $TiSi_3O_4$ ring systems within the silsesquioxane frameworks. This results in an unusual bis(spirocyclic) inorganic ring system in the molecular structure of **124**.

In a more straightforward manner a bis(pentamethylcyclopentadienyl) titanium(III) silsesquioxane complex is formed according to Scheme 40.[78,79] This synthesis has been developed as a new preparative route leading to model compounds for titanium catalysts immobilized on silica surfaces. It involves addition of the silsesquioxane precursors across the Ti–C bond of the "tucked in" fulvene titanium complex Cp*Ti($C_5Me_4CH_2$).[80–82] The main advantage of this "fulvene route" is that it is a salt-free method by which bis(pentamethylcyclopentadienyl) titanium complexes can be obtained without the need of separating any by-products. The method has been first successfully employed by Teuben *et al.*, who prepared various new Cp_2^*Ti derivatives by reacting Cp*Ti($C_5Me_4CH_2$) with protic reagents such as alcohols, thiols etc.[81,82] We found that the fulvene complex Cp*Ti($C_5Me_4CH_2$) is also the reagent of choice to make novel titanium silsesquioxanes. For example, treatment of Cp*Ti($C_5Me_4CH_2$) with one equivalent of the disilylated silsesquioxane precursor **13** resulted in clean formation of the Ti(III) silsesquioxane complex **125** (Scheme 41).
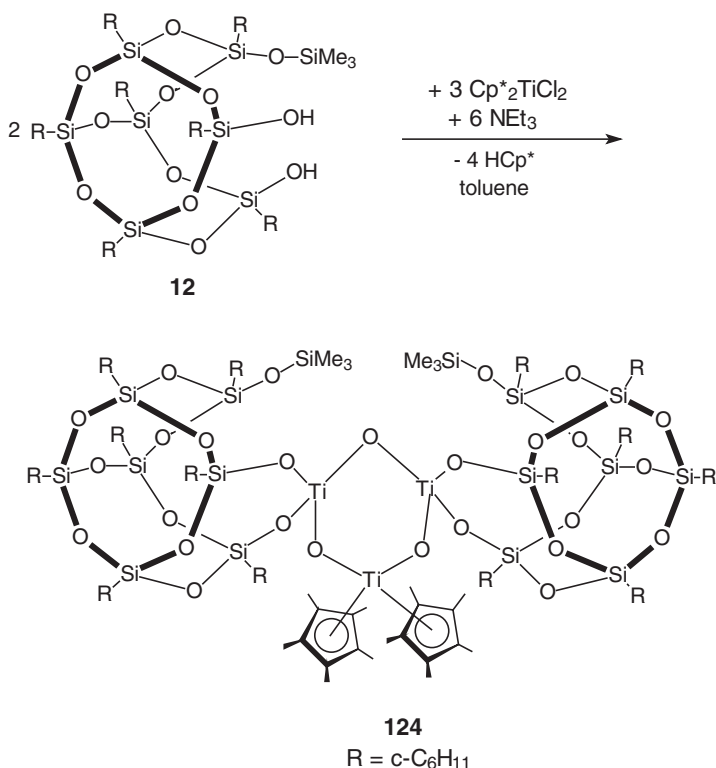
SCHEME 40. Formation of $Cp^*_2Ti_3O_3[Cy_7Si_7O_{11}(OSiMe_3)]_2$ (**124**).

Simple crystallization from the concentrated reaction mixture afforded **125** in the form of air-sensitive, dark-green crystals. The low isolated yield (16%) can be traced back to the very high solubility of **125** even in non-polar organic solvents, which makes it somewhat difficult to recover the material from concentrated solutions in toluene or hexane. The novel titanium(III) silanolate derivative **125** has been fully characterized. An X-ray diffraction study revealed that a Cp^*_2Ti unit has been generated upon protonation of the coordinated tetramethylfulvene ligand. The resulting deprotonated silsesquioxane is coordinated to titanium as a bulky monodentate silanolate ligand. The Ti–O bond length in **125** is 1.927(2) Å.

The "fulvene route" was also successfully employed in the preparation of a compound, which can be regarded as one of the most advanced molecular models for a catalytically active titanium center on a silica surface.[78,79] When $Cp^*Ti(C_5Me_4CH_2)$ was reacted with the monosilylated silsesquioxane precursor **12** in refluxing toluene a color change from deep purple to amber was observed. Crystallization afforded a bright-yellow material, which was subsequently shown to be the novel *mono*(pentamethylcyclopentadienyl) titanium(IV) silsesquioxane complex **126** (69% yield). Its formation is illustrated schematically in Scheme 42.

The surprising outcome of this reaction is the exclusive formation of a Cp^*Ti^{IV} complex in which two silsesquioxanes are bonded in different ways to a single Ti
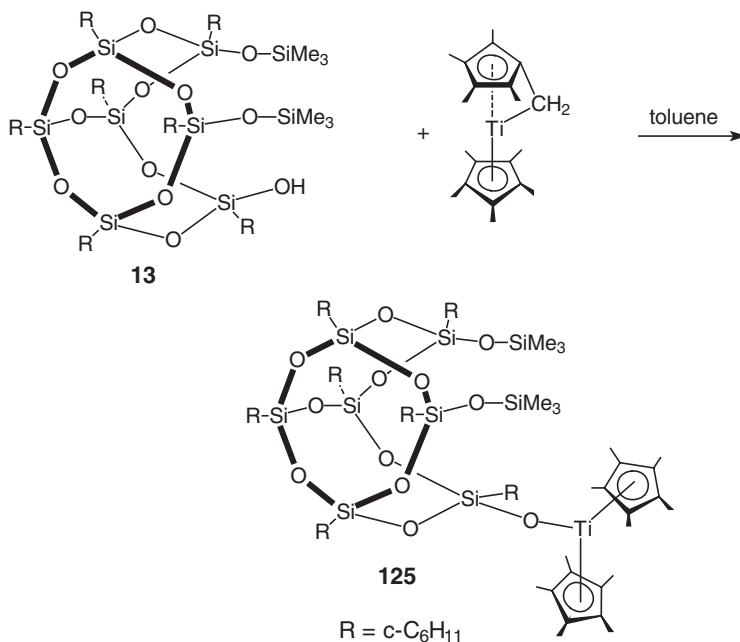
SCHEME 41. Synthesis of **125** *via* the fulvene route.

center. In the course of the reaction one equivalent of pentamethylcyclopentadiene is eliminated. According to an X-ray diffraction analysis a mono(penta-methylclopentadienyl) titanium unit resides on a "model silica surface" formed by one chelating and one monodentate silsesquioxane ligand. With an average of 1.796(3) Å the three Ti–O bond lengths are practically identical. A unique feature of **126**, which makes this compound a particularly "realistic" model system is a silanol function in close proximity to the titanium center. Very weak hydrogen bonding interaction of this silanol group with a cage oxygen atom apparently prevents the molecule from intermolecular protonation of the remaining Cp* ligand, thus "taming" the reactivity of the Si–OH function.

A series of half-sandwich titanium complexes has been prepared with the use of the *closo*-silsesquioxane monosilanol ligand (c-C$_5$H$_9$)$_7$Si$_8$O$_{12}$(OH) (**28**) (Schemes 42 and 43).[64] For example, the reaction of [1,3-C$_5$H$_3$(SiMe$_3$)$_2$]Ti(CH$_2$Ph)$_3$ with one equivalent of silanol **28** resulted in selective substitution of one benzyl group, affording the mono(silsesquioxane) complex **127** in moderate yield (Scheme 43). Introduction of a second bulky silsesquioxane failed.

Deprotonation of **28** with *n*-BuLi in hexane solution at 25 °C readily affords the stable silsesquioxane lithium salt (c-C$_5$H$_9$)$_7$Si$_8$O$_{13}$Li (**128**).[64] The room temperature reaction of **128** with [1,3-C$_5$H$_3$(SiMe$_3$)$_2$]TiCl$_3$ in hexane according to Scheme 44 yielded [1,3-C$_5$H$_3$(SiMe$_3$)$_2$][(c-C$_5$H$_9$)$_7$Si$_8$O$_{13}$]TiCl$_2$ (**129**). The bis(silsesquioxane) product **130** could be selectively prepared by salt metathesis between [1,3-C$_5$H$_3$(SiMe$_3$)$_2$]TiCl$_3$ and two-equivalents of **128** in hexane at 25 °C.

12

126

R = c-C$_6$H$_{11}$
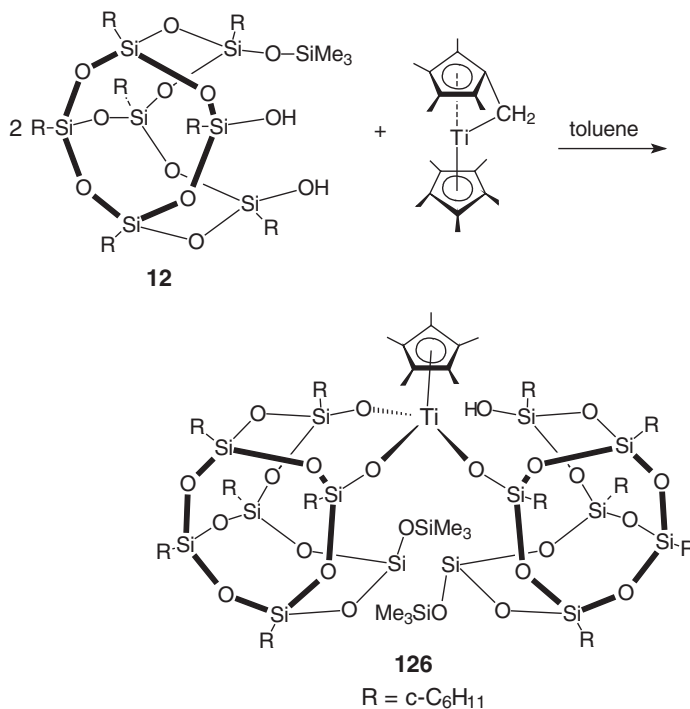
Scheme 42. Preparation of **126** *via* the fulvene route.

28

127
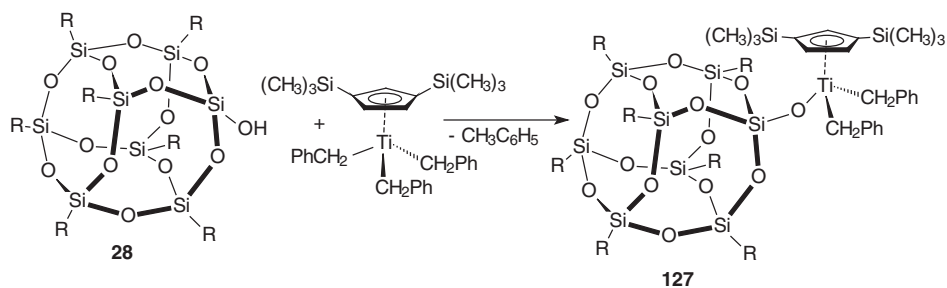
Scheme 43. Synthesis of **127**.

Zirconium silsesquioxane complexes, which have been reported in the literature include the species Cy$_7$Si$_7$O$_{12}$ZrCp* (**131**),[83] [(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSiMe$_3$)]$_2$Zr(THF)$_2$ (**132**),[84] and [{(c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$}Zr(CH$_2$Ph)]$_2$ (**133**),[84] which have all been synthesized by synthetic routes well-established for the corresponding titanium derivatives. The zirconocene complex [(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSiMePh$_2$)]ZrCp$_2$ (**134**) was obtained by treatment of Cp$_2$ZrMe$_2$ with an aluminosilsesquioxane.[51] The availability of permetalated Cy$_7$Si$_7$O$_9$(OLi)$_3$ (**15**) enabled us to prepare the

SCHEME 44. Synthesis of the silsesquioxane titanium half-sandwich complexes **129** and **130**.

first heterobimetallic zirconium silsesquioxane complex. The compound $(Cy_7Si_7O_{12})_2Zr[Li(O\!=\!CMe_2)]_2$ (**135**) was prepared according to Scheme 45 and structurally characterized by X-ray diffraction.[34]

Collins *et al.* reported the use of the borylated silsesquioxane intermediate **136** for the synthesis of the zirconocene derivative **137** according to Scheme 46.[85]

Hafnium-containing metallasilsesquioxanes reported in the literature include the species $Cy_7Si_7O_{12}HfCp^*$ (**138**)[55] and $[(c\text{-}C_5H_9)_7Si_7O_{12}HfCH_2Ph]_2$ (**139**).[84]

A new development in silsesquioxane chemistry is the combination of silsesquioxanes with cyclopentadienyl-type ligands. Recently, several synthetic routes leading to silsesquioxane-tethered fluorene ligands have been developed.[86,87] The scenario is illustrated in Scheme 47. A straightforward access to the new ligand **140** involves the 1:1 reaction of **2** with 9-triethoxysilylmethylfluorene. Alternatively, the chloromethyl-substituted *closo*-silsesquioxane derivative **141** can be prepared first and treated subsequently with lithium fluorenide to afford **140**. Compound **141** has been used as starting material for the preparation of the trimethylsilyl and trimethylstannyl derivatives **142** and **143**, respectively, as well as the novel zirconocene complex **144**. When activated with MAO (methylalumoxane), **144** yields an active ethylene polymerization system.

SCHEME 45. Synthesis of $(Cy_7Si_7O_{12})_2Zr[Li(O{=}CMe_2)]_2$ (**135**).

In a recent paper, Duchateau *et al.* have extended this synthetic approach to a series of silsesquioxane-tethered fluorene ligands and the corresponding zircon-ocenes with various cyclopentadienyl ligands at Zr. The various possibilities are illustrated in Scheme 48.[87]

Yet another interesting variety is the incorporation of functional side-groups in metallasilsesquioxanes of zirconium and hafnium. Mitsudo *et al.* reported the synthesis and structural characterization of novel zirconocene or hafnocene-containing metallasilsesquioxanes with a vinyl group, $Cp_2M[(vinyl)Me_2Si](c\text{-}C_5H_9)_7Si_7O_{12}$ (**145**, M = Zr; **146**, M = Hf).[88] Hydrosilylation of the vinyl group in **145** with $Me_3SiH(OEt)$ in the presence of a $Pt_2(dvs)_3$ catalyst(1 mol% as Pt, dvs = divinyl-tetramethyldisiloxene) in toluene at 30 °C for 72 h cleanly occurred with excellent regioselectivity to give $Cp_2Zr[Me_2(EtO)SiCH_2CH_2SiMe_2](c\text{-}C_5H_9)_7Si_7O_{12}$ (**147**).

A major part of the work described in this section has been carried out with the aim of applying these silsesquioxane complexes of Ti, Zr and Hf in catalytic proc-esses such as ethylene polymerization, olefin epoxidation and Oppenauer oxidation. These catalytic aspects have been highlighted in several recent review articles.[1,2]
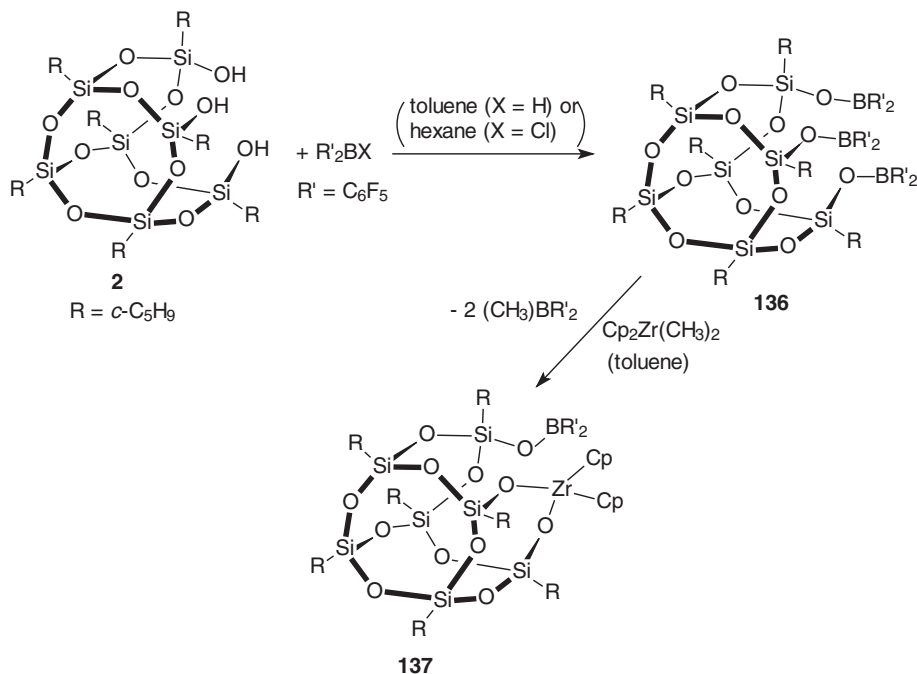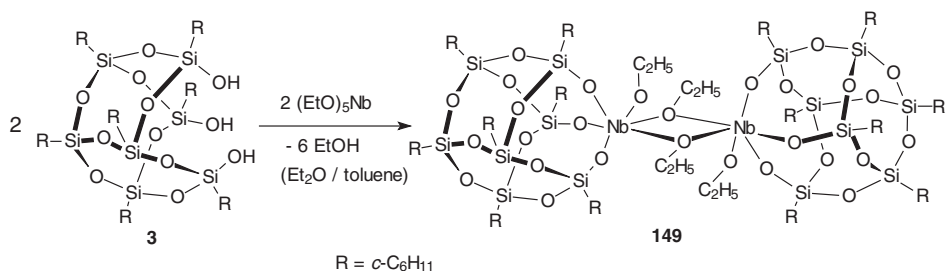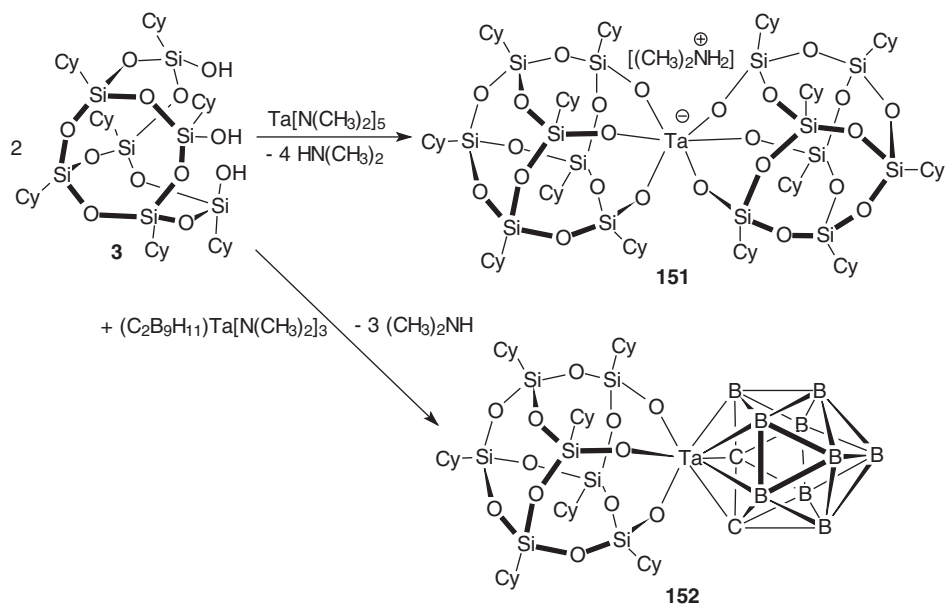
SCHEME 46. Synthesis of the zirconasilsesquioxane **137**.

3. Group 5 Metal Derivatives (V, Nb, Ta)

Significantly less is known about metallasilsesquioxanes incorporating Group 5 metals. The vanadyl silsesquioxane $Cy_7Si_7O_{12}V{=}O$ (**148**) was reported by Feher *et al.* more than 10 years ago and has been shown to be a single-site catalyst for olefin polymerization.[68,89–91] In 1990 Feher and co-workers reported the preparation of the dark-blue dimeric vanadium(III) complex $[Cy_7Si_7O_{12}V(py)_2][Cy_7$-$Si_7O_{12}V]$ (**149**), in which two pyridine ligands are added to one of the vanadium centers.[68] Thus it was surprising that until recently no metallasilsesquioxane had been described for the heavier Group 5 metals, which was presumably due to the lack of suitable synthetic procedures.

Recently, we succeeded in the synthesis and structural characterization of first niobium-containing metallasilsesquioxane complex.[35] In analogy to the corresponding reactions with titanium tetraalkoxides, niobium pentaethoxide cleanly reacts with **3** in a 1:1 molar ratio to give high yields of dimeric $[Cy_7Si_7O_{12}NbOEt(\mu$-$OEt)]_2$ (**149**) as a colorless, crystalline solid (Scheme 49).

During the course of our investigations we found that various tantalum silsesquioxanes are readily accessible *via* a versatile amide route.[92] Commercially available tantalum diethylamide, $Ta(NMe_2)_5$, was chosen as the key starting material for the development of a salt-free route leading to tantalum silsesquioxane derivatives. Clean protonation and liberation of three equivalents of dimethylamine took place upon reaction of $Ta(NMe_2)_5$ with **3** in a 1:1 molar ratio. Pale yellow

SCHEME 47. Synthesis and reactivity of silsesquioxane-tethered fluorene ligands.

SCHEME 48. Synthesis of silsesquioxane-tethered zirconocenes.

$Cy_7Si_7O_{12}Ta(NMe_2)_2$ (**150**) was isolated in 92% yield. Somewhat surprisingly, similar treatment of $Ta(NMe_2)_5$ with **1** in a 1:2 molar ratio did not lead to the formation of the neutral tantalum(V) species $Cy_7Si_7O_{12}Ta[Cy_7Si_7O_{11}(OH)]$ with one Si–OH

SCHEME 49. Synthesis of $[Cy_7Si_7O_{12}NbOEt(\mu\text{-}OEt)]_2$ (**149**).

SCHEME 50. Preparation of tantalasilsesquioxanes.

function remaining intact. Instead, liberation of only four equivalents of dimethyl-amine occurred and the anionic bis(silsesquioxane) "sandwich" complex $[Ta(Cy_7Si_7O_{12})_2]^-$ was obtained in the form of its colorless dimethylammonium salt **151** (89% yield) (Scheme 50). In the resulting anion, the central Ta atom is encapsulated between two silsesquioxane frameworks in a similar manner as in the neutral uranium(VI) species $U(Cy_7Si_7O_{12})_2$ (**100**).[35] We then investigated the possibility of adapting the amide route to more complex systems. Indeed, the amido tantalacarborane species $(C_2B_9H_{11})Ta(NMe_2)_3$ was found to react cleanly with one equivalent of **3** to afford the novel "mixed-sandwich" complex $Cy_7Si_7O_{12}$-$Ta(C_2B_9H_{11})$ (**152**), which was isolated in 82% yield as an orange, crystalline solid. Compound **152** is the first representative of a novel class of inorganic cage compounds in which a carborane and a silsesquioxane framework are linked

through a single metal center. Further examples of such hybrid complexes should be accessible by varying either the central atom or using different carborane and silsesquioxane ligands.

These results clearly demonstrate that the amide route is a versatile synthetic pathway to novel tantalasilsesquioxanes, each of them representing a novel type of metallasilsesquioxane. Suitable tantalum dimethylamides are readily protonated in the presence of silsesquioxanes bearing Si–OH functional groups to form either "half-sandwich" or "sandwich" complexes depending on the stoichiometry. This salt-free method is likely to work equally well with the corresponding Nb derivatives as well as with other Si–OH-functionalized silsesquioxanes. The "mixed-sandwich" complex $Cy_7Si_7O_{12}Ta(C_2B_9H_{11})$ (**152**) is just the first example of an unusual new class of hybrid compounds combining carborane and silsesquioxane chemistry. Tantalum silsesquioxanes have also been investigated by Basset *et al.* as model compounds for the formation of alkylidenetantalum species on silica surfaces.[93]

The dimer of the vanadyl silsesquioxane complex **148** was used by Mitsudo *et al.* to prepare catalysts with a characteristic pore structure and excellent activity toward the selective photoassisted catalytic oxidation of methane into methanal.[94]

C. *Metallasilsesquioxanes of the Middle and Late Transition Metals*

1. Group 6 Metal Derivatives (Cr, Mo, W)

Several Group 6 metallasilsesquioxanes have been reported in the literature and investigated with respect to catalytic applications. However, their number is still scarce, and further exploration of this class of metallasilsesquioxanes is warranted. The disilanol derivative $Cy_7Si_7O_9(OH)_2(OSiMe_3)$ (**12**) reacts with chromium trioxide in CCl_4 in the presence of anhydrous $MgSO_4$ to give the chromate ester $Cy_7Si_7O_9(OSiMe_3)CrO_4$ (**153**), which has been tested as an ethylene polymerization catalyst.[95,96] The chromium(VI) derivative **153** can be regarded as a molecular model of the chromium-based Phillips catalyst. This and related chromium silsesquioxanes have also been demonstrated to be active catalysts for the epoxidation of olefins with *t*-butylhydroperoxide.[97] The chromate ester **153** has also been employed as the starting material for the synthesis of microporous chromium silicate materials (Scheme 51), which catalyze the oxidation of ammonia.[98]

While previously reported Cr silsesquioxane complexes contained chromium in the hexavalent oxidation state, the recently synthesized lithium silsesquioxane precursors such as **15–17** enabled the synthesis of an unprecedented heterobimetallic chromium species.[35] Treatment of **16** with anhydrous $CrCl_3$ in THF resulted in formation of green crystalline **154**, which was structurally characterized by X-ray diffraction (Scheme 52).

The molybdate ester $Cy_7Si_7O_9(OSiMe_3)MoO_4$ (**155**) was made by Feher *et al.*,[32] in 1995 by reacting the thallium intermediate $Cy_7Si_7O_9(OSiMe_3)(OTl)_2$ (**70**) with MoO_2Cl_2. As mentioned earlier, it is one of the advantages of the thallium silsesquioxane reagents that they can be used as precursors in reactions with high-valent

153, R = c-C_6H_{11}
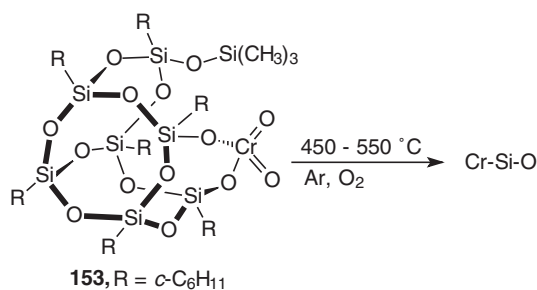
SCHEME 51. Synthesis of microporous chromium silicate materials from **153**.
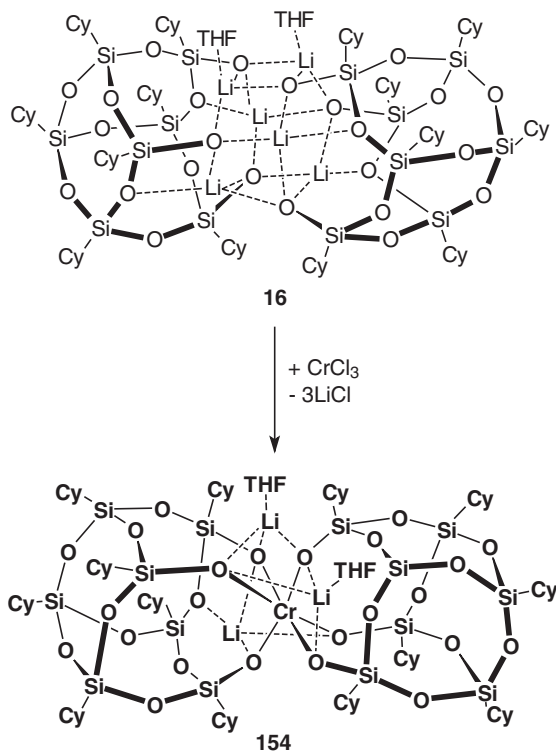
SCHEME 52. Synthesis of the LiCr silsesquioxane complex **154**.

metal halides. Feher et al.[99] also reported the prepartion of the Schrock-type molybdenum carbene complex **156** (Scheme 53).

The first metallasilsesquioxanes containing metal–metal triple bonds have been reported by Chisholm and Feher et al.[100] The reaction between two equivalents of **3** and $Mo_2(OtBu)_6$ in benzene or toluene at room temperature (Scheme 54) led to rapid replacement of all six alkoxide ligands and formation of orange, crystalline
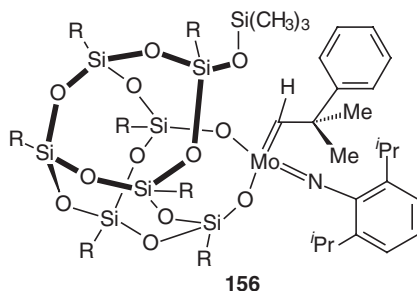
SCHEME 53. Structure of **156**.
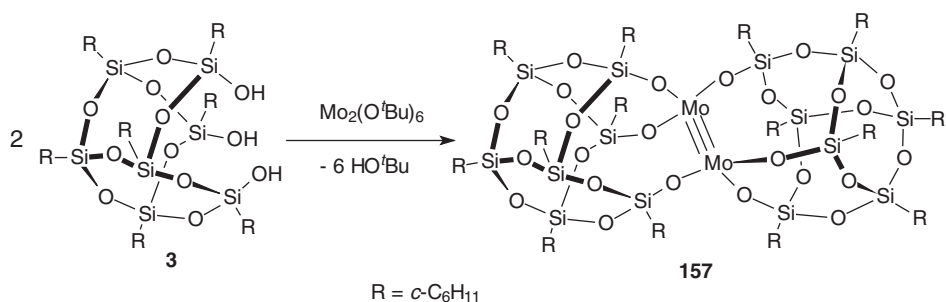
SCHEME 54. Synthesis of the dimeric molybdenum silsesquioxane complex **157**.
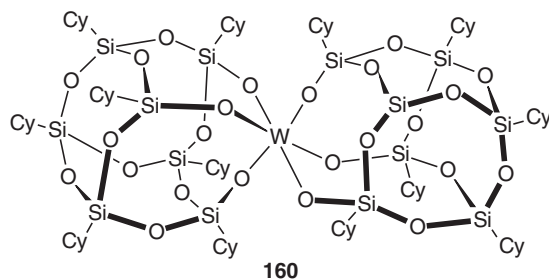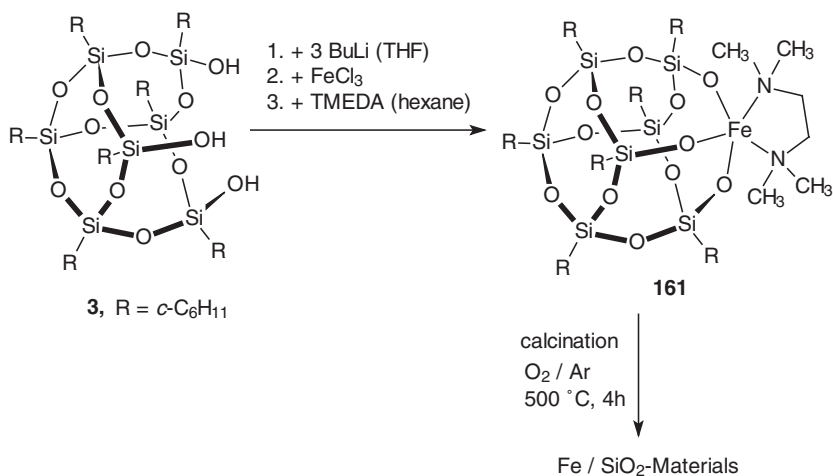
157 in 80% yield. The dimeric structure with a Mo≡Mo triple bond as depicted in Scheme 54 was established by a single-crystal X-ray diffraction study.

The analogous reaction of **3** with $W_2(OtBu)_6$ gave a brown solution, from which a yellow, microcrystalline material could be isolated.[100] Based on spectroscopic data the latter was formulated as $[Cy_7Si_7O_{12}]W_2(\mu\text{-}H)(OtBu)$ (**158**). Cleavage of the Mo≡Mo triple bond in **157** occurred upon treatment of this compound with NO (two equivalents) to afford the dimeric nitrosyl molybdenum silsesquioxane complex $[Cy_7Si_7O_{12}]_2Mo_2(NO)_2$ (**159**).[100]

A metallasilsesquioxane derivative of tungsten(VI), which is an analog of the uranium(VI) complex (**100**) was prepared by Smet et al.[101] Quite remarkably the compound $[Cy_7Si_7O_{12}]_2W$ (**160**) was formed directly by reaction WCl_6 with two equivalents of **3** even without the presence of a base to facilitate the elimination of HCl. According to a single crystal X-ray structure analysis, the tungsten atom in monomeric neutral **160** is encapsulated between the two bulky silsesquioxane cages (Scheme 55).

2. Group 7 Metal Derivatives

No fully characterized metallasilsesquioxane derivatives of Mn, Tc or Re have been reported until now. It has been reported that reactions of **2** or **3** with rhenium(VII) precursors are complicated and often result in dehydration of the silsesquioxane cage without incorporation of rhenium.[1,35] Recently it has been found

160

SCHEME 55. Structure of $[Cy_7Si_7O_{12}]_2W$ (**160**).

1. + 3 BuLi (THF)
2. + FeCl$_3$
3. + TMEDA (hexane)

3, R = c-C$_6$H$_{11}$

161

calcination
O$_2$ / Ar
500 ˚C, 4h

Fe / SiO$_2$-Materials

SCHEME 56. Preparation of the ferrasilsesquioxane complex **161** and its conversion into iron on microporous silica.

that the reaction of **16** with anhydrous MnCl$_2$ in THF affords a colorless hetero-bimetallic Li/Mn silsesquioxane complex of unknown structure.[35]

3. Group 8 Metal Derivatives (Fe, Ru, Os)

The first iron-containing silsesquioxanes which appeared in the literature were compounds containing ferrocenyl units as side-groups.[102–104] However, these are not within the scope of this review as iron is not part of the metallasilsesquioxane skeleton. Meanwhile, several ferrasilsesquioxane complexes have been synthesized. The first iron(III) compound of this type was prepared in our laboratory according to Scheme 56.[105] In **161**, the coordination sphere of iron is completed by TMEDA (N,N,N′,N′-tetramethylethylenediamine) as a chelating amine ligand. Pale yellow, crystalline **161** was isolated in 80% yield and structurally characterized by X-ray diffraction. This compound was later used by Maxim *et al.*[106,107] to prepare iron particles dispersed on microporous silica *via* controlled calcination of the ferra-silsesquioxane precursor as depicted in Scheme 56.
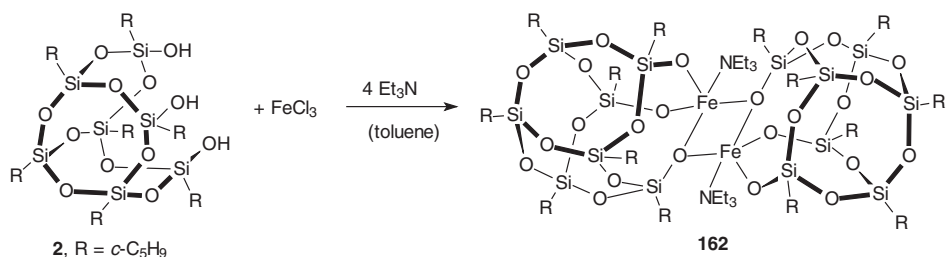
SCHEME 57. Synthesis of the dimeric ferrasilsesquioxane **162**.

More recently Shapley *et al.*[108] carried out a reaction of the cyclopentyl-substituted precursor **2** with FeCl$_3$ in the presence of NEt$_3$ in toluene solution (Scheme 57). In contrast to the formation of **161**[105] this reaction afforded brown, dimeric [(c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$Fe(NEt$_3$)]$_2$ (**162**) in 73% yield.

A series of ferrasilsesquioxanes stabilized by phosphine ligands has been prepared and characterized by Baker *et al.*[109] Reactions of the iron(II) precursor FeCl$_2$(dcpe) (dcpe = bis(dicyclohexylphosphino)ethane) with **2** or the monosilylated precursor (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OSiMe$_3$)(OH)$_2$ (**38**) afforded the (dcpe)iron(II)-silsesquioxane complexes (c-C$_5$H$_9$)$_7$Si$_7$O$_9$(OH)[O$_2$Fe(dcpe)] (**163**, 91% yield) and (c-C$_5$H$_9$)$_7$Si$_7$O$_9$ (OSiMe$_3$)[O$_2$Fe(dcpe)] (**164**, 89% yield), respectively, in the form of colorless crystals. The iron(III) analog (c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$Fe(PCy$_3$) (**165**, colorless crystals, 91% yield) was prepared and isolated in a similar manner from the reaction of **2** with FeCl$_3$(PCy$_3$) in the presence of triethylamine. Compound **165** exhibits some interesting reaction chemistry with water. Treatment of solutions of **165** in benzene with a slight stoichiometric excess of water in the presence of NEt$_3$ leads to formation of the μ-oxo-bridged dianionic complex **166**. The same compound could also be prepared directly in 92% yield by reacting **2** with FeCl$_3$(PCy$_3$) in the presence of water and triethylamine as illustrated in Scheme 58.

Several anionic ferrasilsesquioxane complexes have also been isolated by Shapley *et al.*[108] The high-spin iron(III) silsesquioxane complexes [N(nBu)$_4$][(c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$FeCl] (**167**) and [N(nBu)$_4$][(c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$FeOSiMe$_3$] (**168**) were obtained from reactions of **2** with either [N(nBu)$_4$][FeCl$_4$] or [N(nBu)$_4$][Fe(OSiMe$_3$)$_4$]. Substitution of the terminal chloride or trimethylsilanolate ligands with *t*-butoxide afforded [N(nBu)$_4$][(c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$FeO*t*Bu] (**169**), while a similar substitution reaction with the methyl ester of *N*-acetylcysteine produced the unusual anionic ferrasilsesquioxane complex [N(nBu)$_4$][(c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$Fe{SCH$_2$CH(NHCOMe)-CO$_2$Me}] (**170**). The latter reactions show that complexes **167** and **168** are excellent precursors for the synthesis of other iron(III) silsesquioxanes.

Ruthenium and osmium complexes containing silsesquioxane ligands have also been reported in the literature.[99,108,110–113] A Schrock-type ruthenium carbene complex, Cy$_7$Si$_8$O$_{12}$CH═RuCl$_2$(PCy$_3$)$_2$ (**171**) was made by Feher *et al.* in a similar manner as the molybdenum carbene complex **156**.[108] Other silsesquioxane complexes of Ru and Os contain metal complex fragments bonded to side chains of specially designed silsesquioxane ligands. For example, Braunstein *et al.*[110] used
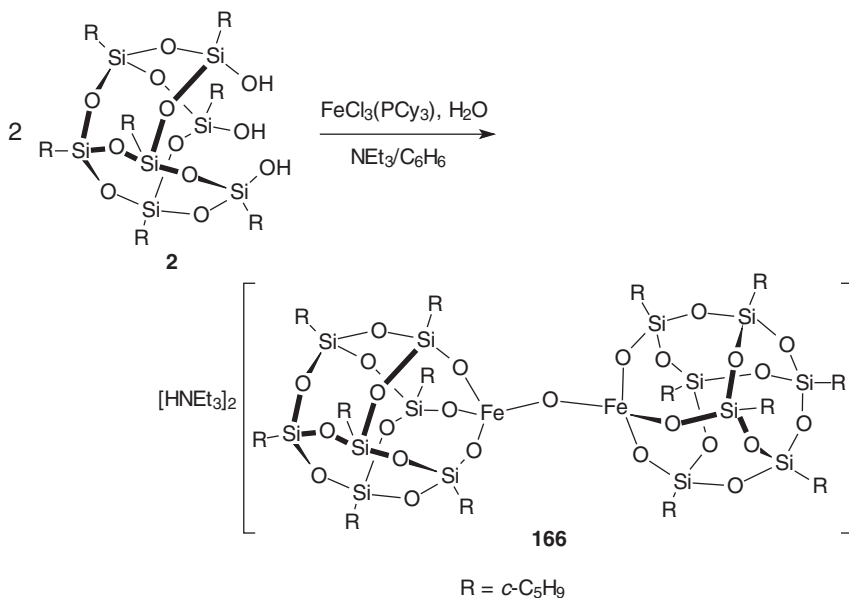
Scheme 58. Direct preparation of **166**.

thiol-functionalized silsesquioxane derivatives such as **172** and **175** to synthesize coordination compounds with ruthenium and osmium clusters as outlined in Scheme 59. All cluster complexes shown in Scheme 59 have been isolated in the form of yellow, crystalline solids.

Ruthenium complexes of a novel silsesquioxane-based tridentate phosphine ligand have been prepared and characterized by Mitsudo et al.[111] The synthesis of the ligand **178** is depicted in Scheme 60. Reactions of **178** with several late transition metal complexes were examined. A typical example is the reaction with three equivalents of [RuCl$_2$(cymene)]$_2$, which produced the red triruthenium complex (c-C$_5$H$_9$)$_7$Si$_7$O$_9$[OSiMe$_2$CH$_2$CH$_2$PPh$_2$RuCl$_2$(cymene)]$_3$ (**179**) in almost quantitative yield.

An osmium cluster complex involving direct bonding of a silanol oxygen atom was reported already in 1990 by Shapley and Feher et al.[112] The reaction shown in Scheme 61 was conducted in cyclooctene at 130 °C for 24 h. The product **180** was isolated as a stable, yellow solid in 13% yield following chromatography. The most striking feature of the molecular structure of **180** is the formation of a siloxane linkage by the cyclodehydration of two silanol groups of **3**.

Several multifunctional donor ligands based on the *closo*-Si$_8$O$_{12}$ silsesquioxane cage have also been reported in the literature, including complexes containing Ru(terpy)$_3$ units.[113] Finally, an unusual anionic osmasilsesquioxane complex containing a nitrido function has recently been described by Shapley et al.[108] The tetraphenylphosphonium salt [PPh$_4$][(c-C$_5$H$_9$)$_7$Si$_7$O$_{11}$(OSiMe$_3$)Os(N)Cl$_2$] (**181**) was isolated as a diamagnetic, air-stable, purple crystalline solid (Scheme 62).
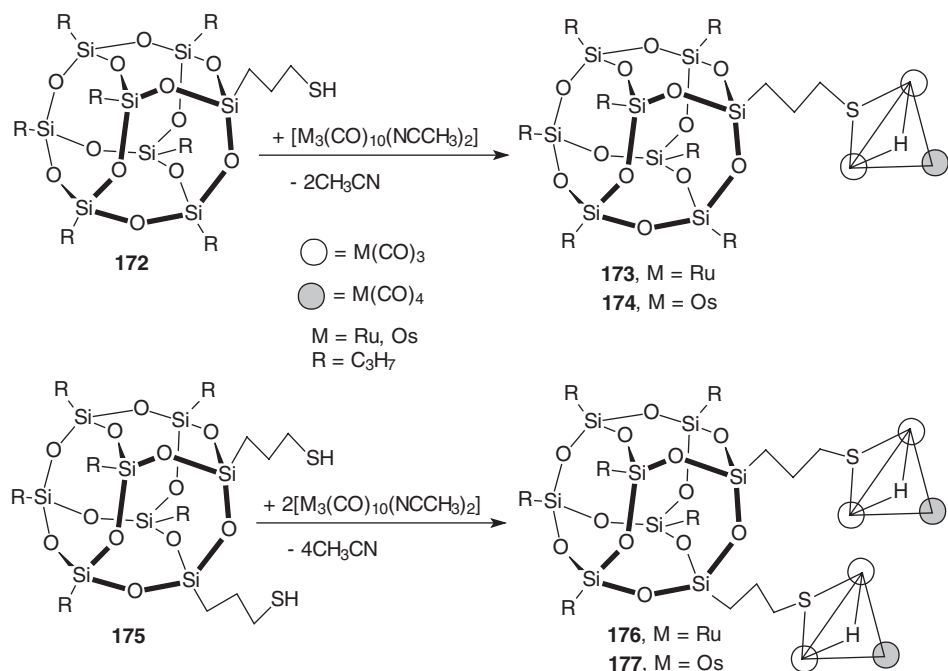
SCHEME 59. Synthesis of silsesquioxane thiol-coordinated ruthenium and osmium clusters.
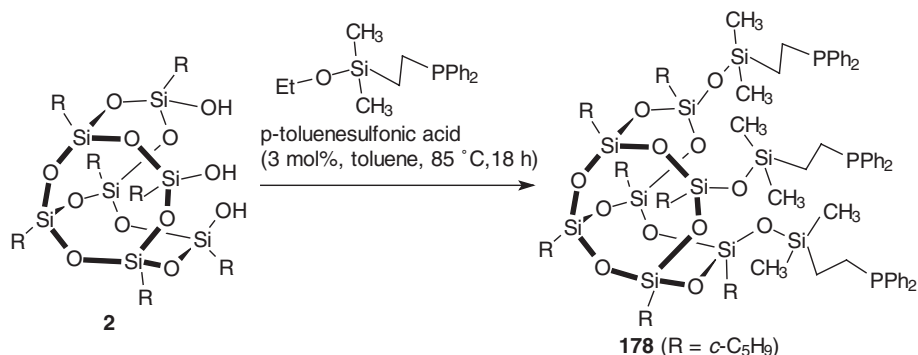
SCHEME 60. Synthesis of the silsesquioxane-based tridentate phosphine ligand **178**.

4. Group 9 Metal Derivatives (Co, Rh)

Apparently "real" metallasilsesquioxanes of cobalt, rhodium or iridium have thus far not been reported in the literature. However, several silsesquioxane ligands containing donor-substituted side chains as well as related silsesquioxane dendrimers have been found to form complexes with cobalt and rhodium complex fragments.[103,114–118]
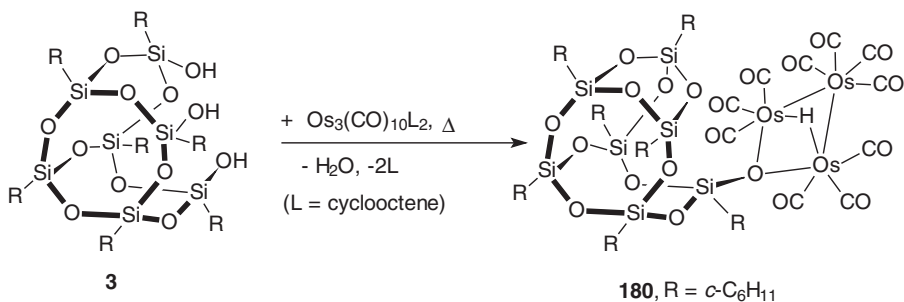
SCHEME 61. Synthesis of the silsesquioxane triosmium cluster compound **180**.
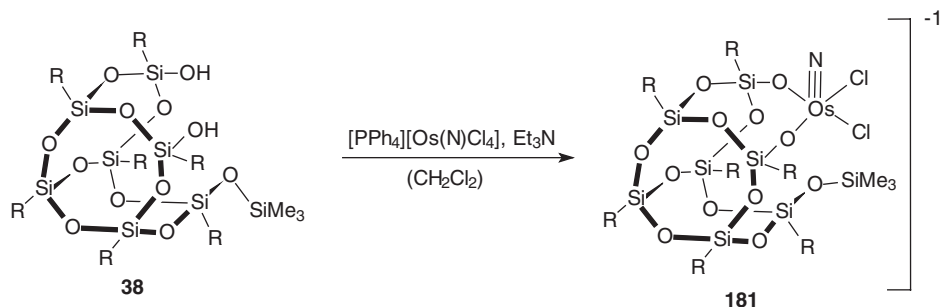
SCHEME 62. Synthesis of the nitrido-osmasilsesquioxane complex **181**.

5. Group 10 Metal Derivatives (Pt)

While apparently no metallasilsesquioxane complexes of nickel and palladium have yet been prepared, several literature reports have appeared on platinum compounds containing silsesquioxane ligands. Abbenhuis reported the synthesis and characterization of three platinum(II) complexes stabilized by the chelating diphosphine ligand dppe (= 1, 2-bis(diphenylphosphino)ethane) as outlined in Scheme 63.[119,120]

After prolonged reaction times (typically 7 days) all three compounds were isolated in good yields (90%) in the form of colorless crystals. The crystal structure of **182** was determined by X-ray diffraction. In other cases reactions of silsesquioxane precursors with platinum complexes have been found to be far less straightforward. Upon treatment of two equivalents of the dithallium intermediate **69** with the square planar platinum(II) complex PtCl$_2$(COD), small amounts of the highly unusual heterobimetallic Pt/Tl silsesquioxane complex **185** were formed (pale yellow needles, 6% yield). A single crystal X-ray diffraction study revealed as the most striking structural feature of **185** the presence of a σ-bond between the silsesquioxane frame and the metal-coordinated cyclooctenyl ligand. A 1:1 reaction of the same reactants also afforded moderate yields of the expected platinasilsesquioxane derivative **186** (Scheme 64).
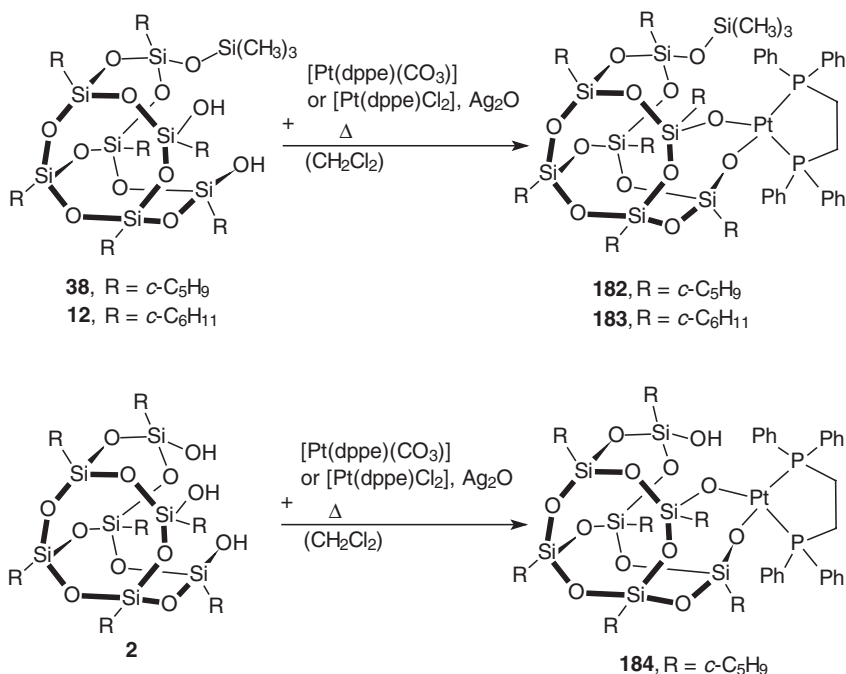
SCHEME 63. Synthesis of the platinum silsesquioxane complexes **182–184**.

6. Group 11 Metal Derivatives (Cu, Au)

The first silsesquioxane derivative of copper was made in our laboratory according to Scheme 65.[121] The reaction of the monosilylated disilanol precursor **12** with tetrameric copper(I)-t-butoxide in a molar ratio of 2:1 afforded the colorless copper(I) silsesquioxane complex **187**, in which the Cu_4O_4 core of copper(I)-t-butoxide is retained.

Thiol-functionalized silsesquioxane ligands such as $(c\text{-}C_5H_9)_7Si_7O_{12}$ $CH_2CH_2CH_2SH$ (**188**) have been successfully employed by Schmid $et\ al.$[122] in the synthesis of gold complexes, especially Au_{55} clusters. More simple gold(I) silsesquioxane derivatives include the complexes $(c\text{-}C_5H_9)_7Si_7O_9(OH)(OAuPPh_3)_2$ (**189**) and $(c\text{-}C_5H_9)_7Si_7O_9(OAuPPh_3)_3$ (**190**).[123] They are readily accessible by reacting the corresponding silanol precursors with appropriate amounts of $Au(O_2CNEt_2)(PPh_3)$.

IV

FUTURE OUTLOOK

During the past 15 years metallasilsesquioxanes have emerged from the status of mere laboratory curiosities and have become a well-investigated and highly valuable

186.
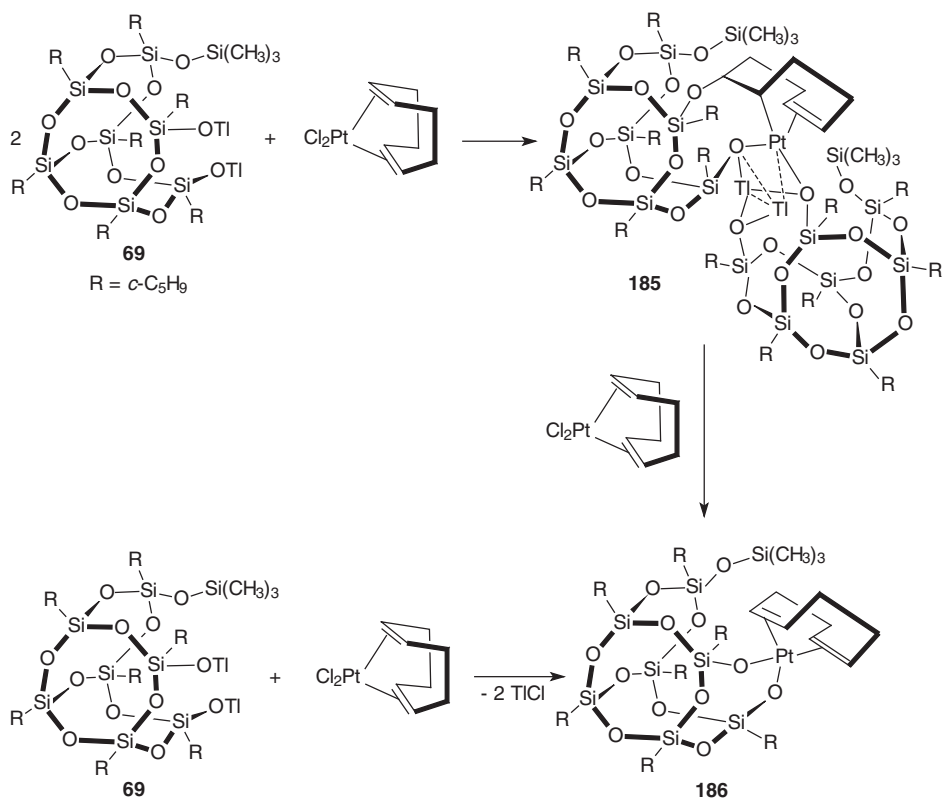
SCHEME 64. Synthesis of the platinum silsesquioxane complexes **185** and **186**.
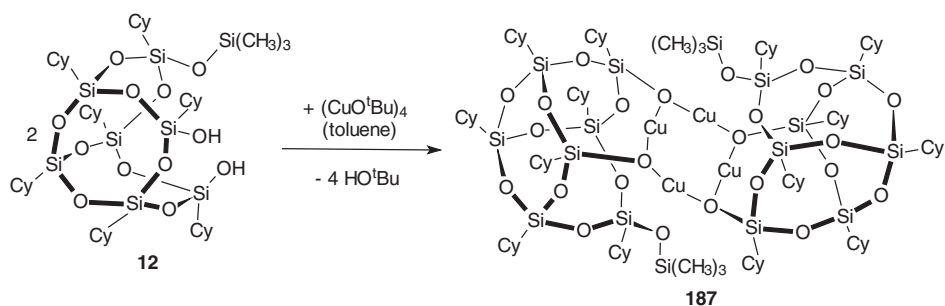
SCHEME 65. Synthesis of the copper(I) silsesquioxane complex **187**.

class of compounds. They are of fundamental interest as "realistic" molecular models of silica-supported metal catalysts. Various metallasilsesquioxanes have meanwhile turned out to be promising catalysts by in their own right. Novel aspects include the tethering of silsesquioxane cages to cyclopentadienyl-type ligands

(cf. Section III.B.2), the copolymerization and cross-linking of vinyl-substituted sil-sesquioxane titanium complexes with siloxane oligomers[124] and the preparation of metal oxide particles on microporous silica by controlled calcination of suitable metallasilsesquioxanes (cf. Sections III.C.1 and III.C.3). These aspects are expected to play an increasing role in future metallasilsesquioxane chemistry. Certainly, the recently discovered alkali metal silsesquioxane reagents such as **15–17** will become key intermediates in the synthesis of complex heterobimetallic metal-lasilsesquioxanes, which in turn could be promising precursors for multi-metallic silicate materials. Clearly, more work needs to be done to extend the "Periodic Table of metallasilsesquioxanes." Various metals (e.g., the heavier alkali and al-kaline earth metals, Mn, Re, Ir, Ni, Ag etc.) have not yet been successfully incor-porated into silsesquioxane derivatives. Strikingly, the vast majority of metallasilsesquioxanes reported thus far are derived from the incompletely con-densed trisilanols $R_7Si_7O_9(OH)_3$ (**2–7**). Extension of this chemistry to other sil-sesquioxane cage compounds remains a largely open field, where many exciting results can be expected for years to come.

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