ELSEVIER

Coordination Chemistry Reviews
206–207 (2000) 321–368

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Disiloxanediolates and polyhedral metallasilsesquioxanes of the early transition metals and *f*-elements

Volker Lorenz [a], Axel Fischer [a], Stephan Gießmann [a],
John W. Gilje [b], Yurii Gun'ko [c], Klaus Jacob [d],
Frank T. Edelmann [a,*]

[a] *Chemisches Institut der Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, Germany*
[b] *Department of Chemistry, James Madison University, Harrisonburg, VA 22807, USA*
[c] *Department of Chemistry, Trinity College, University of Dublin, Dublin 2, Ireland*
[d] *Institut für Anorganische Chemie, Martin-Luther-Universität Halle, Fachbereich Chemie (Merseburg), Geusaer Straße, D-06099 Halle, Germany*

Received 20 September 1999; received in revised form 21 December 1999; accepted 21 December 1999

Dedicated to Professor Karl-Heinz Thiele on the occasion of his 70th birthday

Contents

---

* Corresponding author. Tel.: +49-391-6718327; fax: +49-391-6712933.
E-mail address: frank.edelmann@chemie.uni-magdeburg.de (F.T. Edelmann).

0010-8545/00/$ - see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0010-8545(00)00299-X

Abstract

Two modern areas of metallasiloxane chemistry are reviewed. The first part deals with the preparation and structural characterization of the first *f*-element compounds derived from tetraphenylsisiloxanediol. In the second part recent developments in the chemistry of polyhedral metallasilsesquioxanes are surveyed, with special emphasis being placed on early transition metal and *f*-element derivatives. Also highlighted are applications of these species in catalysis research. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Disiloxanediolates; Metallasilsesquioxanes; Silsesquioxanes; Lanthanides; Actinides; Early transition metals

---

1. Introduction

Metallasiloxanes containing Si–O–M functional groups (M = main group metal, *d*-transition metal or *f*-element) derived from silanediols, disilanols, silanetriols, and trisilanols are in the focus of current interest for various reasons. In *catalysis*, many industrially and commercially important processes are catalyzed by transition metal complexes immobilized on silica surfaces [1–8]. However, due to the heterogeneous nature of the catalysts the catalytic species are normally difficult to characterize and quite often the mechanisms of the catalyzed organic transformations and the metal–silica interactions remain unclear. In these cases metallasiloxanes may serve as highly useful molecular model compounds which can to some extent provide insight into the scenarios occurring on metal-modified silica surfaces [9]. Especially metal compounds derived from polyfunctional silanols such as silanetriols or incompletely condensed silsesquioxanes are generally regarded as ‘realistic’ model compounds in this context as they exhibit the most advanced structural similarity with modified silica surfaces. The concept of studying polyhedral metallasilsesquioxanes to mimic surface sites in heterogeneous silica-supported transition metal catalysts was first proposed by Feher [9a]. In *materials science* certain metallasiloxanes are of interest as molecular precursors for metal-containing inorganic polymers [10,11] and other new materials [12–16]. Metallasiloxanes have also been envisaged as single-source precursors for modified zeolites [17]. Last, but not least, *structural chemistry* greatly benefits from the enormous variety of ring and cage structures found in various metallasiloxane derivatives. A wealth of novel Si–O–M-based polyhedral frameworks and suprastructures has already been uncovered and exciting supramolecular assemblies are emerging from this chemistry [18].

The chemistry of metallasiloxanes, including synthetic and structural aspects, has been extensively covered in excellent recent review articles [17,19] and a book [20]. More specialized reviews covering the chemistry of silanols, disilanols, and silanetriols [21], silicate cages [22], and silsesquioxanes [23–25] are also available. Thus this article will focus mainly on the most recent work in the field of disiloxanediolates and metallasilsesquioxanes. It is divided into two parts. In the first part early transition metal and *f*-element complexes derived from tetraphenyldisiloxanediol, $Ph_2Si(OH)OSiPh_2(OH)$ (**1**), will be surveyed. The second part deals with early transition metal and *f*-element derivatives of the incompletely condensed silsesquioxane cage molecule $Cy_7Si_7O_9(OH)_3$ (**2**) (Cy = cyclohexyl). In addition to *polyhedral* metallasilsesquioxanes, a number of highly interesting transition metal and lanthanide complexes containing cyclo(poly)siloxanolate ligands have been reported. However, these are not within the scope of this review as their preparation and structural characterization have been surveyed elsewhere [17,20,23].

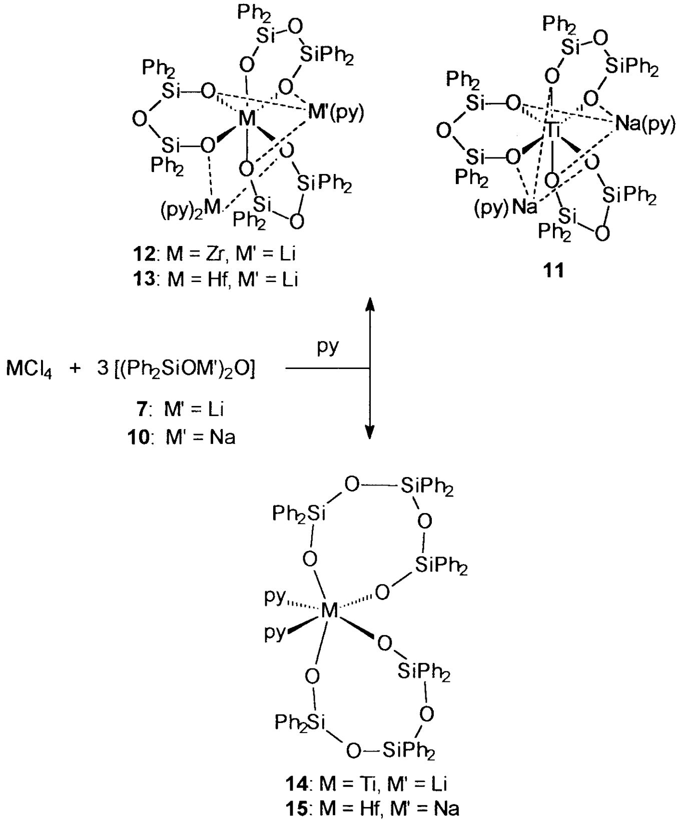
2. Disiloxanediolates

2.1. Starting materials

Disilanols are organosilicon compounds containing two Si–OH functional groups. Among the most often used building blocks in metallasiloxane chemistry are the disiloxanediolate derivatives $Ph_2Si(OH)OSiPh_2(OH)$ (**1**) [26] and $^tBu_2Si(OH)OSi^tBu_2(OH)$ (**3**) [27–31]. Apparently the former is more frequently used in metallasiloxane chemistry as it offers the advantage of being readily preparable from cheap starting materials. Hydrolysis of Ph_2SiCl_2 (**4**) in the presence of ammonium carbonate affords tetraphenyldisiloxanediol **1** in yields up to 51% [26]. Minor products in this synthesis are diphenylsilanediol, $Ph_2Si(OH)_2$ (**5**, 6% yield) and hexaphenyltrisiloxanediol, $Ph_2Si(OH)OSiPh_2OSiPh_2(OH)$ (**6**, 18% yield). The dilithium derivative of **1**, $Ph_2Si(OLi)OSiPh_2(OLi)$ (**7**), can be prepared and isolated in the presence of various Lewis bases such as THF, pyridine, or 1,4-dioxane. Interesting supramolecular structures have been found in the crystalline adducts $Ph_2Si(OLi)OSiPh_2(OLi)\cdot 2py$ (**8**) [32] and $Ph_2Si(OLi)OSiPh_2(OLi)\cdot 3dioxane$ (**9**) [33]. In **8**, dimeric self-assembly leads to the formation of a ladder-type structure consisting of three four-membered Li_2O_2 rings, while **9** is polymeric in the solid state.

2.2. Early transition metal derivatives

Well-defined Lewis-base adducts of **7** as mentioned in the previous section can be used to prepare transition metal derivatives of tetraphenyldisiloxanediol. However, a more convenient preparative route involves in situ formation of **7** by treatment of **1** with two equivalents of *n*-butyllithium in THF followed by treatment with the appropriate main group or transition metal halides. Various metallasiloxanes containing six-membered MSi_2O_3 rings (M = Ti, Zr, Hf, V, Cr, Mn, Co, Cu, Mg, B, Sn) have been synthesized using this method [17]. In these complexes the disiloxanediolate ligand can be either chelating [34–36], bridging [37–44], or chelate-bridging [45,46]. Apparently the latter two coordination modes are generally preferred over simple chelation. Typical examples from early transition metal disiloxanediolate chemistry which have been studied by Sullivan et al. are summarized in Scheme 1. A particularly interesting phenomenon frequently encountered in this chemistry, especially in the case of early transition metals, is the formation of ring-enlarged products containing the hexaphenyltrisiloxanediolate ligand $[Ph_2Si(OSiPh_2O)_2]^{2-}$ [47–50]. This anion can be coordinated to the metal either as a simple chelating ligand or in a chelate-bridging coordination mode, e.g. in certain heterobimetallic complexes. For example, the ring-expanded bis-chelate hafnium complex $[Ph_2Si(OSiPh_2O)_2]_2Hf(py)_2$ (**15**) was the only product when $HfCl_4$ was treated with three equivalents of $Ph_2Si(ONa)OSiPh_2(ONa)$ (**10**) followed by addition of pyridine [50]. As can be seen in Scheme 1, the outcome of these reactions



Scheme 1. Preparation of Group 4 metal disiloxanediolates [50].

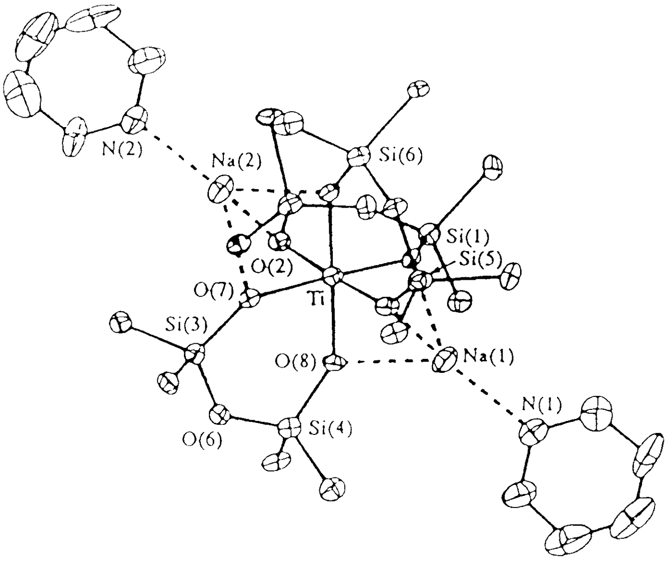


Fig. 1. Molecular structure of **11**.

with Group 4 metal tetrahalides strongly depends on the nature of the chosen disiloxanediolate reagent. The molecular structures of the heterobimetallic titanium complex **11** and the ring-expanded hafnium derivative **15** are shown in the Figs. 1 and 2. The two eight-membered rings in **15** are only slightly puckered.

Thus far metallasiloxanes derived from tetraphenyldisiloxanediol have been reported for the early transition metals titanium, zirconium, hafnium, and vanadium [17,33,39,47,50–53]. Apparently, no related Group 3 metal complex has been

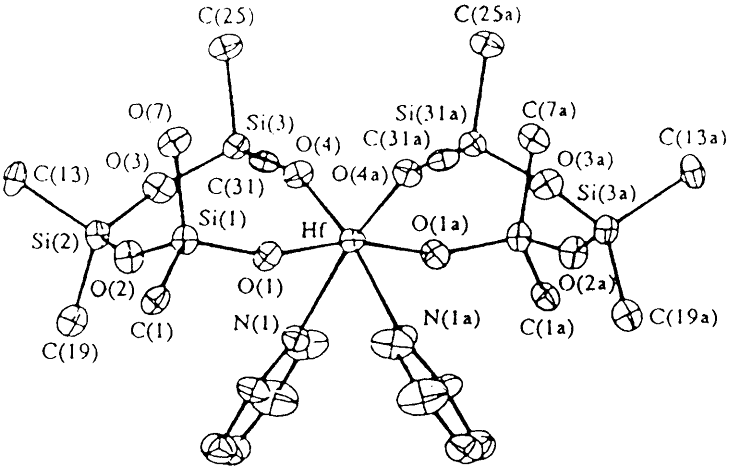
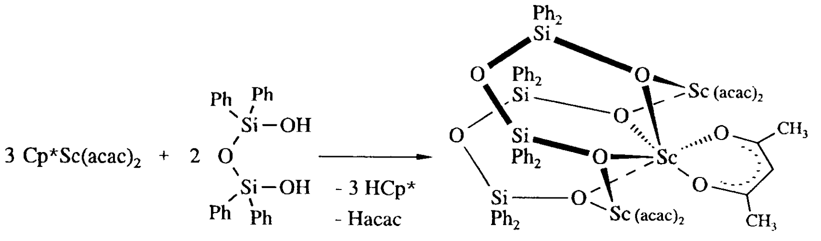


Fig. 2. Molecular structure of **15**.

reported in the literature [17,21b]. Recently the first scandium disiloxanediolate was prepared via a rather unexpected synthetic route. (Pentamethylcyclopentadienyl)scandium-bis(acetylacetonate), Cp*Sc(acac)$_2$ (**16**) [54], was treated with **1** (molar ratio 3:2) in refluxing toluene according to Eq. (1). Recrystallization of the crude product from diethylether afforded the trinuclear scandium disiloxanediolate [(Ph$_2$SiO)$_2$O]$_2$Sc$_3$(acac)$_5$ (**17**) in 72% yield.



16 **1** **17** (1)

During the course of this reaction the Cp* ligand in the starting material was completely replaced upon protonation by **1**. An X-ray structure analysis of **17** (Fig. 3) confirmed the presence of a trinuclear scandium complex containing the tetraphenyl-disiloxanediolate ligand in a novel chelate-bridging coordination mode involving three scandium ions.

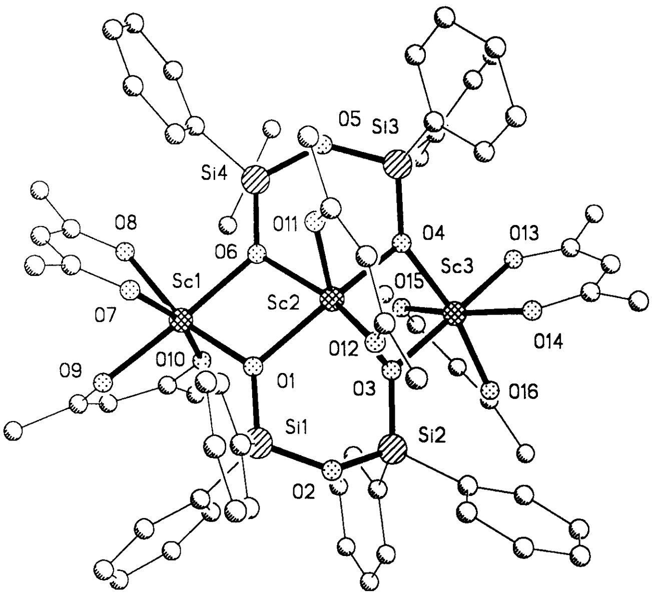
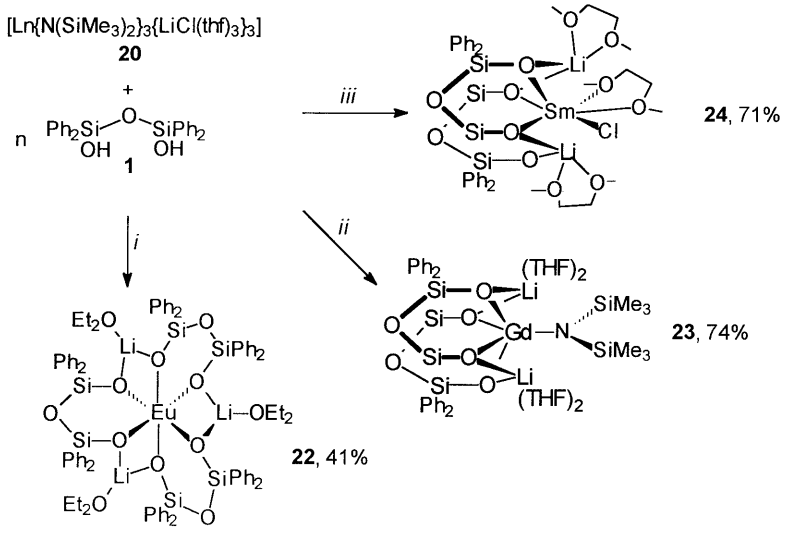


Fig. 3. Molecular structure of **17**.

2.3. Lanthanide derivatives

Apart from a series of very interesting cyclosiloxanolates [55,56], which have been reviewed elsewhere [17,20,23], the lanthanide (and actinide) elements had mostly been excluded from metallasiloxane chemistry. There have been reports on trialkyl and triphenylsilanolates of cerium and some other lanthanides [57], and most recently several tris(trimethylsilyl)siloxides of lanthanum and gadolinium have been prepared and structurally characterized. [58] However, no information on tetraphenyldisiloxanediolates of the rare earth elements was available. The only closely related lanthanide siloxane derivative which has been reported in the literature is (μ-OSiMe$_2$OSiMe$_2$O)[Cp$_2^*$Sm(THF)]$_2$ (**18**), which was first obtained from a reaction of the highly reactive organosamarium hydride [Cp$_2^*$Sm(μ-H)]$_2$ (**19**) with dimethylsilicone joint grease. A more straightforward preparation of **18** (88% yield) involves treatment of **19** with hexamethylcyclotrisiloxane in THF solution [59]. Our investigations in this field focussed on the chemistry of lanthanide complexes containing the tetraphenyldisiloxanediolate ligand. A ‘silylamide route’ [60] was found to be the method of choice for making such species. The silylamide precursors Ln[N(SiMe$_3$)$_2$]$_3$[LiCl(THF)$_3$]$_3$ (**20a**: Ln = Eu, **20b**: Ln = Gd, **20c**: Ln = Sm) are readily accessible by reacting anhydrous lanthanide trichlorides with three equivalents of LiN(SiMe$_3$)$_2$ (**21**) in THF [61]. The silylamides **20** were prepared in situ and subsequently reacted with **1** in different stoichiometries according to Scheme 2 [62].

In all cases heterobimetallic complexes are formed which formally contain lithium disiloxanediolate ligands acting as monoanionic ligands. Thus it is impor-



Scheme 2. Synthesis of the lanthanide disiloxanediolates **22**–**24**. Reagents and conditions: *i*, Ln = Eu, $n = 3$, toluene-Et$_2$O; *ii*, Ln = Gd, $n = 2$, THF; *iii*, Ln = Sm, $n = 2$, DME (four phenyl groups in **23** and **24** have been omitted for clarity).

tant to employ the in situ prepared silylamide precursors which still contain a large amount of lithium chloride. Another interesting result of these experiments is the finding that the nature of the products strongly depends on both the stoichiometry of the precursors and the size of the Ln^{3+} ion. The three complexes **22**–**24** have been isolated in the form of colorless crystalline solids. They were fully characterized by elemental analyses, spectroscopic data, and X-ray-crystallography. A homoleptic complex is obtained in the case of trivalent europium as central ion. The X-ray analysis (Fig. 4) reveals the presence of a heterobimetallic metallasiloxane, in which the Eu^{3+} ion is surrounded by three mono-anionic chelating $(Et_2O)Li[(Ph_2SiO)_2O]^-$ units.

Even more remarkable are the molecular structures of the gadolinium and samarium derivatives **23** and **24**. Both compounds are disubstituted lanthanide metallasiloxanes comprising two lithium disiloxanediolate units while retaining one functional ligand [Cl or $N(SiMe_3)_2$, respectively] (Figs. 5 and 6). The latter should make these complexes suitable candidates for carrying out derivative chemistry. The most striking structural feature of the species, however, is their similarity with certain lanthanide metallocenes such as $Cp^*_2LnN(SiMe_3)_2$, **25**, (cf. **23**) [63,64] or $Cp^*_2LnCl(THF)$, **26**, (cf. **24**) [65,66]. Such organolanthanide complexes are important as catalyst precursors or highly active catalysts in a variety of organic transformations [67,68]. It can be anticipated that the lithium disiloxanediolate units in the 'inorganic metallocenes' **22**–**24** are quite robust spectator ligands as they involve only lanthanide–oxygen coordination. Thus there might be a chance of

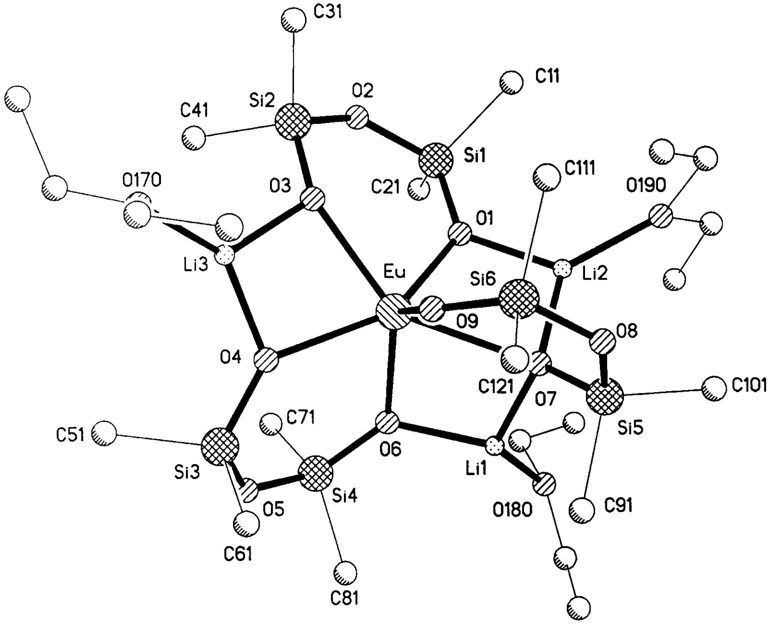


Fig. 4. Molecular structure of **22**.

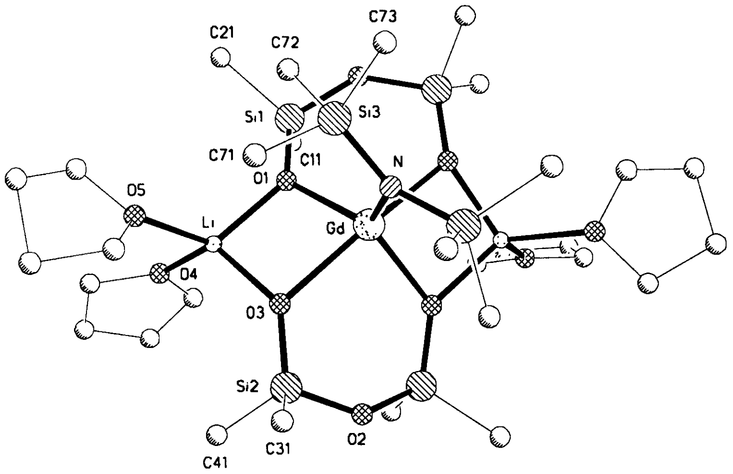
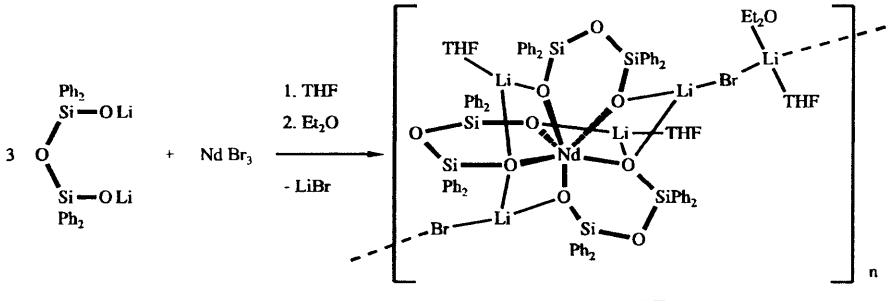


Fig. 5. Molecular structure of **23**.

using these materials to prepare organolanthanide catalysts which are less sensitive to air and moisture than the catalytically active lanthanide metallocenes. In the literature there is only one previous report on Li-containing anionic ligands formally replacing the Cp* ligands in lanthanide metallocenes, i.e. the $[Li(DAD)]^-$ units (DAD = 1,4-diazadiene dianion) [69].

While the reactions of tetraphenyldisiloxanediol with the lanthanide silylamide reagents proceed in a clear and straightforward manner, a completely different picture is seen when anhydrous lanthanide trihalides are allowed to react with $Ph_2Si(OLi)OSiPh_2(OLi)$ (**7**). Some products resulting from these reactions still remain to be fully characterized, but it appears that they are all different from those shown in Scheme 1. An interesting example in which retention of lithium halide leads to a self-assembled polymeric structure is the product obtained from the reaction of anhydrous $NdBr_3$ with three equivalents of **7** in THF solution. Extraction of the crude product with diethyl ether afforded the heterobimetallic neodymium disiloxanediolate **27** as a blue crystalline solid (Eq. (2)).



7 **27** (2)

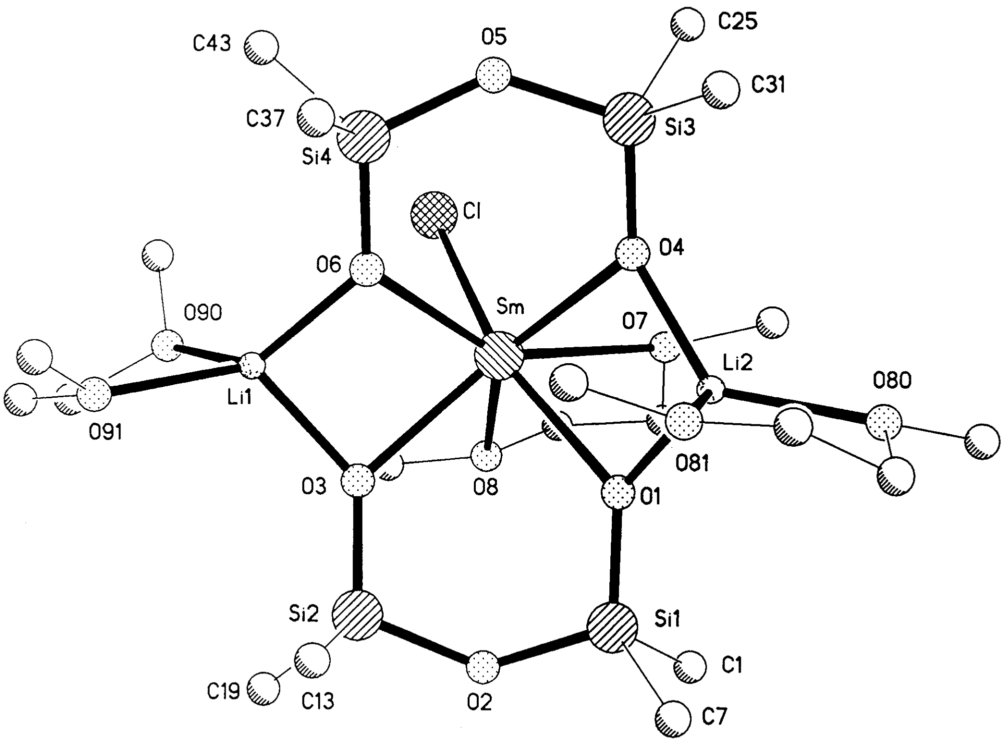


Fig. 6. Molecular structure of **24**.

According to the X-ray analysis the neodymium complex **27** contains a central core which is similar to that of the monomeric europium derivative **22** (Fig. 7). Three formally monoanionic lithium disiloxanediolate ligands are coordinated to Nd and the coordination sphere of two lithium ions is completed by an additional THF ligand. A polymeric superstructure results from retention of lithium bromide, which connects these monomeric units to give a linear chain polymer (Fig. 8). Clearly more structural investigations are needed to corroborate the nature of lanthanide disiloxanediolates resulting from reactions of anhydrous lanthanide trihalides with the lithium reagent **7**. A further structural variety can be expected when other alkali metal derivatives of tetraphenyldisiloxanediol are employed.

The derivative chemistry of lanthanide disiloxanediolates such as **23** and **24** is currently under active investigation in our laboratory. Especially the preparation of related σ-alkyl and hydride derivatives would be of interest as potential catalytically active species. A preliminary result was obtained from a reaction of **23** with diphenylsilanediol, $Ph_2Si(OH)_2$ (**5**). Plausible reaction pathways were thought to be either replacement of the silylamido ligand with formation of a diphenylsilanediolate complex or ring-enlargement. In fact, the latter did occur, but in a rather unexpected way. Treatment of **23** with two equivalents of **5** resulted in the formation

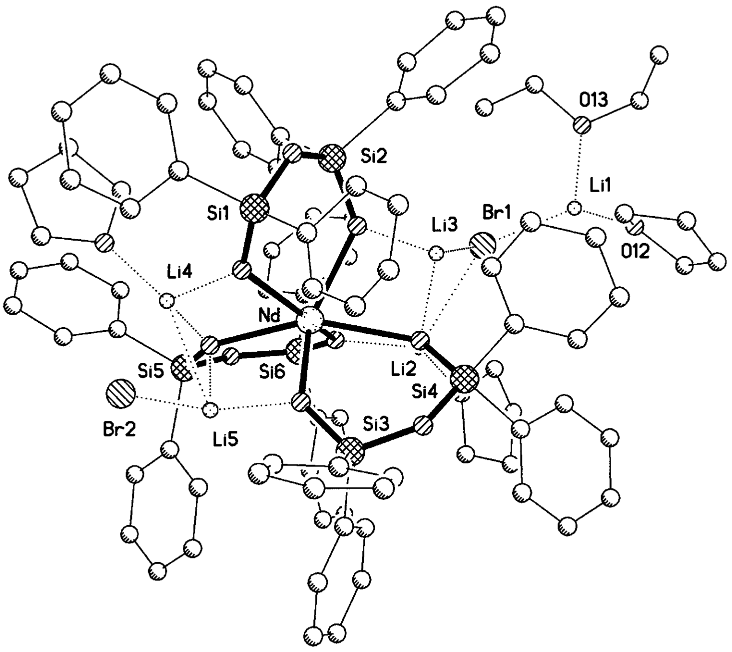


Fig. 7. Molecular structure of **27**.

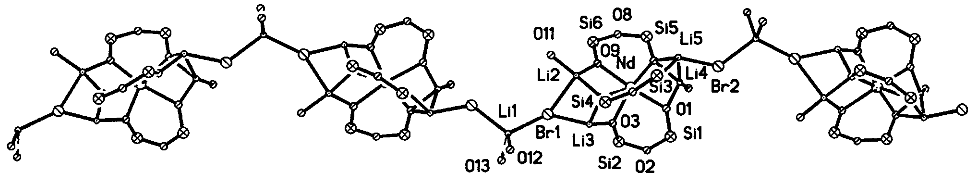
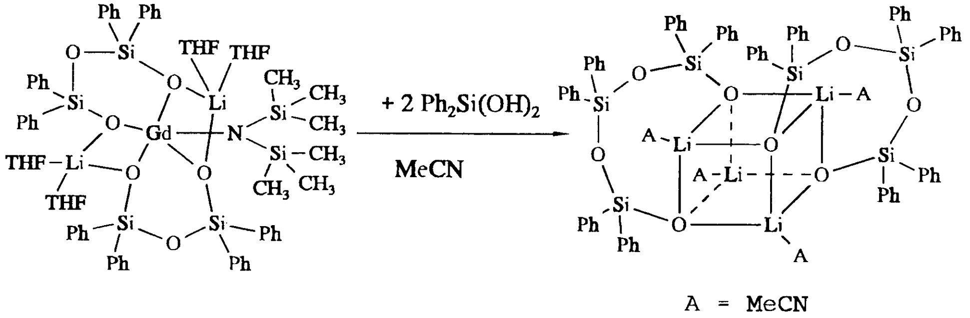


Fig. 8. Supramolecular chain structure of **27**.

of a colorless crystalline solid after recrystallization from acetonitrile. Spectroscopic evidence and X-ray diffraction revealed this material to be the acetonitrile solvate of the dilithium derivative of hexaphenyltrisiloxanediol (**28**, Eq. (3); Fig. 9).



23 **28** (3)

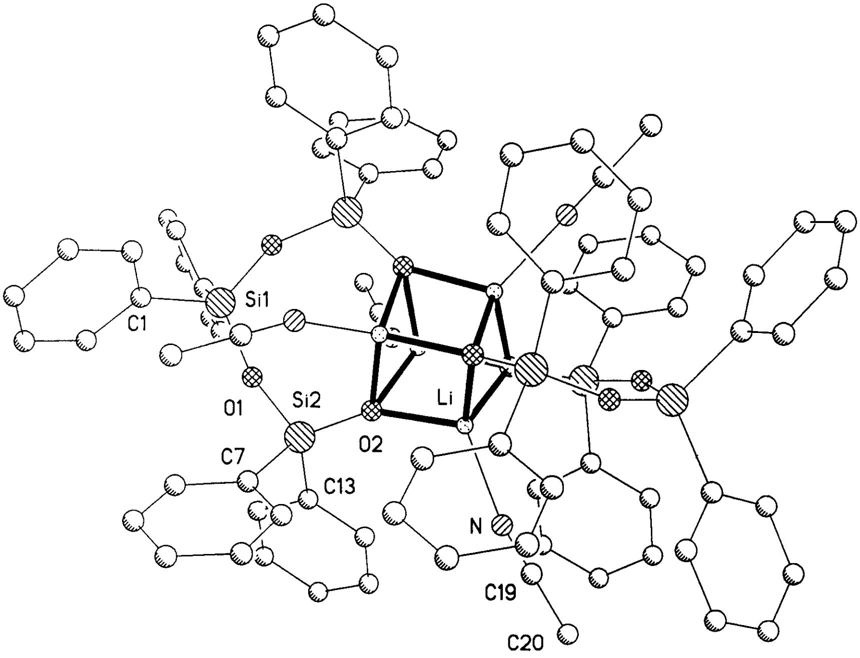
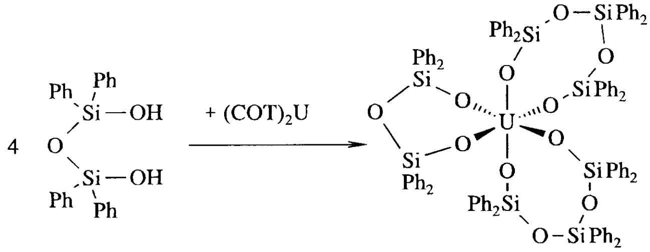


Fig. 9. Molecular structure of **28**.

The molecular structure of **28** consists of an Li_4O_4 heterocubane in which an acetonitrile ligand is coordinated to each lithium ion. The two hexaphenyltrisiloxanediolate ligands are arranged in a perpendicular fashion with respect to each other. The reaction leading to **28** is of interest as a deliberate way of achieving the ring-enlargement starting from a tetraphenyldisiloxanediolate and a monosilicon building block. In addition, the dilithium derivative **28** may well serve as a useful reagent for the preparation of other metal hexaphenyltrisiloxanediolates.

2.4. Actinide derivatives

Like the rare earth elements, actinides were virtually non-existent in metallasiloxane chemistry until recently. In this context it is interesting to note that even the chemistry of simple uranium trialkylsilanolates is very little developed and no structural information is available. The few existing reports in the literature are mainly concerned with uranium(V) and uranium(VI) siloxides such as $U(OSiR_3)_5$ (**29**; R = Me, Et) or $U(OSiR_3)_6$ (**30**; R = Me, Et) [70–73]. It was found that reactions of UCl_4 with two or three equivalents of **7** were always accompanied by complete decolorization of the reaction mixtures, indicating oxidation to uranium(VI) species. However, it proved difficult to isolate pure compounds from these mixtures. Finally this became possible by employing a salt-free synthetic route starting with the long-known uranium sandwich complex uranocene, $(COT)_2U$ (**31**, COT = η^8-C_8H_8) [74]. Treatment of uranocene with an excess of tetraphenyldisiloxanediol in toluene solution resulted in clean formation of the colorless uranium(VI) complex $U[Ph_2Si(OSiPh_2O)_2]_2[(Ph_2SiO)_2O]$ (**32**) according to Eq. (4) [62].



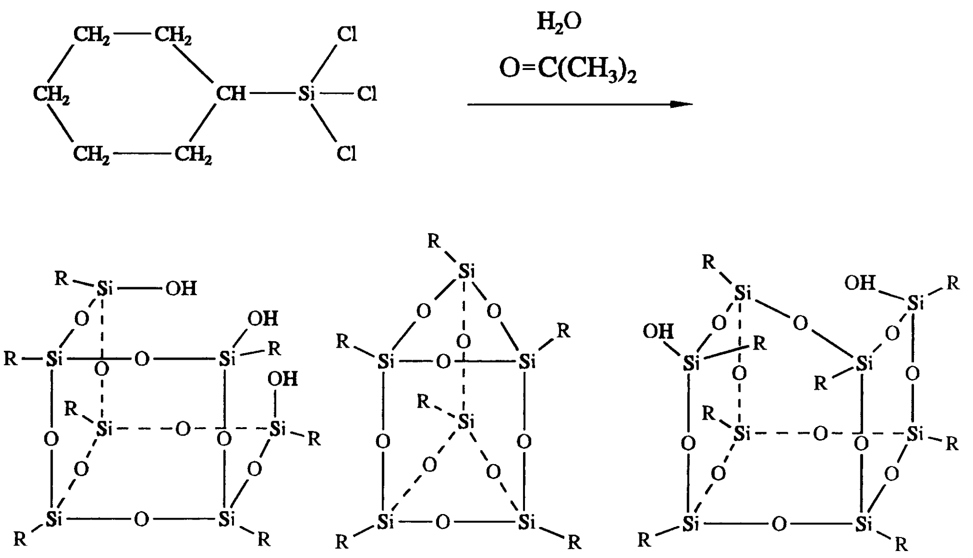
1 **32** (4)

This reaction and the nature of the product are quite remarkable in several ways. First of all, the replacement of both cyclooctatetraene ligands upon treatment with the disiloxane reagent is an unprecedented reaction pathway for uranocene. Secondly, clean oxidation to uranium(VI) readily takes place in the presence of **1** and not even traces of uranium(IV) disiloxanediolate species have been detected. Finally, an X-ray structure analysis revealed that **32** represents the first example of a mixed-ligand metallasiloxane containing both the original tetraphenyldisiloxanediolate dianion and the ring-expanded hexaphenyltrisiloxanediolate chelating ligand [47–50] (Fig. 10). Thus the monomeric molecule contains one six-membered and two eight-membered metallasiloxane ring systems.

3. Metallasilsesquioxanes

3.1. Starting materials

Silsesquioxanes are silicon–oxygen cage compounds of the general formula $(RSiO_{1.5})_n$ which can be prepared by hydrolysis of the corresponding trifunctional organosilicon monomers $RSiCl_3$ or $RSi(OMe)_3$ [75]. Various aspects of their chemistry, including the preparation and structure of metallasilsesquioxanes, have been documented in a number of review articles [17,22–25,76–81]. Among the fully condensed silsesquioxane polyhedra are trigonal prisms ($R_6Si_6O_9$, $n = 6$), cubes ($R_8Si_8O_{12}$, $n = 8$), and drum-shaped frameworks ($R_{10}Si_{10}O_{15}$, $n = 10$; D_{2d}-$R_{12}Si_{12}O_{18}$, $n = 12$). Especially interesting for the preparation of metallasilsesquioxanes and other functional derivatives are incompletely condensed silsesquioxanes which can be regarded as intermediates in the formation of the fully condensed frameworks. The most prominent representative of this class of organosilicon compounds is the trisilanol derivative $Cy_7Si_7O_9(OH)_3$ (**2**), which was first reported by Brown and Vogt [82,83] and more recently investigated in great detail by Feher and co-workers [25]. An improved synthetic route developed by the latter research group involves kinetically controlled hydrolysis of trichlorocyclohexylsilane according to Eq. (5) [84].



2 (R = Cy) **33** (R = Cy) **35** (R = Cy)

(5)

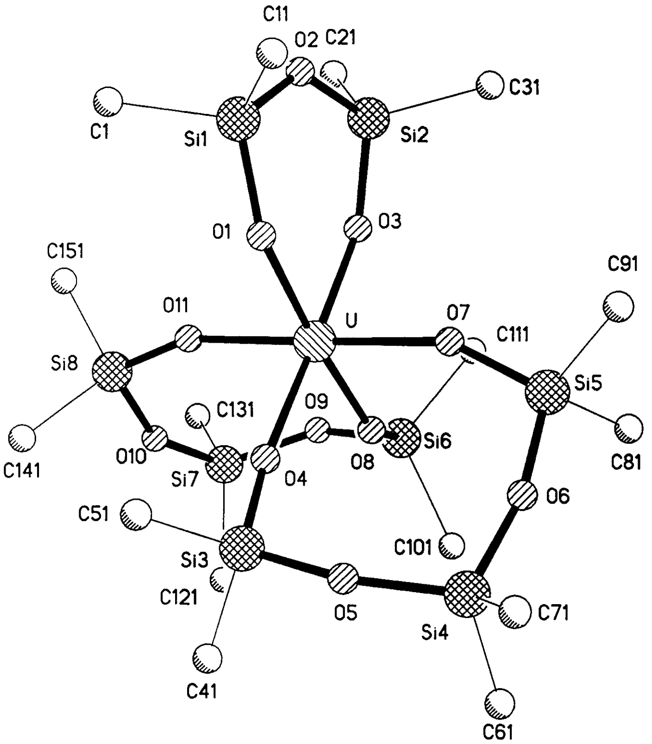
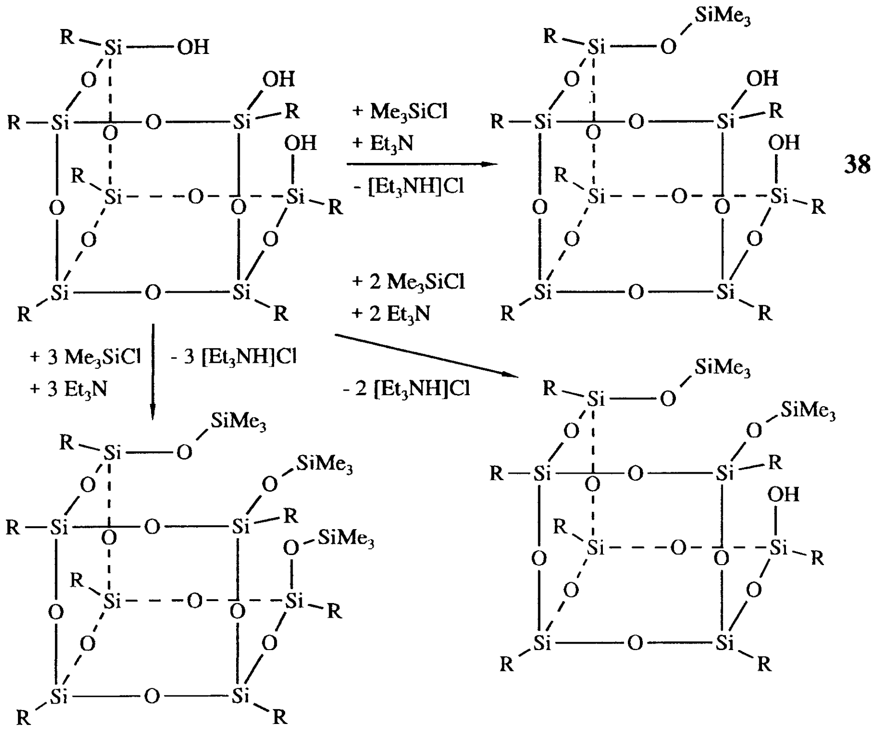


Fig. 10. Molecular structure of **32**.



40 **39**

Scheme 3. Synthesis of the silylated silsesquioxanes **38**–**40** (R = Cy). Reagents and conditions: Me_3SiCl/NEt_3, THF, r.t.

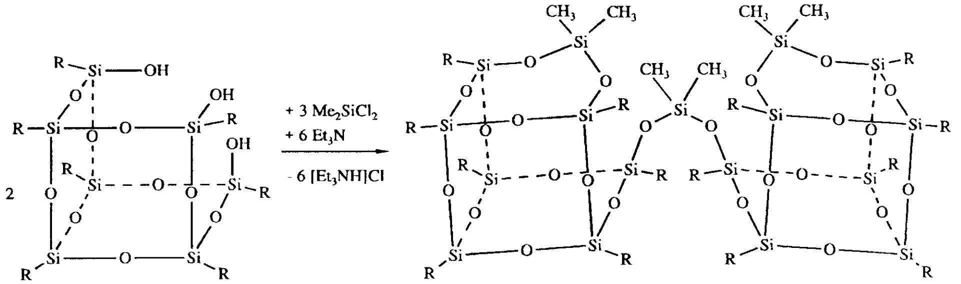
Other products resulting from this reaction are the fully condensed silsesquioxane **33** and the disilanol derivative **34**, from which **2** can be readily separated by an extraction procedure. A certain drawback of this synthesis is that the kinetically controlled hydrolytic polycondensation of the in situ formed cyclohexylsilanetriol, $CySi(OH)_3$ (**35**), takes up to 3 years to proceed to completion. However, synthetically useful quantities of **2** can already be isolated after a reaction time of several months. Related trisilanols based on a silsesquioxane cube have been isolated with R = cyclopentyl (**36**) and cycloheptyl (**37**) [85]. In these cases, and quite in contrast to the formation of **2**, the rates of the hydrolysis reactions can be dramatically improved by refluxing the reaction mixtures.

The derivative chemistry of **2** and especially the study of related metallasilsesquioxanes as molecular models for silica-supported metal catalysts have been pioneered by Feher et al. [9a]. Synthesis, characterization, and reactivity of these compounds have been surveyed in a recent review article [25]. Thus the present contribution focuses mainly on new results published after 1995. The preparation of metal derivatives of **2** generally involves treatment of the parent trisilanol with the appropriate metal halide in the presence of a base such as triethylamine [17,25]. In addition, Feher et al. have demonstrated that the reactivity of **2** can be modified and tuned by silylation of the Si–OH functions [84,86] or by preparing the corresponding thallium silanolates [87]. The latter offer the advantage that thallium reagents are non-reducing and thus allow the preparation of transition metal derivatives in high oxidation states. On the other hand, silylation is an effective way to protect one or two Si–OH functions and thus prepare the corresponding mono- and disilanol derivatives. Scheme 3 illustrates the selective preparation of mono-, di- and trisilylated silsesquioxanes starting from **2**.

The silylated products **38** and **40** can be readily isolated as pure materials by fractional crystallization from pentane or hexane. The disilylated silsesquioxane **39** is not as easily prepared as it is very soluble in hydrocarbon solvents and thus somewhat difficult to purify. Recently an analytically pure sample of **39** was obtained by repeated crystallization from acetonitrile and this enabled us to determine its molecular structure. Figure 11 depicts how the single Si–OH function is sterically shielded by a cyclohexyl substituent and two -OSiMe$_3$ units.

In contrast to the monomeric nature of **39**, the parent trisilanol **2** had previously been reported to crystallize as a hydrogen-bonded dimer [9a].

In an extension of this chemistry the reaction of **2** with the difunctional reagent dichlorodimethylsilane was studied [88]. A pure reaction product, the bis(-silsesquioxane) derivative **41**, can be isolated when the reaction is carried out in a 2:3 molar ratio according to Eq. (6).



41 (R = Cy) (6)

The white crystalline solid was structurally characterized by X-ray diffraction (Fig. 12). In this molecule one corner of the original incompletely condensed silsesquioxane is capped by a Me$_2$Si unit. A third Me$_2$Si group connects two of these partially closed silsesquioxane cages.

Lithium, sodium or potassium silanolates derived from the trisilanol **2** would be of paramount interest as they could also serve as useful starting materials for the preparation of other polyhedral metallasilsesquioxanes. In fact, it was first demonstrated by Feher et al. that deprotonation of the trisilanols **2**, **36** or **37** with one equivalent of sodium *t*-butoxide cleanly affords the corresponding mono-sodium derivatives, but these products were found to be stable only for short periods of time in solution and could not be isolated as crystalline materials [25]. Another

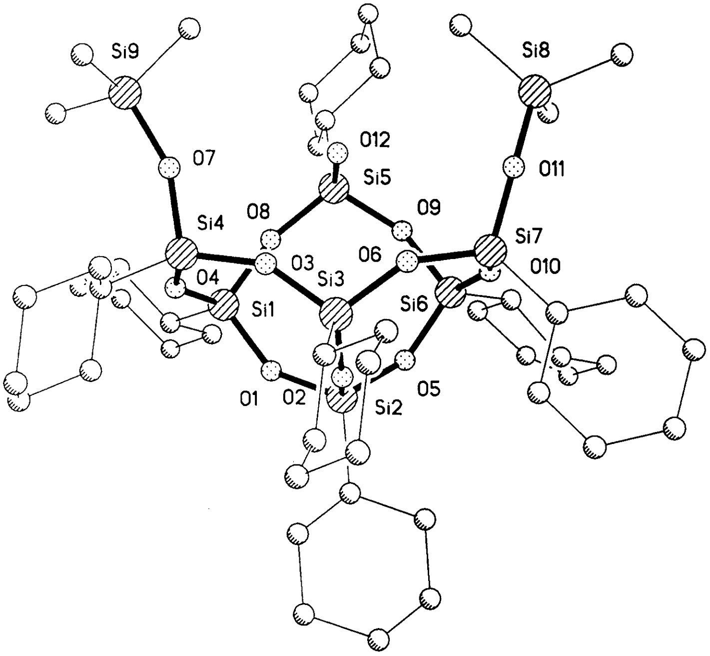


Fig. 11. Molecular structure of **39**.

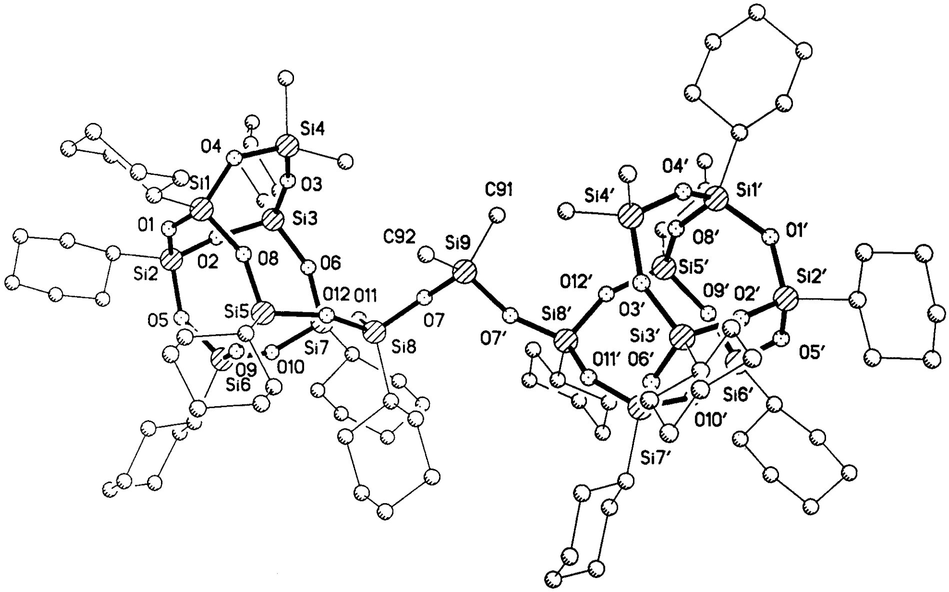
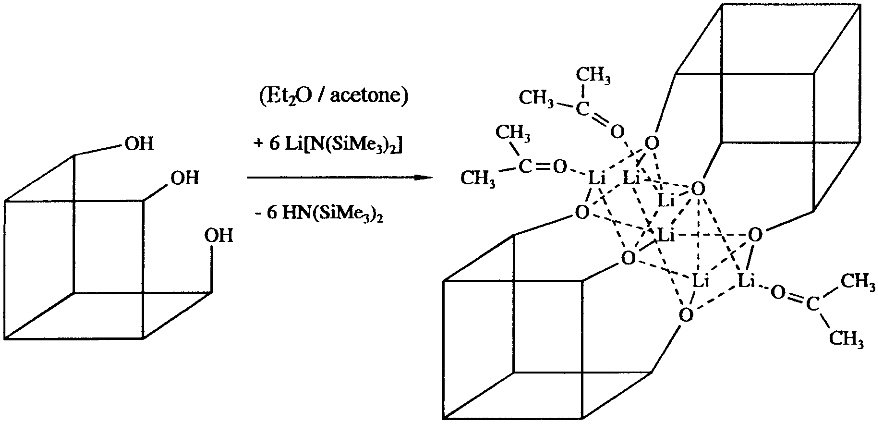


Fig. 12. Molecular structure of **41**.

route to remarkably stable mono-anionic derivatives involves the comproportionation reaction of **2** with $Cy_7Si_7O_9(OTl)_3$ (**42**) [87] followed by reaction with $[PPh_4]Cl$, $[P^nBu_4]Cl$, or $[N^nBu_4]Br$ to produce the corresponding salts of $[Cy_7Si_7O_{10}(OH)_2]^-$, i.e. the monoanion derived from deprotonation of **2** [89a]. A single-crystal X-ray diffraction study revealed that the salt $[N^nBu_4][Cy_7Si_7O_{10}(OH)_2]$ (**43**) exists in the solid state as isolated ion pairs with strong intramolecular hydrogen bonding (Fig. 13) [89a].

Quite in contrast, early attempts to exhaustively deprotonate the Si–OH functions with the use of strong bases such as NaO^tBu resulted in decomposition, presumably owing to skeletal degradation of the silsesquioxane cage [25]. Recently it was discovered that a successful preparation of fully deprotonated trisilanols strongly depends on the proper choice of the base [89b,c]. It was found that the silsesquioxane cage remains intact and all three Si–OH functions are deprotonated when **2** is treated with three equivalents of $LiN(SiMe_3)_2$. Diethyl ether, THF or toluene are suitable solvents for these reactions. When the deprotonation reaction between **2** and $LiN(SiMe_3)_2$ (**21**) is carried out in toluene, the unsolvated lithium silanolate $Cy_7Si_7O_9(OLi)_3$ (**44**) precipitates as an amorphous, presumably polymeric material. However, crystalline adducts are readily obtained in the presence of suitable Lewis bases. Eq. (7) illustrates the preparation of the acetone solvate $[Cy_7Si_7O_9(OLi)_3]_2{\cdot}3Me_2CO$ (**45**), which was the first adduct of this type to be isolated and structurally characterized [89a].

2



2 **45**

(7)

As shown by X-ray diffraction, supramolecular self-assembly of **45** leads to the formation of an unsymmetrical dimer in the solid state (Fig. 14).

The central structural unit of **45** consists of a box-shaped Li_6O_6 polyhedron. Acetone ligands are coordinated to three lithium ions while the other three interact with framework oxygen atoms of the silsesquioxane cages. This results in tetracoordination around each lithium. Structurally related box-shaped Li_6O_6 or Li_6S_6 polyhedra have previously been reported for some hexameric lithium phenoxides or

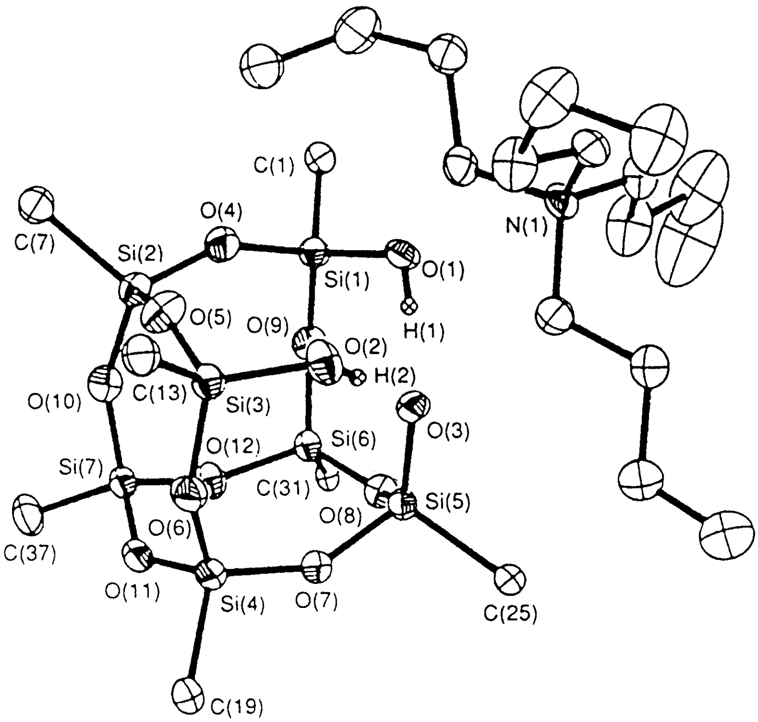


Fig. 13. Molecular structure of **43**.

arenethiolates [18]. The structural investigation of **45** clearly demonstrated that fully deprotonated trisilanols can be generated without concomitant break-down of the silsesquioxane cage structure and that the products can be isolated as stable crystalline solids. In a similar manner the well-defined adducts $[Cy_7Si_7O_9(OLi)_3]_2 \cdot 3Et_2O$ (**46**) and $[Cy_7Si_7O_9(OLi)_3]_2 \cdot 3THF$ (**47**) have been isolated in high yields and fully characterized. The dimeric molecular structure of **47** is shown in Fig. 15.

Most recently, Aspinall et al. also succeeded in preparing fully deprotonated silsesquioxanes [89c]. These authors demonstrated that it is possible to isolate the unsolvated lithium silanolate $Cy_7Si_7O_9(OLi)_3$ (**44**) by reacting **2** with three equivalents of ^{n}BuLi in hexanes. Under these conditions **44** was obtained in high yield as a white solid, which was found to be indefinitely stable in the air at room temperature! Hydrolysis of a 1-year-old sample with HCl in THF resulted in clean and quantitative formation of **2**, indicating that no noticeable degradation of the silsesquioxane cage had occurred. In a similar manner, mono-silylated **38** could be deprotonated in the presence of *n*-butyllithium to afford $Cy_7Si_7O_9(OSiMe_3)(OLi)_2$ in moderate yield [89c]. Initial experiments indicate that other alkali metal derivatives of fully deprotonated **2** can be readily prepared using the corresponding alkali metal bis(trimethylsilyl) amides [89b]. For example, treatment of **2** with three equivalents of $KN(SiMe_3)_2$ (**48**) in DME solution afforded the potassium silanolate

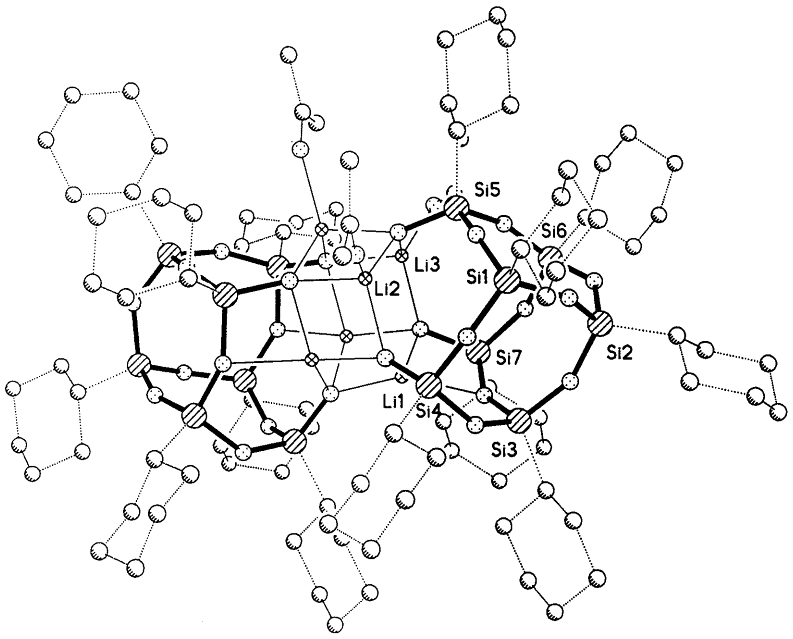
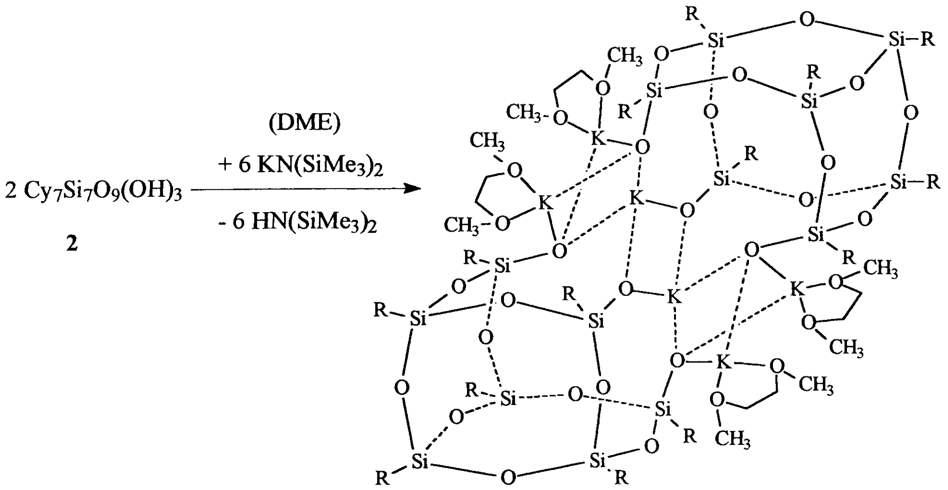


Fig. 14. Molecular structure of **45**.

$[Cy_7Si_7O_9(OK)_3]_2 \cdot 4DME$ (**49**) in almost quantitative yield as a colorless, moisture-sensitive crystalline solid (Eq. (8)) [89b]. According to the X-ray analysis the crystal structure of **49** consists of dimeric molecules formed by self-assembly of two fully deprotonated silsesquioxane cages and six potassium ions (Fig. 16).



2

49
(R = Cy)

(8)

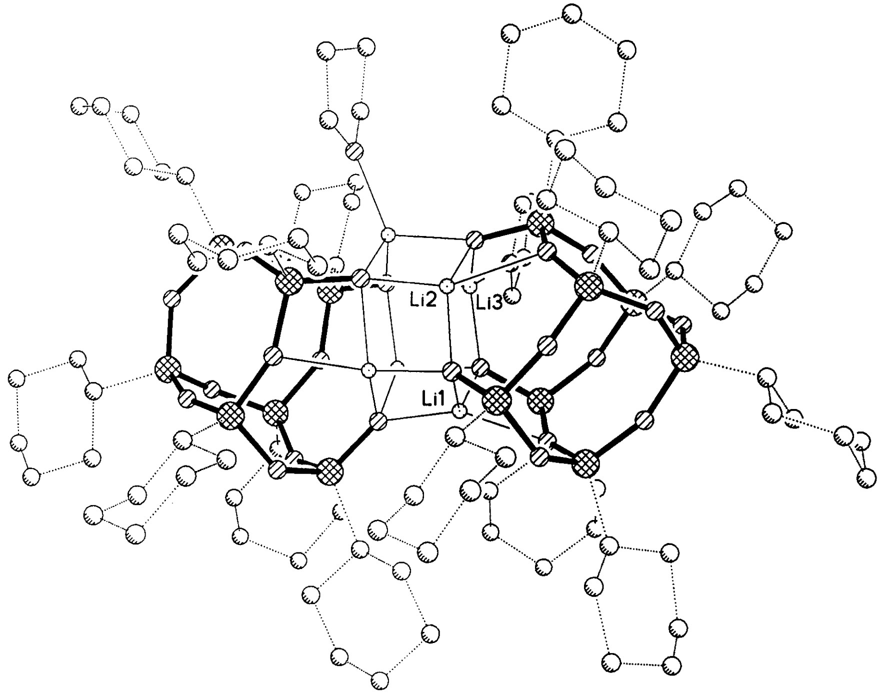
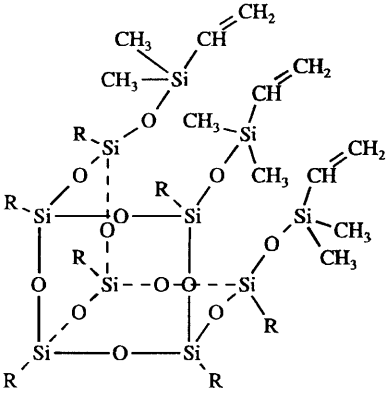


Fig. 15. Molecular structure of **47**.

Similar to the lithium silanolates **44**–**47** a box-shaped K_6O_6 arrangement forms the central structural unit of the dimer. Four chelating dimethoxyethane ligands are needed to saturate the coordination sphere of the potassium ions owing to the larger ionic radius of potassium.

The first reactivity studies have already demonstrated, that the novel alkali metal silsesquioxanes **44**–**47** and **49** are excellent building blocks for the construction of heterobimetallic metallasiloxanes (vide infra) [89b,c]. New silylated derivatives are also readily prepared from these starting materials, as exemplified by the reaction of **44** with three equivalents of $ClSiMe_2(CH{=}CH_2)$ according to Eq. (9). White crystalline $Cy_7Si_7O_9[OSiMe_2(CH{=}CH_2)]_3$ (**50**) can be isolated in ca. 90% yield. Oligo(vinylsilane) derivatives such as **50** may be of interest as precursors for the synthesis of carbosilane dendrimers based on the incompletely condensed silsesquioxane cage of **2**.

$$\underset{\mathbf{44}}{Cy_7Si_7O_9(OLi)_3} + 3\ CH_2{=}CHSiMe_2Cl \xrightarrow[-\ 3\ LiCl]{Et_2O}$$



50 (R = Cy)

(9)

It should be noted at this stage that until recently the number of incompletely condensed silsesquioxanes which were available in preparatively useful quantities was quite limited [82–85,90–92]. In fact, virtually all studies directed towards the synthesis of metallasilsesquioxanes or silsesquioxane-derived hybrid organic-inorganic polymers have been carried out using **2** or its cyclopentyl-substituted analog **36**. However, a new synthetic route to incompletely condensed silsesquioxanes has

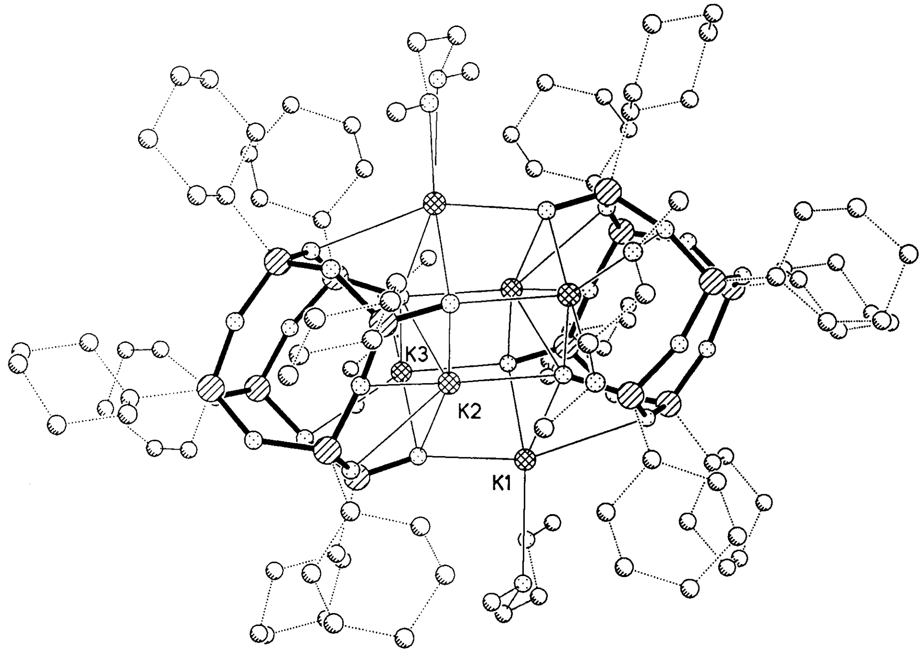


Fig. 16. Molecular structure of **49**.

recently been developed by Feher et al. [93–96]. It involves the acid-mediated cleavage and — in some cases — rearrangement of fully condensed silsesquioxane frameworks such as trigonal prismatic $Cy_6Si_6O_9$ (**51**) or cubic $Cy_8Si_8O_{12}$ (**52**). The resulting silanediols (e.g. C_2–$Cy_6Si_6O_8(OH)_2$ (**53**)) are a valuable addition to the current pool of incompletely condensed silsesquioxanes and it can be anticipated that they will exhibit a rich derivative chemistry and provide access to interesting new Si–O frameworks [96].

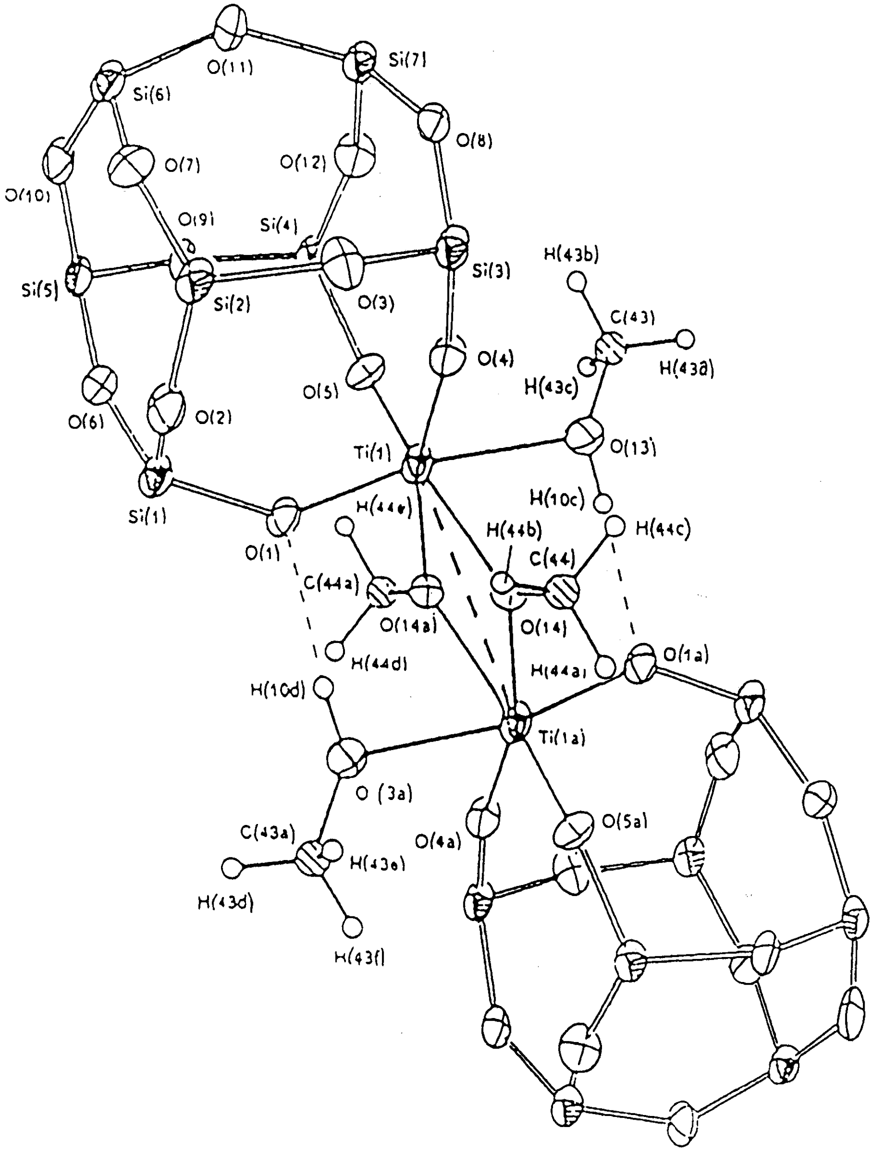


Fig. 17. Molecular structure of **65**.

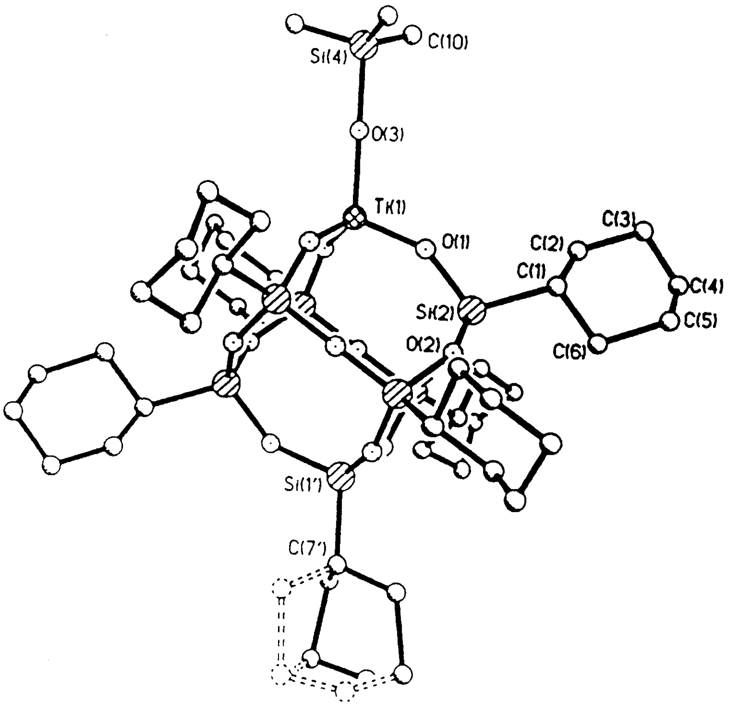
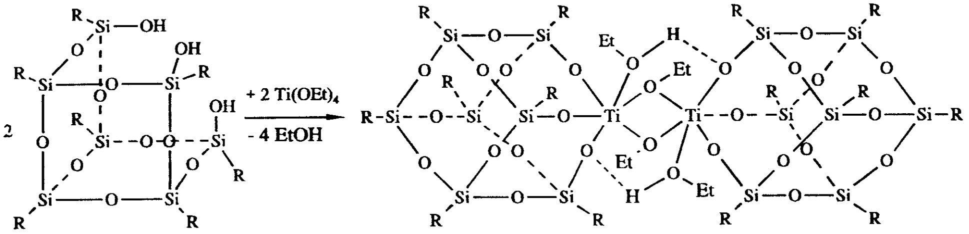


Fig. 18. Molecular structure of **73**.

3.2. Early transition metal derivatives

Thus far, metallasilsesquioxane derivatives containing the Group 3 elements scandium, yttrium, and lanthanum are unknown [17]. Previously reported Ti compounds include titanium(III) [97] and titanium(IV) silsesquioxanes [98]. The former have been prepared by allowing **2** to react with either $Ti[N(SiMe_3)_2]_3$ (**54**) or $TiCl_3(NMe_3)_2$ (**55**). The initial product in these reactions is the blue dimeric complex $[Cy_7Si_7O_{12}Ti]_2$ (**56**). Treatment of **56** with pyridine afforded the bis-adduct $[Cy_7Si_7O_{12}Ti(py)]_2$ (**57**) in virtually quantitative yield. Both **56** and **57** have been structurally characterized by X-ray analyses [97]. Corner-capping of the silsesquoxane framework with a TiCp unit is readily achieved by treatment of either $Cy_7Si_7O_9(OSbMe_4)_3$ (**58**) or the thallium silanolate $Cy_7Si_7O_9(OTl)_3$ (**42**). In both cases the product is monomeric $Cy_7Si_7O_{12}TiCp$ (**59**) [98]. Other titanasilsesquioxanes have been designed as model compounds for titanosilicates, which are industrially important as oxidation catalysts [99]. Prominent examples of such realistic models include $(MeC_5H_4)_4Ti_4(Si^tBu)_4O_{12}$ (**60**) [100], $[2,6\text{-}^iPr_2C_6H_3NH_3]$-$[(RSiO_3)_3Ti_4Cl_4(\mu_3\text{-}O)]$ [**61**, $R = 2,6\text{-}^iPr_2C_6H_3N(SiMe_3)$] [101], $[Cy_7Si_7O_{12}MgTiCl_3]_n$ (**62**, $n = 1,2$) [102], and $[R_7Si_7O_{12}TiO^iPr]_n$ (**63**, $R = c\text{-}C_5H_9$, **64**, $R = c\text{-}C_6H_{11}$; $n = 1,2$) [103]. In the presence of triethylaluminum, compound **62** was found to exhibit high catalytic activity for ethylene polymerization, while the model compounds **63** and **64** display catalytic activity in the epoxdation of cyclohexene (cf. Section 4.2). The high catalytic performance of these two complexes was attributed to a monomer–dimer equilibrium which could create free coordination sites at titanium. Treatment of **64** with methanol affords the six-coordinate titanasilsesquioxane dimer $[Cy_7Si_7O_{12}Ti(\mu\text{-}OMe)(MeOH)]_2$ (**65**), which was structurally characterized (Fig. 17) [103]. The same type of alkoxide-bridged dimer can also be obtained directly by the reaction of the trisilanols **2** and **32** with titanium tetraethoxide in a 1:1 molar ratio (Eq. (10)) [104,105].



2, R = Cy **66**, R = Cy

36: R = c-C_5H_9 **67**, R = c-C_5H_9 (10)

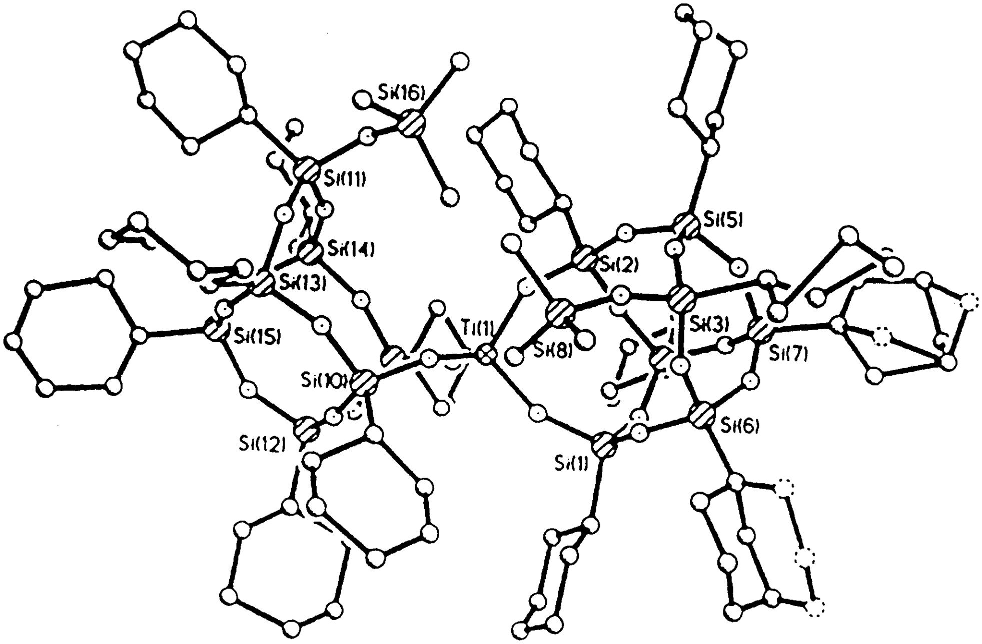


Fig. 19. Molecular structure of **75**.

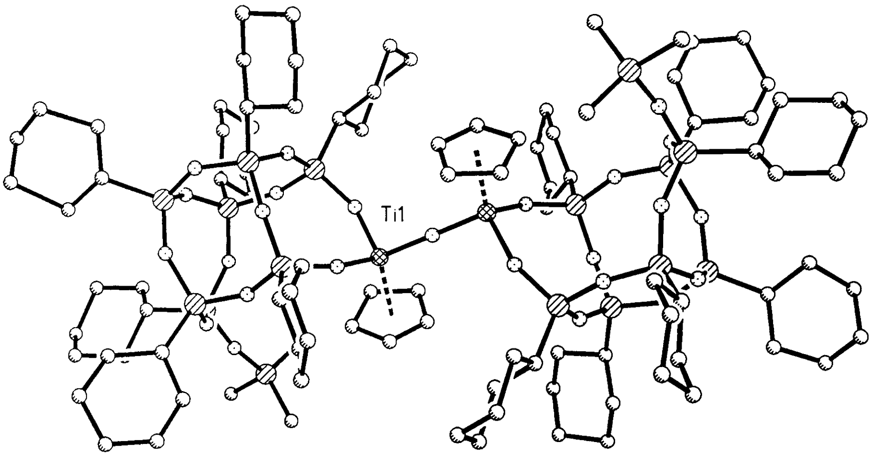


Fig. 20. Molecular structure of **83**.

The solid state dimeric molecular structure was established by an X-ray diffraction analysis of **66** [104]. As in **65**, two titanium-capped silsesquioxane cages are connected through alkoxide bridges. One ethanol ligand, which is a by-product in the formation of these compounds, is coordinated to each Ti atom. In solution, compound **66** also exists in a monomer–dimer equilibrium as evidenced by ^{1}H-NMR studies [105]. The protonolytic reaction exemplified in Eq. (10) is not limited to titanium tetraalkoxides. Related complexes, although monomeric, have also been

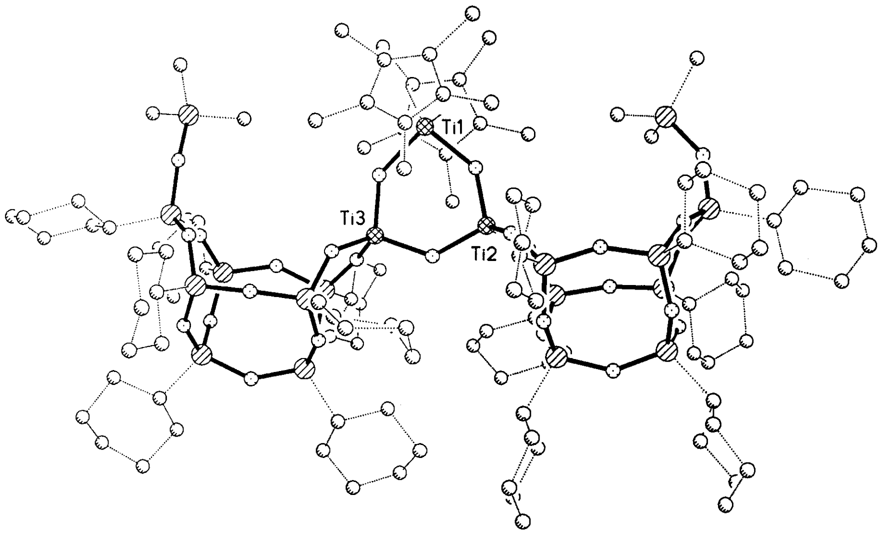


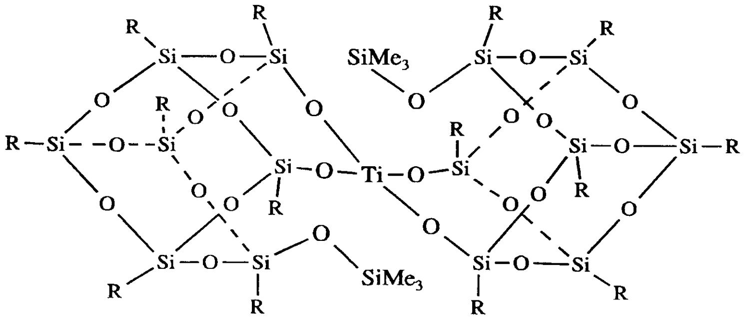
Fig. 21. Molecular structure of **85**.

isolated from reactions of **2** with $Ti(CH_2Ph)_4$ (**68**), $Ti(NMe_2)_4$ (**69**) or $Ti(OSiMe_3)_4$ (**70**) [105]. The products, $Cy_7Si_7O_{12}TiCH_2Ph$ (**71**), $Cy_7Si_7O_{12}TiNMe_2$ (**72**) and $Cy_7Si_7O_{12}TiOSiMe_3$ (**73**) were characterized on the basis of elemental analysis and NMR data as well as an X-ray structural analysis in the case of **65**. The molecular structure of **73** is depicted in Fig. 18.

Similar reactions have also been carried out with the difunctional monosilylated silsesquioxane precursor **38** [105]. Treatment of **38** with one equivalent of $Ti(O^{i}Pr)_4$ smoothly produced monomeric $Cy_7Si_7O_{11}(OSiMe_3)[Ti(O^{i}Pr)_2]$ (**74**) as the sole product. A bis(silsesquioxane) titanium complex, $[Cy_7Si_7O_{11}(OSiMe_3)]_2Ti$ (**75**), can be prepared using either $Ti(CH_2Ph)_4$ (**68**) [105] or, as shown in Eq. (11), $Ti(OEt)_4$ as reagent.

$$2\,Cy_7Si_7O_9(OH)_2(OSiMe_3) + Ti(OEt)_4 \xrightarrow{\text{toluene}} 4\,EtOH +$$

38

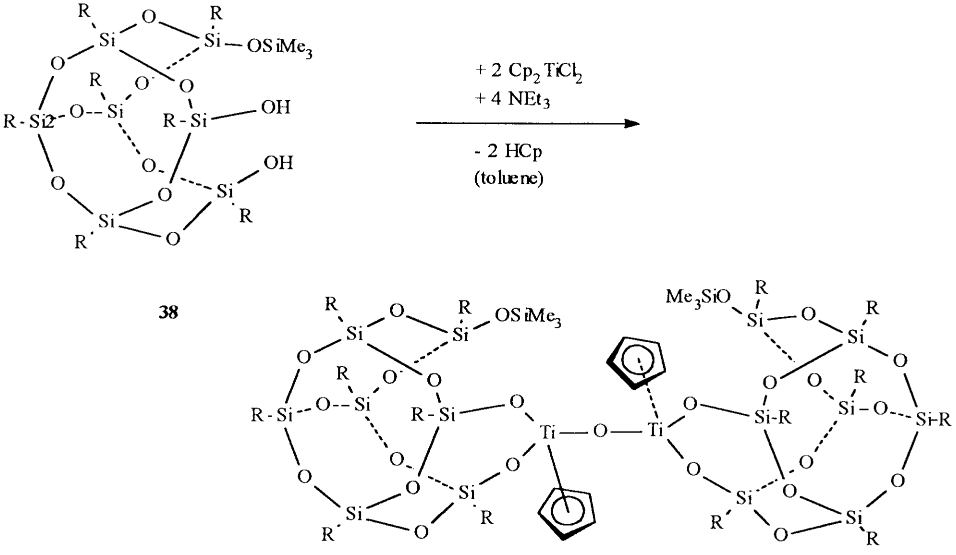


75 (11)

According to an X-ray diffraction study [104,105b] the central titanium atom is tetrahedrally coordinated by the two dianionic silsesquioxane cages (Fig. 19).

Currently, titanium appears to be the metal which displays the richest metallasiloxane chemistry when combined with silsesquioxane frameworks. Crocker and co-workers recently published a detailed investigation of an extensive series of monomeric titanasilsesquioxanes including $Cy_7Si_7O_{12}TiL$ ($L = CH_2Ph$ (**71**), NMe_2 (**72**), $OSiMe_3$ (**73**), $O^{i}Pr$ (**76**)) and $(c\text{-}C_5H_9)_7Si_7O_{12}TiL$ ($L = CH_2Ph$ (**77**), $O^{i}Pr$ (**78**)) [105b]. Treatment of $Cy_7Si_7O_{12}TiO^{i}Pr$ (**76**) with phenols was found to be an effective synthetic route to the corresponding aryloxide derivatives $Cy_7Si_7O_{12}TiL$ ($L = OPh$ (**79**), $OC_6H_4F\text{-}p$ (**80**), $OC_6H_4NO_2\text{-}p$ (**81**)).

Other recent additions include several metallocene derivatives containing silsesquioxane ligands. Thus far it has turned out that reactions of **2** with titanocene dihalides are not straightforward and usually lead to the formation of product mixtures. Several crystalline materials have been isolated from such reactions but not all of them have been fully characterized. 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 ruled out, we assume that the oxygen-bridges in these complexes result from degradation of the silsesquioxane frameworks. A typical example is the reaction of **38** with Cp_2TiCl_2 (**82**) in toluene solution in the presence of triethylamine. In this case the μ-oxo dititanium complex $(\mu\text{-}O)[Cy_7Si_7O_{11}(OSiMe_3)Ti]_2$ (**83**) has been isolated in ca. 70% yield in the form of orange crystals (Eq. (12)).



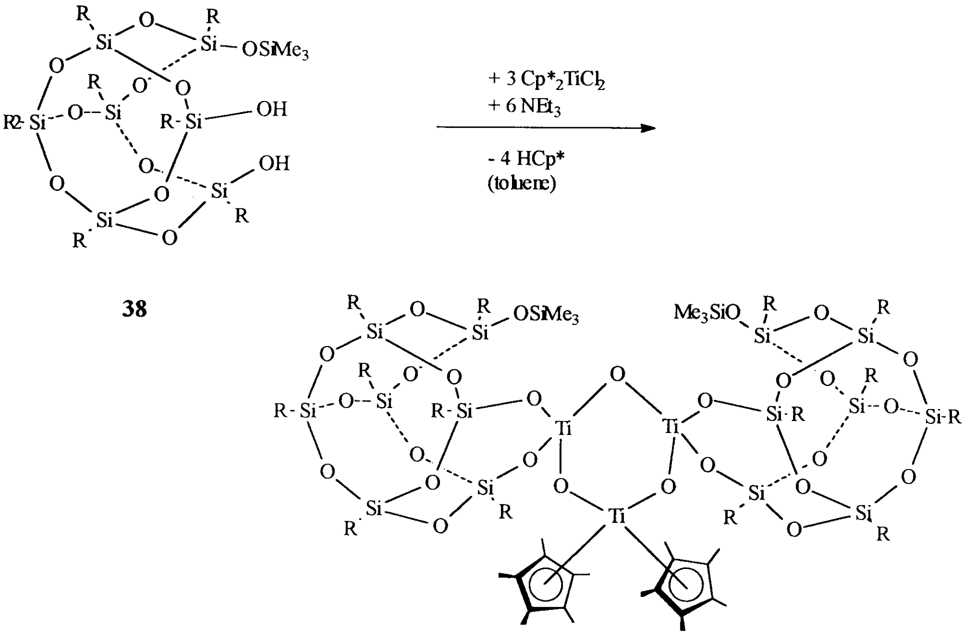
38

83 (R = Cy)

(12)

The molecular structure of **83** has been established by an X-ray diffraction analysis (Fig. 20) [104]. It shows the presence of a dinuclear metallasilsesquioxane with a central Ti–O–Ti unit. During the course of the reaction one cyclopentadienyl ligand per titanium atom is eliminated upon protonolysis to give the observed mono(cyclopentadienyl) titanium(IV) derivative.

At least two different products are formed when **38** is allowed to react with the corresponding pentamethylcyclopentadienyl titanium complex $Cp^*_2TiCl_2$ (**84**) in the presence of triethylamine. While a yellow component has not yet been identified, it was possible to isolate and fully characterize the red crystalline trinuclear 1,3,5-tritritana-2,4,6-trioxane derivative $Cp_2^*Ti_3O_3[Cy_7Si_7O_{11}(OSiMe_3)]_2$ (**85**) (Eq. (13)). [104] The molecular structure of **85** has been elucidated by an X-ray structural analysis (Fig. 21).



38

85 (R = Cy)

(13)

The central structural motif of **85** 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 **85**.

In a more straightforward manner a bis(pentamethylcyclopentadienyl)titanium-(III) silsesquioxane complex became available according to the preparative route outlined in Eq. (14). It involves addition of the monofunctional silsesquioxane precursor **39** across the Ti–C bond of the 'tucked in' fulvene titanium complex $Cp^*Ti(C_5Me_4CH_2)$ (**86**) [106].

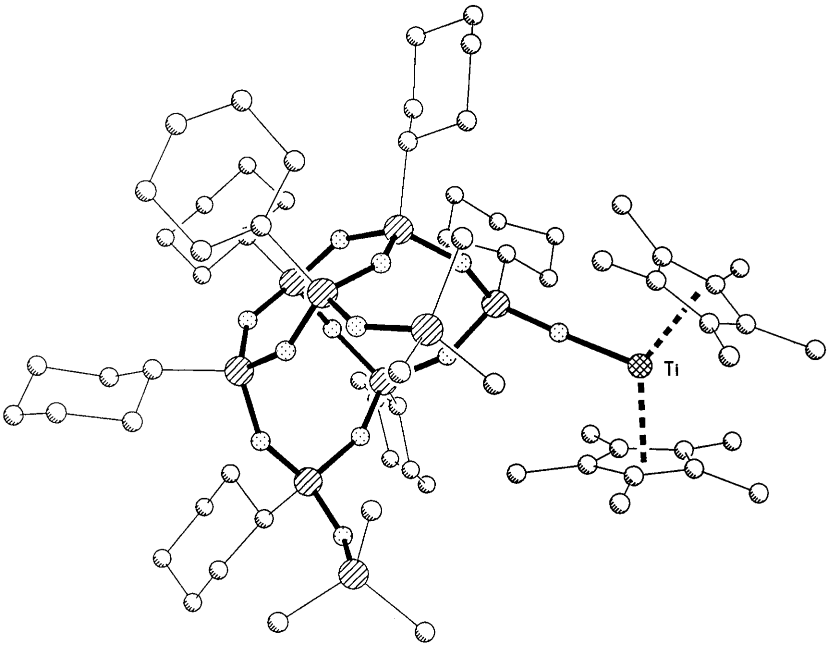
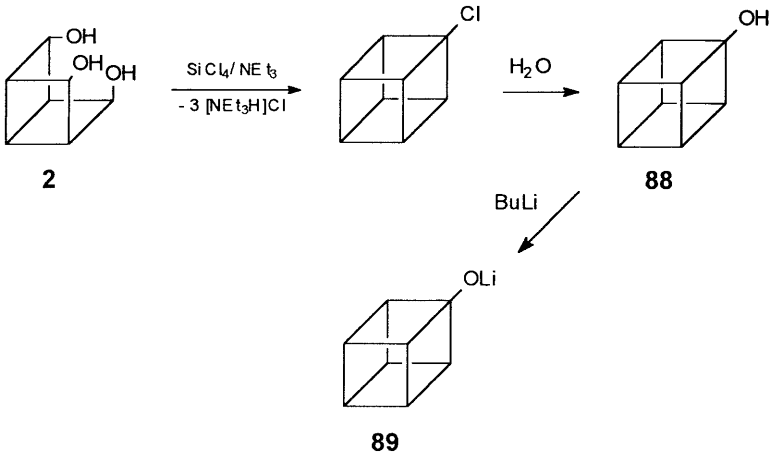
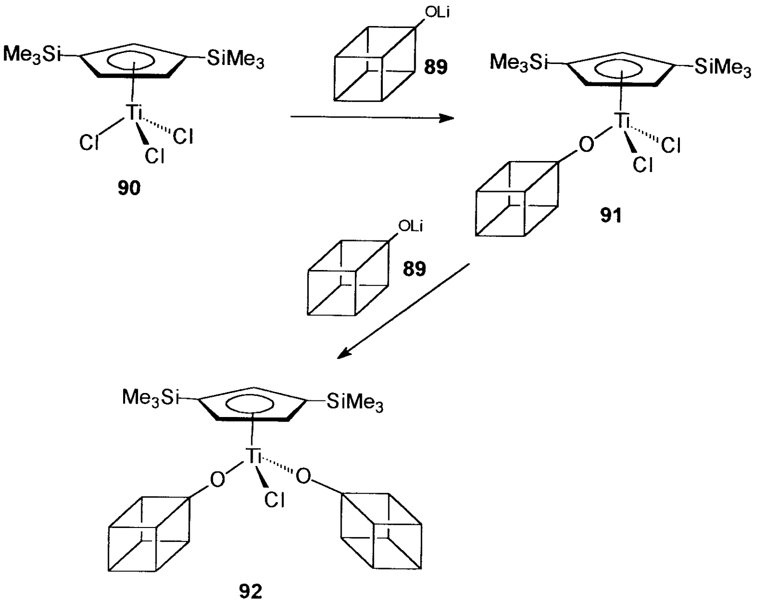


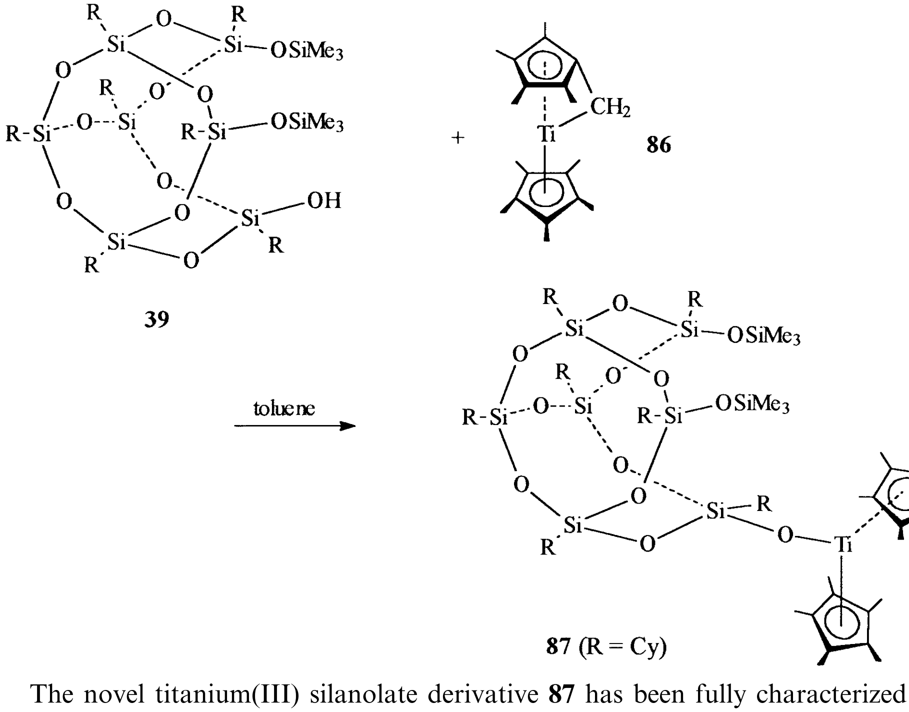
Fig. 22. Molecular structure of **87**.



Scheme 4. Preparation of the silsesquioxane mono(silanol) **88** and its lithium salt **89** (the cube stands for the (c-C_5H_9)$_7$$Si_7O_{12}$ cage).



Scheme 5. Preparation of titanium complexes derived from **89**.



(14)

The novel titanium(III) silanolate derivative **87** has been fully characterized and its molecular structure has been elucidated by an X-ray diffraction study [104]. As shown in Fig. 22 a Cp_2^*Ti 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.

In the search for simple yet realistic model compounds for isolated silanol functionalities as found in partially dehydroxylated silica, Duchateau et al. recently published a promising new approach [107]. In contrast to incorporating metal atoms in a silsesquioxane skeleton, it involves attaching a fully condensed silsesquioxane cage to a metal through an oxygen bridge. In the first stage, the silsesquioxane mono(silanol) $(c\text{-}C_5H_9)_7Si_7O_{12}(OH)$ (**88**) was prepared in high yield according to Scheme 4 by allowing **2** to react with $SiCl_4$ in the presence of triethylamine followed by hydrolysis of the intermediate chlorosilane derivative.

Mono(silanol) **88** itself is an interesting model compound which mimics isolated silanol sites in partially dehydroxylated silica. Deprotonation with *n*-butyllithium cleanly affords the stable lithium salt $(c\text{-}C_5H_9)_7Si_7O_{12}(OLi)$ (**89**), which can be used as a precursor in the preparation of transition metal complexes in which the silsesquioxane cage is coordinated to the metal via an oxygen bridge. As shown in Scheme 5 one or two chloride ligands in $Cp''TiCl_3$ ($Cp'' = 1,3\text{-}C_5H_3(SiMe_3)_2$) (**90**) can be substituted by the novel siloxide ligand [107].

Several attempts to replace the chloride ligands in the complexes **91** and **92** by alkyl substituents failed. However, a protolytic reaction of the parent mono-silanol **88** and $Cp''Ti(CH_2Ph)_3$ (**93**) selectively afforded the mono(silsesquioxane) titanium-trialkyl complex (Eq. (15)) [107].

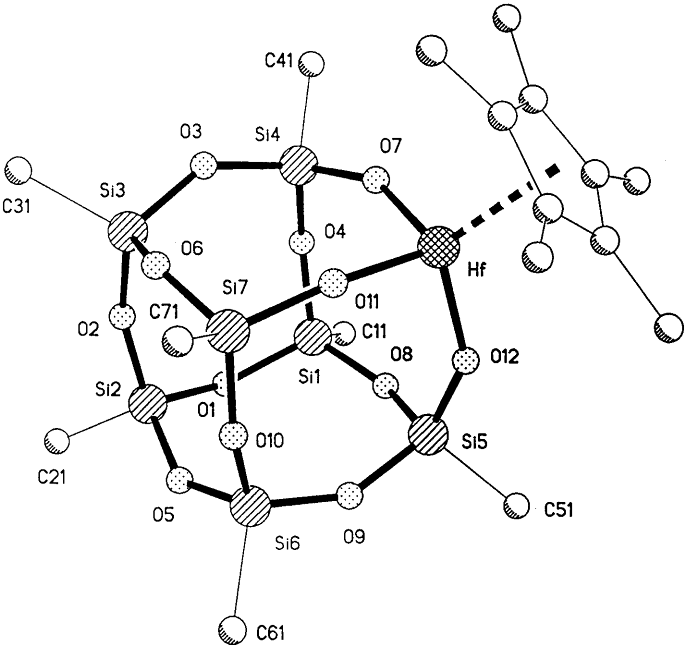
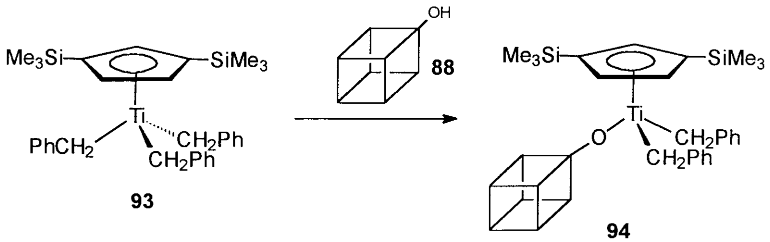


Fig. 23. Molecular structure of **99**.



(15)

The other Group 4 metals, zirconium and hafnium, have also been successfully incorporated into the silsesquioxane framework of **2**. Capping with a Cp*Zr unit has been achieved by treatment of **2** with Cp*Zr(CH_2Ph)$_3$ (**95**) to give $Cy_7Si_7O_{12}$ZrCp* (**96**) [9a]. An alternative preparative route involves the reaction of **2** with Cp*ZrCl_3 (**97**) in CH_2Cl_2 in the presence of triethylamine. The zirconium derivative **96** was the first polyhedral metallasilsesquioxane reported in the literature [9a]. In a similar manner, **2** has been found to react smoothly with Cp*HfMe_3 (**98**) under elimination of methane to afford $Cy_7Si_7O_{12}$ZrCp* (**99**) as a colorless crystalline solid in 78% yield (Eq. (16)). [108] The formation of a closo-silsesquioxane cage has been confirmed by an X-ray structure determination of **99** (Fig. 23).

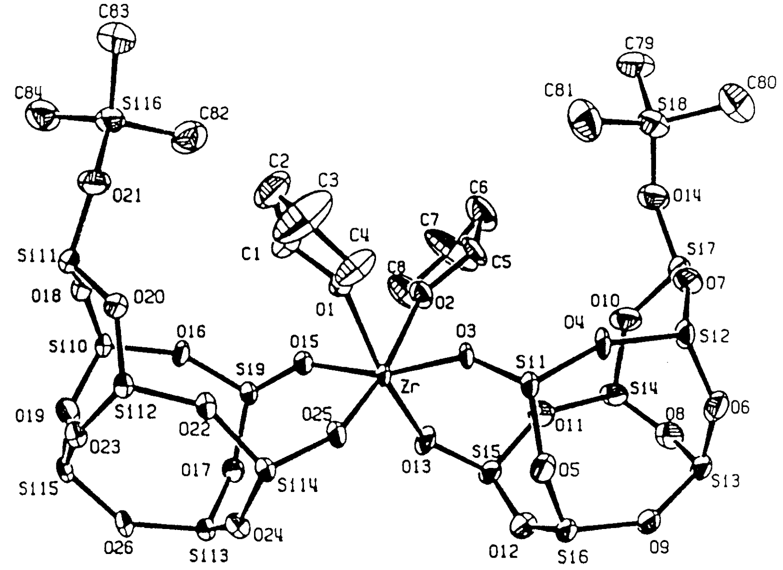
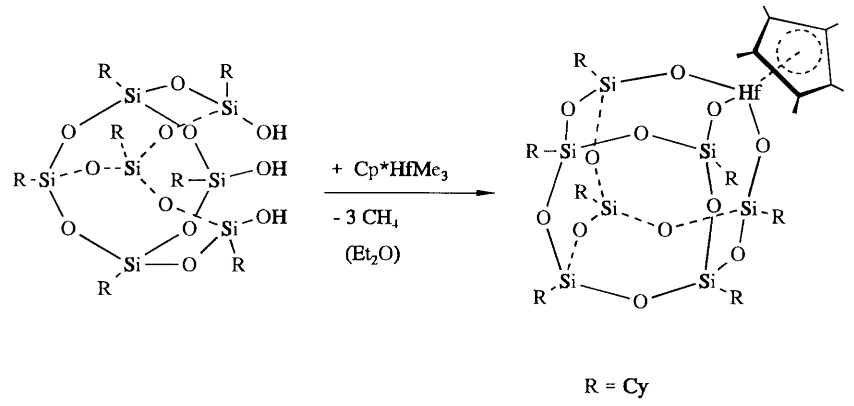


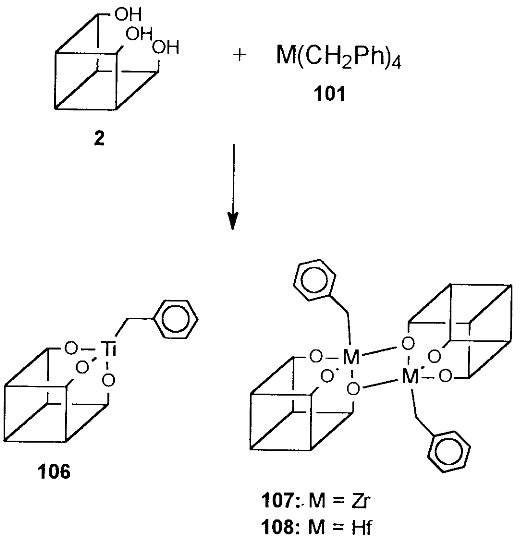
Fig. 24. Molecular structure of **103**.



2 **99** (16)

An interesting series of monomeric and dimeric zirconium and hafnium silsesquioxane complexes, including σ-alkyl derivatives, has recently been reported by Duchateau et al. [109]. A zirconium analog of **75**, $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2Zr$ (**100**) was obtained in excellent yield by reacting $Zr(CH_2Ph)_4$ (**101b**) two equivalents of $(c\text{-}C_5H_9)_7Si_7O_9(OH)_2(OSiMe_3)$ (**102**). In contrast to the titanium derivative **75**, the tetracoordinated Zr center in **100** is able to add THF to give the bis-adduct $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2Zr(thf)_2$ (**103**). As shown in Fig. 24, the THF ligands in **103** are positioned *cis* to each other.

A monomeric zirconium silsesquioxane complex, $[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]$–$ZrCl_2(thf)_2$ (**104**) is accessible in high yield through the reaction of the mono-sily-



Scheme 6. Preparation of the Group 4 benzyl complexes **106–108**.

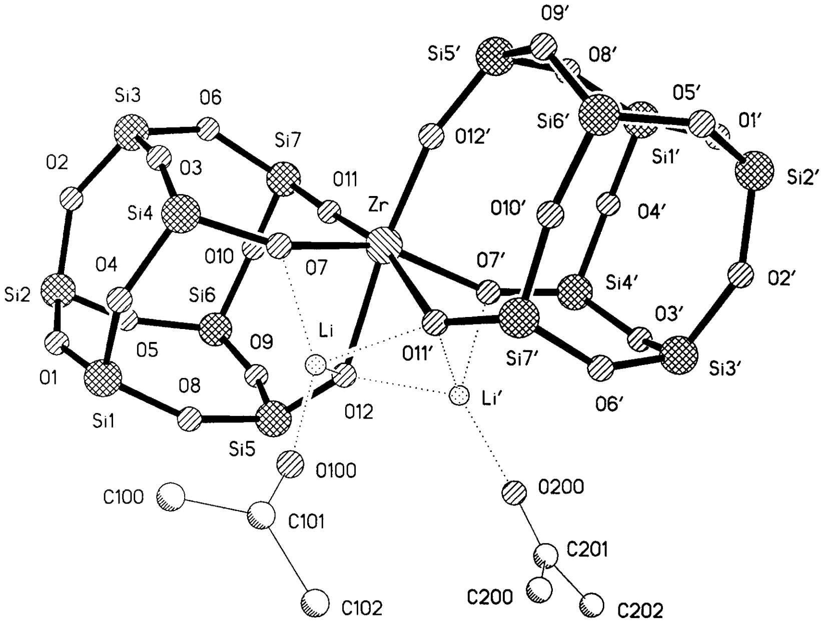


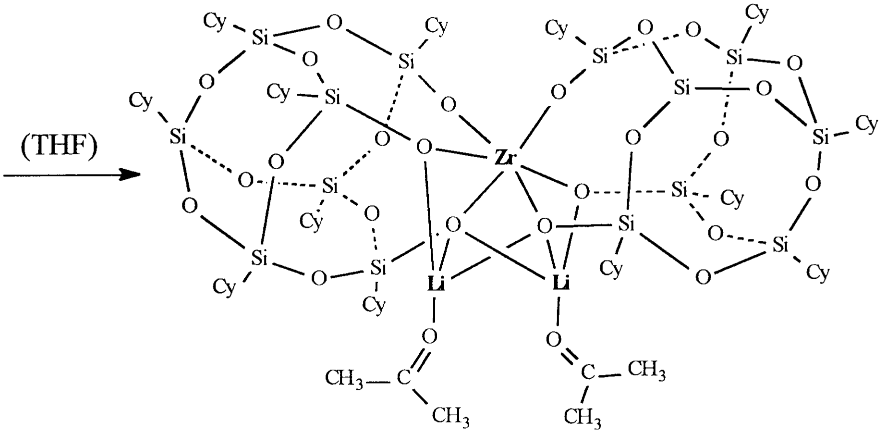
Fig. 25. Molecular structure of **111**.

lated precursor **102** with $(\mathrm{PhCH_2})_2\mathrm{ZrCl_2{\cdot}OEt_2}$ (**105**). A surprising selectivity is found when the trisilanol **2** is reacted with the homoleptic Group 4 metal benzyl complexes $\mathrm{M(CH_2Ph)_4}$ (**101**, M = Ti, Zr, Hf) [109]. In the case of titanium a monomeric corner-capped metallasilsesquioxane complex is formed, while the zirconium and hafnium benzyl complexes are dimeric in the solid state (Scheme 6).

Crocker et al. also described the preparation of a related zirconium silsesquioxane complex, namely $\mathrm{Cy_7Si_7O_{12}Zr(O^tBu)}$ (**109**). This compound was made by reacting **2** with $\mathrm{Zr(O^tBu)_4}$ (**110**) and it was shown by NMR spectroscopy to exist as a monomer–dimer mixture in solution [105b]. Other novel aspects of Group 4 metallasilsesquioxane chemistry are currently evolving from the use of the recently discovered alkali metal silsesquioxanes **44**–**47** and **49** [110]. As an instructive example the preparation of the heterobimetallic zirconium silsesquioxane complex $\mathrm{[Li(Me_2CO)]_2Zr(Cy_7Si_7O_{12})_2}$ (**111**) shall be described here. High yields of the colorless crystalline material can be isolated according to Eq. (17) by reacting the lithium derivative **45** with $\mathrm{ZrCl_4}$ in THF (molar ratio 2:1).

$2\,[Cy_7Si_7O_9(OLi)_3]_2 \cdot 3\,Me_2CO + ZrCl_4$

45



111

(17)

Although **111** is not very soluble even in THF, it was possible to grow X-ray quality single crystals from this solvent. As shown in Fig. 25, the central zirconium atom is encapsulated by two silsesquioxane cages resulting in an approximate octahedral coordination geometry around Zr. Two $Li(Me_2CO)$ units are attached to this formally dianionic $Zr(Cy_7Si_7O_{12})_2^{2-}$ moiety. Tetracoordination at each lithium ion is achieved through coordinative interaction with three silanolate oxygen atoms. Heterobimetallic metallasilsesquioxanes such as **111** can be expected to be valuable new precursors for the assembly of unusual metal-containing Si–O frameworks. The use of lithium salt **44** in the preparation of heterobimetallic lanthanide silsesquioxane complexes will be outlined in the following section.

3.3. Lanthanide derivatives

Lanthanide derivatives are a more recent addition to the chemistry of metallasilsesquioxanes. The first rare earth complexes derived from the cyclopentyl-substituted trisilanol **36** were reported by Herrmann et al. in 1994 [111]. Yttrium and neodymium complexes were prepared via a ‘silylamide route’ [60] by reacting **36** with the corresponding bis(trimethylsilyl)amides $Ln[N(SiMe_3)_2]_3$ (**112a,b**, Ln = Y, Nd) and the dimeric yttrium derivative was structurally characterized. In view of the industrial importance of lanthanide-doped zeolite catalysts [112–115], such rare earth metallasilsesquioxanes are of interest as realistic molecular model compounds. Since these first reports on lanthanide silsesquioxanes this class of compounds has been extensively investigated in our laboratory. In addition to the original silylamide route other synthetic pathways have been studied, including reactions involving anhydrous lanthanide trichlorides or certain organolanthanide complexes. A considerable body of results has been accumulated and numerous lanthanide-containing silsesquioxane derivatives have been prepared and characterized by spectroscopic methods and elemental analyses. However, it turned out that many of these complexes are difficult to obtain as single crystals suitable for X-ray diffraction. In most cases this behavior can be attributed to the very high solubility of these materials even in non-polar hydrocarbon solvents such as pentane or hexane. Structural information is still scarce and many molecular structures of lanthanide silsesquioxanes remain rather speculative. It is noteworthy that Herrmann and co-workers apparently were also confronted with this problem of a rather low tendency to from suitable crystals. They finally succeeded in crystallizing the yttrium derivative with the use of triphenylphosphine oxide as an auxiliary ligand [111]. Thus, in the context of this review the description of lanthanide silsesquioxane chemistry will be limited to a few instructive and well-characterized examples, keeping in mind that many other compounds of this type are still awaiting further elucidation.

Taking cerium as a representative member of the lanthanide series, several methods for preparing metallasilsesquioxanes containing this element have been developed. As shown in Eq. (18), the silylamide route can easily be extended to cerium.

$$\underset{\mathbf{2}}{\mathrm{Cy_7Si_7O_9(OH)_3}} + \underset{\mathbf{112c}}{\mathrm{Ce[N(SiMe_3)_2]_3}} \xrightarrow[-\,2\mathrm{HN(SiMe_3)_2}]{\text{toluene}} \underset{\mathbf{113}}{\mathrm{Cy_7Si_7O_9Ce[HN(SiMe_3)_2]}} \qquad (18)$$

In this case the reaction product, pink crystalline **113**, contains one molecule of hexamethyldisilazane coordinated to cerium.

A generally applicable synthetic pathway to rare earth silsesquioxane complexes involves treatment of **2** with the corresponding lanthanide trichlorides in the presence of stoichiometric amounts of triethylamine. Anhydrous lanthanide triflates can also be successfully employed instead of the trichlorides. Such reactions have been carried out with various members of the lanthanide series. The preparation of the cerium(III) complex **114** is depicted in Eq. (19) as a typical example. In this case the analytical data show that the coordination sphere of cerium is completed by triethylamine ligands. Once again, however, the seemingly simple reactions are far more complicated and the products are often difficult to characterize. One of the reasons for this behavior is the tendency of the lanthanide ions to achieve high coordination numbers i.e. by coordination of solvent molecules, by retaining metal halides or by formation of anionic 'ate-complexes'.

$$\underset{\mathbf{2}}{\mathrm{Cy_7Si_7O_9(OH)_3}} + \mathrm{CeCl_3} + 3\mathrm{NEt_3} \xrightarrow[-\,2[\mathrm{HNEt_3}]\mathrm{Cl}]{\text{THF}} \underset{\mathbf{114}}{\mathrm{Cy_7Si_7O_9Ce(NEt_3)}_n} \qquad (19)$$

Similar routes have been followed to prepare related cerium(IV) species. In this case stable cerium(IV) precursors such as ceric ammonium nitrate ('CAN', **115**) or cerium(IV) tetra-*t*-butoxide (**117**) can be employed. In the first case it has been found advantageous to utilize the non-reducing thallium silsesquioxane reagent **42** [87] in order to avoid the formation of cerium(III) by-products (Eq. (20)). The product **116** is readily soluble in THF and can be isolated as a pale yellow crystalline material after filtering off the inorganic reaction products ($TlNO_3$, NH_4NO_3). Protonolysis of cerium(IV) tetra-*t*-butoxide upon treatment with one equivalent of trisilanol **2** cleanly affords the mono-*t*-butoxide derivative **118** as outlined in Eq. (21). Compound **118** also forms pale yellow crystals which are soluble even in hydrocarbon solvents. It can be anticipated that such cerium(IV) metallasilsesquioxane might exhibit catalytic activity e.g. in oxidation reactions.

$$\underset{\mathbf{42}}{\mathrm{Cy_7Si_7O_9(OTl)_3}} + \underset{\mathbf{115}}{\mathrm{(NH_4)_2[Ce(NO_3)_6]}} \xrightarrow[-2\mathrm{TlNO_3},\ -2\mathrm{NH_4NO_3}]{\mathrm{THF}} \underset{\mathbf{116}}{\mathrm{Cy_7Si_7O_9CeNO_3(thf)_2}} \tag{20}$$

$$\underset{\mathbf{2}}{\mathrm{Cy_7Si_7O_9(OH)_3}} + \underset{\mathbf{117}}{\mathrm{Ce(O^tBu)_4(thf)_2}} \xrightarrow[-3^t\mathrm{BuOH}]{\text{toluene, reflux}} \underset{\mathbf{118}}{\mathrm{Cy_7Si_7O_9Ce(O^tBu)}} \tag{21}$$

Quite likely the chemistry of lanthanide silsesquioxane complexes too will greatly benefit from the use of the new alkali metal silsesquioxane precursors **44**–**47** and

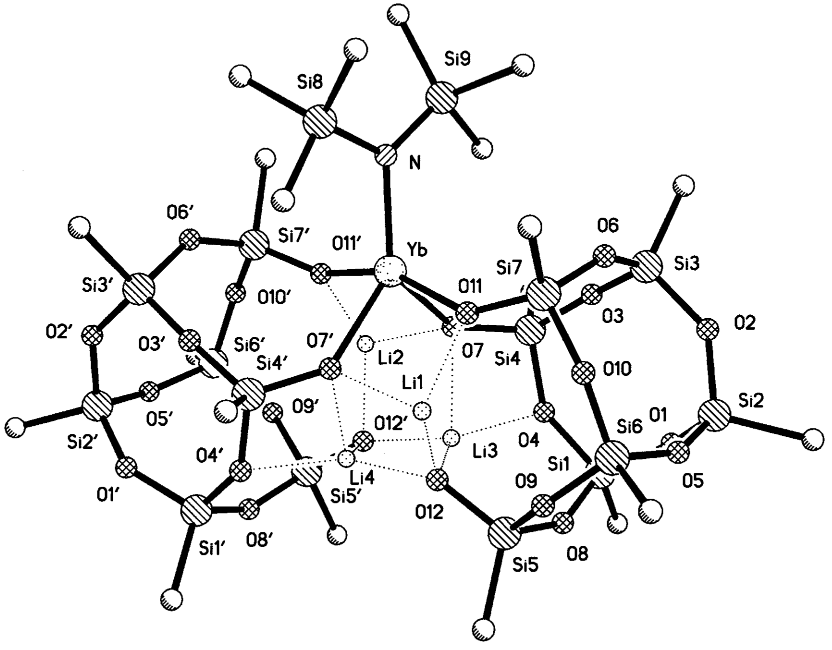


Fig. 26. Molecular structure of **119**.

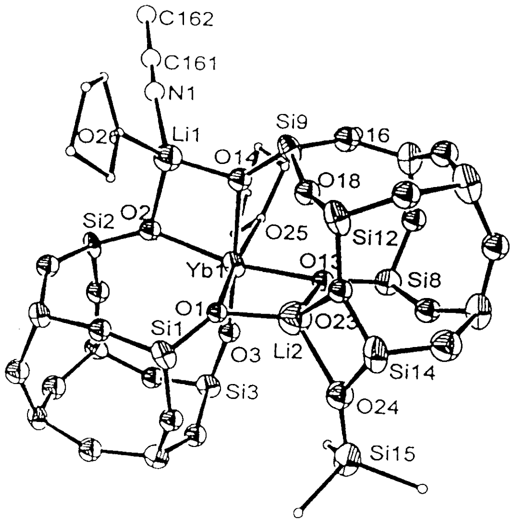
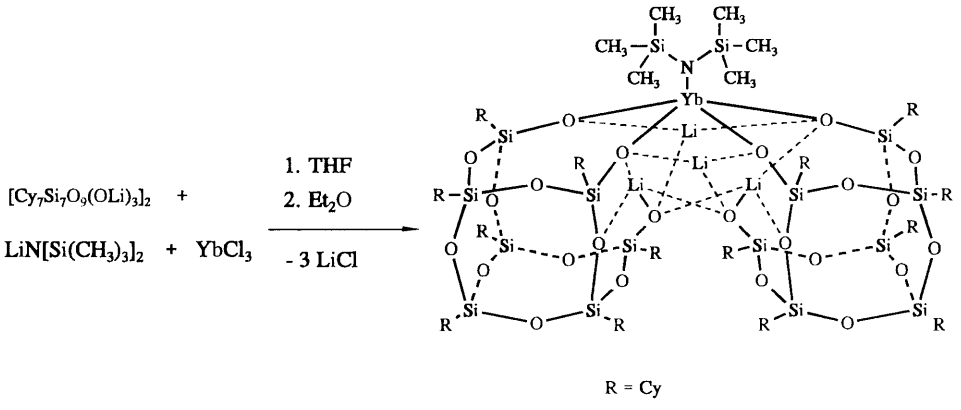


Fig. 27. Molecular structure of **122a**.

49. Initial experiments in this direction are already very encouraging [89c,110]. Interesting new frameworks can be accessed through reactions involving these alkali metal derivatives and the resulting bimetallic metallasilsesquioxanes have generally been found to exhibit a much better crystallinity than the corresponding pure rare earth derivatives. One of the first examples of a reaction product to be structurally characterized was $[Cy_7Si_7O_{12}Li_2]_2YbN(SiMe_3)_2$ (**119**), which was prepared as outlined in Eq. (22) [110].



119 (22)

The ytterbium complex **119** represents a novel type of heterobimetallic lanthanide metallasilsesquioxanes. Ytterbium is coordinated via oxygen to a lithium silsesquioxane framework made up of two $Cy_7Si_7O_{12}Li_2$ units (Fig. 26). There are no additional ligands such as $\mathrm{Et_2O}$ or THF present in this molecule owing to the involvement of cage oxygen atoms in the coordination to lithium. The overall structure of **119** resembles that of typical bent lanthanide metallocenes such as $\mathrm{Cp^*_2LnN(SiMe_3)_2}$ (**25**) [63,64]. The extension of this chemistry to other rare earth elements as well as the preparation of potential new catalysts such as $\mathrm{[Cy_7Si_7O_{12}Li_2]_2LnCH(SiMe_3)_2}$ or $\mathrm{[\{Cy_7Si_7O_{12}Li_2\}_2Ln(\mu\text{-}H)]_2}$ (cf. $\mathrm{Cp^*_2LnCH(SiMe_3)_2}$ (**120**) and $\mathrm{[Cp^*_2Ln(\mu\text{-}H)]_2}$ (**121**) [63,64]) is currently an area under active investigation in our laboratory. Initial results already indicate that the new precursors **44**–**47** and **49** are the starting materials of choice in this chemistry.

Similar reactions have recently been studied by Aspinall et al. [89c] The monosilylated ytterbium complex $\mathrm{[\{Cy_7Si_7O_{12}\}\{Cy_7Si_7O_{11}(OSiMe_3)\}]YbLi_2(thf)_2(MeCN)\cdot 2.5THF}$ (**122a**) was crystallized in minor quantities from a reaction mixture containing $\mathrm{Yb[N(SiMe_3)_2]_3}$ (**112c**) and **2** in the presence of PMDTA (*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine). The main product of this reaction was analyzed as $\mathrm{Cy_7Si_7O_{12}Yb(pmdta)}$ (**123**). The origin of the siloxy function in **122a** can be explained by the presence of small amounts of $\mathrm{HN(SiMe_3)_2}$. It was found that a rational synthetic route leading to **122a** can be realized by reacting $\mathrm{Cy_7Si_7O_{12}Yb(thf)_2}$ (**124**) with $\mathrm{Cy_7Si_7O_9(OH)_2(OSiMe_3)}$ (**38**). The yttrium derivative $\mathrm{[\{Cy_7Si_7O_{12}\}\{Cy_7Si_7O_{11}(OSiMe_3)\}]YLi_2(thf)_2(MeCN)\cdot 2.5THF}$ (**122b**) was prepared analogously. The molecular structure of **122a** was determined by X-ray diffraction and is shown in Fig. 27 [89c].

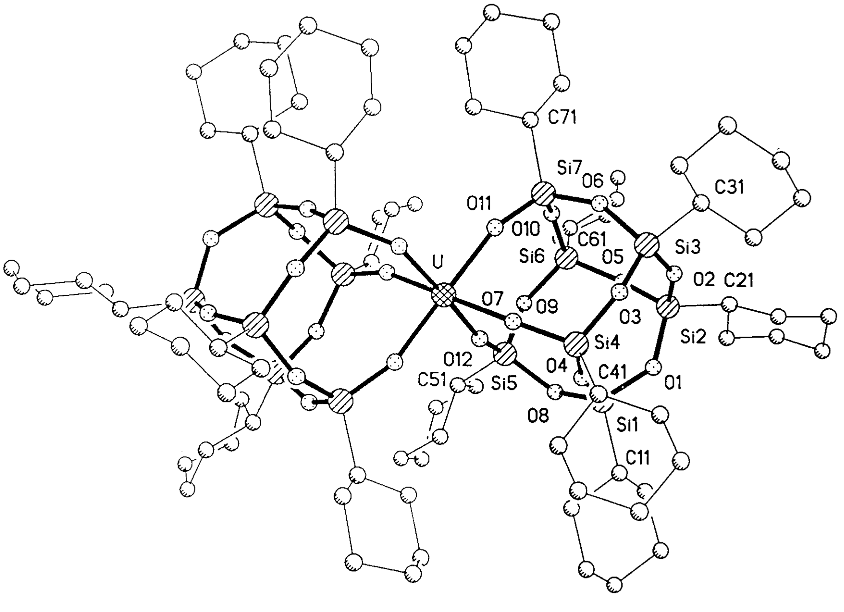


Fig. 28. Molecular structure of **125**.

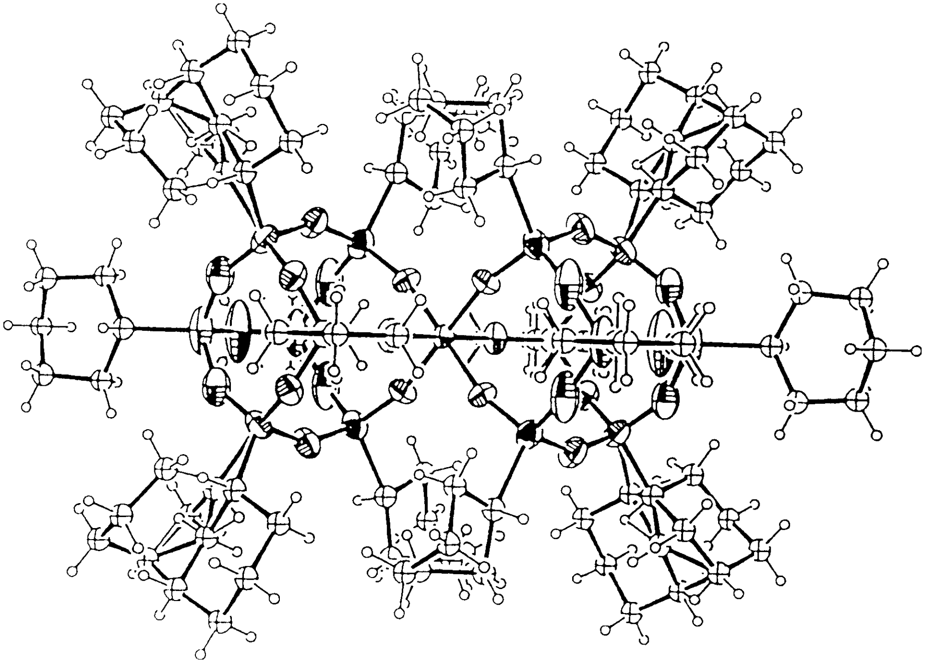
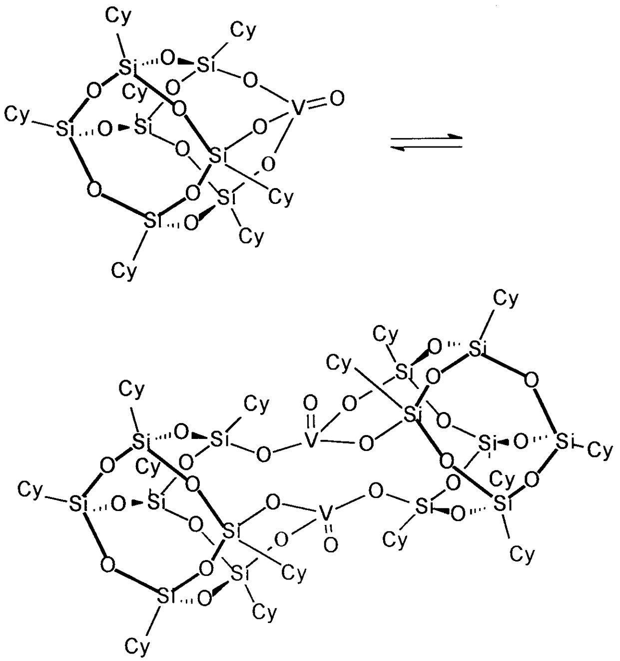


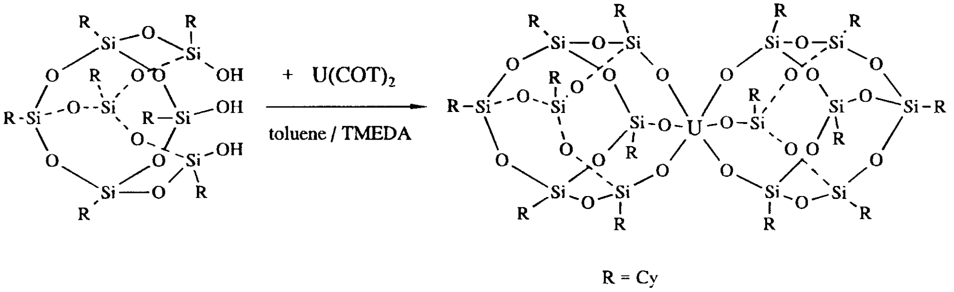
Fig. 29. Molecular structure of **126**.

3.4. Actinide derivatives

Very little is known about the incorporation of actinide elements into silsesquioxane frameworks. Thus far the only experiments in that direction have been dealing with uranium. When reactions of uranium compounds such as UCl_4 or uranyl nitrate with **2** were carried out under various conditions it was soon discovered that in all cases uranium(VI) species were formed regardless of the oxidation state of uranium in the starting material [110]. This behavior was not totally surprising in view of earlier experiences with uranium disiloxandediolate systems as described in Section 2.4. There too oxidation under formation of uranium(VI) species took place in all cases. For example, treatment of green anhydrous UCl_4 with two equivalents of **2** in THF solution in the presence of triethylamine produced a colorless reaction mixture, from which colorless $[Cy_7Si_7O_{12}]_2U$ (**125**) could eventually be isolated. As in the case of the disiloxanediolate reactions (cf. Section 2.4) it was demonstrated that a highly useful starting material for the preparation of **125** is uranocene, $U(COT)_2$ (**31**). As depicted in Eq. (23), uranocene cleanly reacts with **2** to afford the uranium(VI) silsesquioxane **125** in more than 80% isolated yield.



Scheme 7. Monomer–dimer equilibrium of the vanadyl silsesquioxane **127** [118].



2 **125** (23)

$\mathrm{Cy_7Si_7O_9(OH)_3}$ + BuEtMg
2

$\xrightarrow[\text{- BuH, -EtH}]{} [\mathrm{Cy_7Si_7O_{11}(OH)Mg}]_n$ (n = 1,2)
128

$\xrightarrow[\text{- HCl}]{\mathrm{TiCl_4}} [\mathrm{Cy_7Si_7O_{12}MgTiCl_3}]_n$ (n = 1,2)
129

Scheme 8. Synthesis of the heterobimetallic silsesquioxane complex **129** [102].

Crystalline **125** freely dissolves in various organic solvents including pentane or hexane. This is quite reasonable considering the fact that the outer shell of the molecule is covered by no less than fourteen cyclohexyl groups. An X-ray structure determination clearly show how the central uranium atom is encapsulated between the two silsesquioxane cages (Fig. 28). A closely related structure has recently been reported for the analogous tungsten(VI) silsesquioxane derivative $[Cy_7Si_7O_{12}]_2W$ (**126**), which was made by the reaction of **2** with WCl_6 [116]. Compound **126** was selectively formed regardless whether **2** was allowed to react with one or two equivalents of tungsten hexachloride. The structure of **126** was confirmed by MALDI-TOF mass spectrometry as well as an X-ray diffraction analysis (Fig. 29).

4. Catalysis

This is a very recent development in the chemistry of metallasilsesquioxanes which can be expected to have a strong impact on catalysis research well into the next millennium. Today, certain metallasilsesquioxanes, especially titanium derivatives, are emerging as highly promising new catalysts especially for olefin polymerizations and oxidation processes. In addition, a high-valent imidomolybdenum silsesquioxane complex has been found to be an excellent catalyst for the metathesis of olefins [25,117].

4.1. Olefin polymerization

The first report on catalytic activity of a metallasilsesquioxane originates from Feher's work in 1991 [118]. The vanadyl compound $Cy_7Si_7O_{12}VO$ (**127**), which can be prepared by reacting **2** with $(^nPrO)_3VO$, $(Me_3SiCH_2)_3VO$, or $VOCl_3$, exists in solution in a monomer-dimer equilibrium as shown in Scheme 7. It was found that addition of Me_3Al to benzene or hexane solutions of **2** at 25°C produces a straw-colored solution (deep red in the case where $Al(CH_2SiMe_3)_3$ is used) which readily polymerizes ethylene or 1,3-butadiene. Other olefins were also polymerized, but not as efficiently as ethylene [118].

Several Group 4 metal silsesquioxanes have already been proven to exhibit high catalytic activity for olefin polymerization. For example, trisilanol **2** reacts with butylethylmagnesium to give the magnesium intermediate **128**, which exists as a monomer–dimer equilibrium [102]. Subsequent treatment with $TiCl_4$ afforded the heterobimetallic Mg/Ti silsesquioxane complex **129** (cf. Section 3.2). The synthesis is summarized in Scheme 8. Bimetallic **129** has also been found to exist as a monomer–dimer mixture. In the presence of triethylaluminum as co-catalyst it shows a high catalytic activity for ethylene polymerization. The properties of the resulting polyethylene were similar to those obtained with a commercial silica-supported catalyst with the same components [102].

Other authors have recently pointed out, however, that the high affinity of aluminum alkyls for the silsesquioxane oxo functions could make them unsuitable as co-catalysts for silsesquioxane complexes [107,109]. In the case of the titanium complexes **92** and **94** (cf. Section 3.2) cation-generating boron reagents such as $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ have been found to be superior reagents for the generation of silsesquioxane-based olefin polymerization catalysts [107]. Duchateau et al. also used this approach to synthesize the cationic mono(benzyl) complexes $[\{c\text{-}C_5H_9)_7Si_7O_{12}\}_2M_2(CH_2Ph)]^+$ (**130**, M = Zr, Hf). These species have been found to be active single-site ethylene polymerization catalysts (activity: $(2–8) \times 10^6$ g PE/(mol·h)) [109].

4.2. Oxidation reactions

The second area where metallasilsesquioxanes are currently emerging as promising catalysts are oxidation and epoxidation reactions. It was first recognized by Maschmeyer and Johnson et al. that the silsesquioxane titanium alkoxides **65** and **76** display catalytic activity in the epoxidation of cyclohexane. [103]. These compounds react with peroxides such as tetrabutylperoxyhydroxide (TBPH) with formation of yellow solutions ($\lambda_{max} = 320$ nm), indicative of η^2-coordinated peroxide. Catalytic epoxidation of cyclohexene with TBPH was achieved using a catalyst–substrate ration of 1:70:70 resulting in up to 93% conversion with 98% selectivity towards the epoxide.

Most recently these investigations were extended by Crocker et al. to a large series of titanium silsesquioxanes (**71**–**74** and **76**–**81**, cf. Section 3.2) [105b]. These authors studied the catalytic epoxidation of oct-2-ene with ^{t}BuOOH (TBHP). It was concluded from these experiments that the most active site in titanium silicate epoxidation catalysts corresponds to a four-coordinate site possessing tripodal geometry. Thus the titanium silsesquioxanes **71–74** and **76–81** can serve as soluble models for putative tripodal sites in titanium silicates. Other coordination geometries such as in **75** (tetrapodal) lead to significantly lower activities in the case of olefin epoxidation [105b]. A heterogeneous epoxidation catalyst has been obtained by Abbenhuis et al. through immobilization of $Cy_7Si_7O_{12}TiCp$ (**59**) on silica or MCM-41 molecular sieve [119]. Finally, a silica-supported vanadium-containing silsesquioxane catalyst was prepared from **127**. This material showed excellent activity towards the selective photo-assisted catalytic oxidation of methane to formaldehyde [120].

5. Future outlook

There is no doubt that the beginning of the new millennium will witness the chemistry of metallasiloxanes as an area of vigorous research activities. Fascinating new metal-containing Si–O frameworks will be discovered at a rapid pace. This is the more likely as most of the structural varieties known to date have been realized with only one polyhedral Si–O framework, i.e. the cube-derived nido-silsesquioxane cage **2** (and its cyclopentyl analog **32**). Further development of the field can be expected from the use of new polyhedral silsesquioxanes containing Si–OH functions. A highly promising aspect is the application of metallasilsesquioxanes in homogeneous and heterogeneous catalysis. Initial studies on titanium silsesquioxanes have already revealed, that such compounds are not only realistic model compounds for silica-supported metal catalysts, but that they may be active catalysts by themselves (cf. Section 4) This area is expected to continue to be an exciting topic of research in the future. Further opportunities for future applications are in materials sciences. Silsesquioxane have already been demonstrated to be useful building blocks in the construction of novel hybrid organic–inorganic polymers [77,78]. An interesting novel aspect would be the incorporation of metallasilsesquioxanes in such new materials which could lead to unusual properties. Thus it needs no prophet to foresee that the near future will witness a dramatic increase in research activities dealing with metallasiloxanes and their applications in catalysis and materials science.

Acknowledgements

Financial support of our own work described in this review by the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm 'Spezifische Phänomene in der Siliciumchemie'), the Fonds der Chemischen Industrie, and the Otto-von-Guericke-Universität Magdeburg is gratefully acknowledged. We also thank the Alexander von Humboldt-Stiftung for granting a Senior Research Award to J.W.G. During his stay at Göttingen in 1992 this work was initiated by setting up the first 100 l of reaction mixture for the preparation of **2**.

References

[1] C.L. Thomas, Catalytic Processes and Proven Catalysts, Academic Press, New York, 1970.
[2] T. Seiyama, K. Tanabe, New Horizons in Catalysis, Elsevier, Amsterdam, 1980.
[3] Y.I. Yermakov, B.N. Kuznetsov, V.A. Zakharov, Catalysis by Supported Complexes, Elsevier, New York, 1981.
[4] R. Pearce, W.R. Patterson, Catalysis and Chemical Processes, Blackie and Son, Glasgow, 1981.
[5] F.R. Hartley, Supported Metal Complexes, Reidel, Dordrecht, 1985.
[6] Y. Iwasawa, Tailored Metal Catalysts, Reidel, Dordrecht, 1986.
[7] T. Keii, K. Soga, Catalytic Polymerization of Olefins, Studies in Surface Science and Catalysis, Elsevier, New York, 1986.
[8] W. Kaminsky, H. Sinn, Transition Metals and Organometallics as Catalysts for Olefin Polymerization, Springer-Verlag, Heidelberg, 1988.
[9] (a) F. Feher, J. Am. Chem. Soc. 108 (1986) 3850. (b) Review: F.T. Edelmann, Angew. Chem. 104 (1992) 600; Angew. Chem. Int. Ed. Engl. 31, (1992) 586.
[10] S.N. Borisov, M.G. Voronkov, E.Y. Lukevits, Organosilicon Heteropolymers and Hetero Compounds, Plenum, New York, 1970.
[11] J.C. Saam, in: J.M. Zeigler, F.W.G. Fearon (Eds.), Silicon Based Polymer Science, Advances in Chemistry 224, American Chemical Society, Washington, 1990.
[12] G.A. Sigel, R.A. Bartlett, D. Decker, M.M. Olmstead, P.P. Power, Inorg. Chem. 26 (1987) 1773.
[13] D.C. Hrncir, G.D. Skiles, J. Mater. Res. 3 (1988) 410.
[14] A.K. McMullen, T.D. Tilley, A.L. Rheingold, S.J. Geib, Inorg. Chem. 28 (1989) 3772.
[15] A.R. Barron, C.C. Landry, L.K. Cheatham, A.N. MacInnes, J. Mater. Chem. 1 (1991) 143.

[16] M. Baier, P. Bissinger, J. Blümel, H. Schmidbaur, Chem. Ber. 126 (1993) 947.
[17] R. Murugavel, A. Voigt, M.G. Walawalkar, H.W. Roesky, Chem. Rev. 96 (1996) 2205.
[18] I. Haiduc, F.T. Edelmann, Supramolecular Organometallic Chemistry, Wiley-VCH, Weinheim, 1999.
[19] R. Corriu, P. Jutzi, Tailor-Made Silicon–Oxygen Compounds: From Molecules to Materials, Vieweg, Braunschweig, 1996.
[20] M.G. Voronkov, E.A. Maletina, V.K. Roman, in: M.E. Vol'pin, K. Gingold (Eds.), Heterosiloxanes, Soviet Scientific Review Supplement, Series Chemistry, vol. 1, Academic Press, London, 1988.
[21] (a) P.D. Lickiss, Adv. Inorg. Chem. 42 (1995) 147. (b) L. King, A.C. Sullivan, Coord. Chem. Rev. 189 (1999) 19.
[22] P.G. Harrison, J. Organomet. Chem. 542 (1997) 141.
[23] M.G. Voronkov, V.I. Lavrent'yev, Top. Curr. Chem. 102 (1982) 199.
[24] R.H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, Chem. Rev. 95 (1995) 1409.
[25] F.J. Feher, T.A. Budzichowski, Polyhedron 14 (1995) 3239.
[26] G.I. Harris, J. Chem. Soc. (1963) 5978.
[27] L.H. Sommer, L.J. Tyler, J. Am. Chem. Soc. 76 (1954) 1030.
[28] M. Weidenbruch, H. Pesel, D.V. Hieu, Z. Naturforsch. 35 (1980) 31.
[29] W. Clegg, U. Klingebiel, G.M. Sheldrick, Z. Naturforsch. 37 (1982) 423.
[30] O. Graalmann, U. Klingebiel, W. Clegg, M. Haase, G.M. Sheldrick, Chem. Ber. 117 (1984) 2988.
[31] P.D. Lickiss, S.A. Litster, A.D. Redhouse, C.J. Wisener, J. Chem. Soc. Chem. Commun. (1991) 173.
[32] M.B. Hursthouse, M.A. Hossain, M. Motevalli, M. Sanganee, A.C. Sullivan, J. Organomet. Chem. 381 (1990) 293.
[33] M. Motevalli, D. Shah, A.C. Sullivan, J. Chem. Soc. Dalton Trans. (1993) 2849.
[34] M.B. Hursthouse, M.A. Hossain, Polyhedron 3 (1984) 95.
[35] D.A. Foucher, A.J. Lough, I. Manners, Inorg. Chem. 31 (1992) 3034.
[36] S. Schütte, U. Klingebiel, D. Schmidt-Bäse, Z. Naturforsch. 48 (1993) 263.
[37] H. Puff, M.P. Böckmann, T.R. Kök, W. Schuh, J. Organomet. Chem. 268 (1984) 197.
[38] H. Puff, T.R. Kök, P. Nauroth, W. Schuh, J. Organomet. Chem. 281 (1985) 141.
[39] O. Graalmann, M. Meyer, U. Klingebiel, Z. Anorg. Allg. Chem. 534 (1986) 109.
[40] A. Mazzah, A. Haoudi-Mazzah, M. Noltemeyer, H.W. Roesky, Z. Anorg. Allg. Chem. 604 (1991) 93.
[41] A. Haoudi-Mazzah, A. Mazzah, H.-G. Schmidt, M. Noltemeyer, H.W. Roesky, Z. Naturforsch. 46 (1991) 587.
[42] F.-Q. Liu, H.-G. Schmidt, M. Noltemeyer, C. Freire-Erdbrügger, G.M. Sheldrick, H.W. Roesky, Z. Naturforsch. 47 (1992) 1085.
[43] J.A. Darr, S.R. Drake, D.J. Williams, A.M.S. Slawin, J. Chem. Soc. Chem. Commun. (1993) 866.
[44] B.J. Brisdon, M.F. Mahon, K.C. Molloy, P.J. Schofield, J. Organomet. Chem. 465 (1994) 145.
[45] M.B. Hursthouse, M.A. Mazid, M. Motevalli, M. Sanganee, A.C. Sullivan, J. Organomet. Chem. 381 (1990) C43.
[46] M.B. Hursthouse, M. Motevalli, M. Sanganee, A.C. Sullivan, J. Chem. Soc. Chem. Commun. (1991) 1709.
[47] M.A. Hossain, M.B. Hursthouse, A.A. Ibrahim, M.A. Mazid, A.C. Sullivan, J. Chem. Soc. Dalton Trans. (1989) 2347.
[48] M. Motevalli, D. Shah, A.C. Sullivan, J. Chem. Soc. Chem. Commun. 1994, 2427.
[49] M. Motevalli, S.A.A. Shah, A.C. Sullivan, J. Organomet. Chem. 492 (1995) 99.
[50] M. Lazell, M. Motevalli, S.A.A. Shah, C.K.S. Simon, A.C. Sullivan, J. Chem. Soc. Dalton Trans. (1996) 1449.
[51] K.A. Andrianov, N.A. Kurasheva, L.I. Kuteinikova, Zh. Obshch. Khim. 46 (1976) 1533.
[52] D.C. Hrncir, Mater. Res. Symp. Proc. 121 (1988) 127.
[53] M. Motevalli, D. Shah, S.A.A. Shah, A.C. Sullivan, Organometallics 13 (1994) 4109.
[54] W.E. Piers, E.E. Bunel, J.E. Bercaw, J. Organomet. Chem. 407 (1991) 51.

[55] (a) V.A. Igonin, S.V. Lindeman, Y.T. Struchkov, O.I. Shchegolikhina, Y.A. Molodtsova, Y.A. Pozdnyakova, A.A. Zhdanov, Izv. Akad. Nauk Ser. Khim. (1993) 184; Russ. Chem. Bull. 42 (1993) 168. (b) V.A. Igonin, S.V. Lindeman, Y.T. Struchkov, Y.A. Molodtsova, Y.A. Pozdnyakova, O.I. Shchegolikhina, A.A. Zhdanov, Izv. Akad. Nauk Ser. Khim. (1993) 193; Russ. Chem. Bull. 42 (1993) 176.

[56] O.I. Shchegolikhina, Y.A. Pozdnyakova, S.V. Lindeman, A.A. Zhdanov, R. Psaro, R. Ugo, G. Gavioli, R. Battistuzzi, M. Borsari, T. Rüffer, C. Zucchi, G. Páli, J. Organomet. Chem. 514 (1996) 29.

[57] (a) J.M. Batwara, R.C. Mehrotra, J. Inorg. Nucl. Chem. 32 (1970) 411. (b) P.S. Gradeff, K. Yünlü, A. Gleizes, J. Galy, Polyhedron 8 (1989) 1001. (c) P.S. Gradeff, K. Yünlü, J. Less-Common Met. 149 (1989) 81. (d) P.S. Gradeff, K. Yünlü. T.J. Deming, J.M. Olofson, R.J. Doedens, W.J. Evans, Inorg. Chem. 29 (1990) 420.

[58] A.N. Kornev, T.A. Chesnokova, E.V. Zhezlova, L.N. Zakharov, G.K. Fukin, Y.A. Kursky, G.A. Domrachev, P.D. Lickiss, J. Organomet. Chem. 587 (1999) 113.

[59] W.J. Evans, T.A. Ulibarri, J.W. Ziller, Organometallics 10 (1991) 134.

[60] R. Anwander, Rev. Top. Organomet. Chem. 2 (1999) 1.

[61] D.C. Bradley, J.S. Gothra, F.A. Hart, J. Chem. Soc. Dalton Trans. (1973) 1021.

[62] V. Lorenz, A. Fischer, K. Jacob, W. Brüser, T. Gelbrich, P.G. Jones, F.T. Edelmann, Chem. Commun. (1998) 2217.

[63] K. den Haan, L.L. de Boer, J.H. Teuben, A.L. Spek, B. Kojic-Prodic, G.R. Hays, R. Huis, Organometallics 5 (1986) 1726.

[64] W.J. Evans, R.A. Keyer, J.W. Ziller, Organometallics 12 (1993) 2618.

[65] R.G. Finke, S.R. Keenan, D.F.A. Schiraldi, P.L. Watson, Organometallics 6 (1987) 1356.

[66] H. Yasuda, H. Yamamoto, K. Yokota, A. Nakamura, Chem. Lett. (1989) 1309.

[67] F.T. Edelmann, Top. Curr. Chem. 179 (1996) 247.

[68] H. Yasuda, Top. Organomet. Chem. 2 (1999) 255.

[69] H. Görls, B. Neumüller, A. Scholz, J. Scholz, Angew. Chem. 107 (1995) 732; Angew. Chem. Int. Ed. Engl. 34 (1995) 673.

[70] D.C. Bradley, R.N. Kapoor, B.C. Smith, J. Inorg. Nucl. Chem. 24 (1962) 863.

[71] D.C. Bradley, R.N. Kapoor, B.C. Smith, J. Chem. Soc. (1963) 204.

[72] E. Stumpp, V. Stoeven, 17th Int. Conf. Coord. Chem., Hamburg, (1976) Abstr. p. 252; cited in Gmelin Hanbuch, U Suppl. vol. C 13, p. 378.

[73] V. Stoeven, Ph.D. Thesis, Technische Universität Clausthal, Germany, 1974.

[74] A. Streitwieser Jr., U. Müller-Westerhoff, J. Am. Chem. Soc. 90 (1968) 7364.

[75] D.W. Scott, J. Am. Chem. Soc. 68 (1946) 356.

[76] H. Bürgy, G. Calzaferri, D. Herren, A. Zhdanov, Chimia 45 (1991) 3.

[77] J.D. Lichtenhan, Comments Inorg. Chem. 17 (1995) 115.

[78] J.D. Lichtenhan, in: J.C. Salamone (Ed.), Polymeric Material Encyclopedia, CRC Press, New York, 1996.

[79] R. Murugavel, V. Chandrasekhar, H.W. Roesky, Acc. Chem. Res. 29 (1996) 183.

[80] A. Provatas, J.G. Matisons, Trends Polym. Sci. 5 (1997) 327.

[81] D.A. Loy, K.J. Shea, Chem. Rev. 95 (1995) 1431.

[82] J.F. Brown, L.H. Vogt, J. Am. Chem. Soc. 87 (1965) 4313.

[83] J.F. Brown, L.H. Vogt, J. Am. Chem. Soc. 87 (1965) 4317.

[84] F.J. Feher, D.A. Newman, J.F. Walzer, J. Am. Chem. Soc. 111 (1989) 1741.

[85] F.J. Feher, T.A. Budzichowski, R.L. Blanski, K.J. Weller, J.W. Ziller, Organometallics 10 (1991) 2526.

[86] F.J. Feher, D.A. Newman, J. Am. Chem. Soc. 112 (1990) 1931.

[87] F.J. Feher, K. Rahimian, T.A. Budzichowski, J.W. Ziller, Organometallics 14 (1995) 3920.

[88] V. Lorenz, M. Spoida, A. Fisher, F.T. Edelmann, J. Organomet. Chem. (2000) in press.

[89] (a) F.J. Feher, S.H. Phillips, J.W. Ziller, Chem. Commun. (1997) 829. (b) V. Lorenz, A. Fischer, F.T. Edelmann, unpublished results. (c) J. Annand, H.C. Aspinall, A. Steiner, Inorg. Chem. 38 (1999) 3941.

[90] T.W. Hambley, T. Maschmeyer, A.F. Masters, Appl. Organomet. Chem. 6 (1992) 253.

[91] M. Unno, K. Takada, H. Matsumoto, Chem. Lett. (1998) 489.

[92] O.I. Shchegolikhina, V.A. Igonin, Yu.A. Holodtsova, YuA. Pozdniakova, A.A. Zhdanov, T.V. Strelkova, S.V. Lindemann, J. Organomet. Chem. 562 (1998) 141.

[93] F.J. Feher, D. Soulivong, G.T. Lewis, J. Am. Chem. Soc. 119 (1997) 11323.

[94] F.J. Feher, D. Soulivong, A.E. Eklund, Chem. Commun. (1998) 399.

[95] F.J. Feher, D. Soulivong, F. Nguyen, Chem. Commun. (1998) 1279.

[96] F.J. Feher, F. Nguyen, D. Soulivong, J.W. Ziller, Chem. Commun. (1999) 1705.

[97] (a) F.J. Feher, S.L. Gonzales, J.W. Ziller, Inorg. Chem. 27 (1988) 3440. (b) F.J. Feher, J.F. Walzer, Inorg. Chem. 29 (1990) 1604.

[98] F.J. Feher, T.A. Budzichowski, K. Rahimian, J.W. Ziller, J. Am. Chem. Soc. 114 (1992) 3859.

[99] R. Murugavel, H.W. Roesky, Angew. Chem. 109 (1997) 491; Angew. Chem. Int. Ed. Engl. 36 (1997) 476.

[100] N. Winkhofer, A. Voigt, H. Dorn, H.W. Roesky, A. Steiner, D. Stalke, A. Reller, Angew. Chem. 106 (1994) 1414; Angew. Chem. Int. Ed. Engl. 33 (1994) 1352.

[101] A. Voigt, R. Murugavel, M.L. Montero, H. Wessel, F.-Q. Liu, H.W. Roesky, I. Usón, T. Albers, E. Parisini, Angew. Chem. 109 (1997) 1020; Angew. Chem. Int. Ed. Engl. 36 (1997) 1001.

[102] J.-C. Liu, Chem. Commun. (1996) 1109.

[103] T. Maschmeyer, M.C. Klunduk, C.M. Martin, D.S. Shephard, J.M. Thomas, B.F.G. Johnson, Chem. Commun. (1997) 1847.

[104] S. Gießmann, A. Fischer, F.T. Edelmann, J. Organomet. Chem. (2000) in press.

[105] (a) M. Crocker, R.H.M. Herold, A.G. Orpen, Chem. Commun. (1997) 2411. (b) M. Crocker, R.H.M. Herold, A.G. Orpen, M.T.A. Overgaag, J. Chem. Soc. Dalton Trans. (1999) 3791.

[106] J.W. Pattiasina, C.E. Hissink, J.L. de Boer, A. Meetsma, J.H. Teuben, A.L. Spek, J. Am. Chem. Soc. 107 (1985) 7758.

[107] R. Duchateau, H.C.L. Abbenhuis, R.A. van Santen, S.K.-H. Thiele, M.F.H. van Tol, Organometallics 17 (1998) 5222.

[108] Yu K. Gun'ko, L. Nagy, W. Brüser, V. Lorenz, A. Fischer, S. Gießmann, F.T. Edelmann, K. Jacob, A. Vértes, Monatsh. Chem. 130 (1999) 45.

[109] R. Duchateau, H.C.L. Abbenhuis, R.A. van Santen, A. Meetsma, S.K.-H. Thiele, M.F.H. van Tol, Organometallics 17 (1998) 5663.

[110] V. Lorenz, A. Fischer, F.T. Edelmann, unpublished work.

[111] W.A. Herrmann, R. Anwander, V. Dufaud, W. Scherer, Angew. Chem. 106 (1994) 1338; Angew. Chem. Int. Ed. Engl. 33 (1994) 1285.

[112] M. Bruzzone, in: T.J. Marks, I.L. Fragalá (Eds.), Fundamental and Technological Aspects of Organo-*f*-Element Chemistry, Reidel, Dordrecht, 1985.

[113] W. Hölderich, M. Hesse, F. Näumann, Angew. Chem. 100 (1988) 232; Angew. Chem. Int. Ed. Engl. 27 (1988) 226.

[114] T. Baba, R. Koide, Y. Ono, J. Chem. Soc. Dalton Trans. (1991) 691.

[115] S.L. Suib, Chem. Rev. 93 (1993) 803.

[116] P. Smet, B. Devreese, F. Verpoort, T. Pauwels, I. Svoboda, S. Foro, J. Van Beeumen, L. Verdonck, Inorg. Chem. 37 (1998) 6583.

[117] F.J. Feher, T.L. Tajima, J. Am. Chem. Soc. 116 (1992) 2145.

[118] (a) F.J. Feher, J.F. Walzer, R.L. Blanski, J. Am. Chem. Soc. 113 (1991) 3618. (b) F.J. Feher, R.L. Blanski, J. Am. Chem. Soc. 114 (1992) 5886.

[119] (a) H.C.L. Abbenhuis, S. Krijnen, R.A. van Santen, Chem. Commun. (1997) 331. (b) S. Krijnen, H.C.L. Abbenhuis, R.W.J.M. Hanssen, J.H.C. van Hooff, R.A. van Santen, Angew. Chem. 119 (1998) 374; Angew. Chem. Int. Ed. Engl. 37 (1998) 356.

[120] K. Wada, M. Nakashita, A. Aamamoto, T. Mitsudo, Chem. Commun. (1998) 133.