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Synthesis and Reactivity of Core-Functionalized Polyhedral Titanasiloxanes

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Condensation reactions of cyclopentadienyl silanetriols with titanium alkoxides yield oligomeric titanasiloxanes in high yields. Two types of polyhedral structures can be obtained by small structural modifications at the reactants ($Cp^RSi(OH)_3$, $Ti(OR)_4$) or by variation of reaction parameters. Thus, reaction of the silanetriols 9-(Me_3Si)Fluorenyl-$Si(OH)_3$ (**1**) and $Cp^*Si(OH)_3$ (**2**) with $Ti(O^tBu)_4$ leads to the cubic $Ti_4O_{12}Si_4$ polyhedrons [9-(Me_3Si)Fluorenyl-$Si]_4O_{12}[TiO^tBu]_4$ (**3**) and $[Cp^*Si]_4O_{12}[TiO^tBu]_4$ (**4**), respectively, while co-condensations of **1** with $Ti(O^iPr)_4$ afford either the polyhedral titanasiloxane [9-(Me_3Si)Fluorenyl-$Si]_4O_{12}[Ti$-$O^iPr]_6[\mu_2$-$^iPrO]_2[\mu_3$-$O]_2$ (**6**) or the cubic polyhedron [9-(Me_3Si)Fluorenyl-$Si]_4O_{12}[TiO^iPr]_4$ (**5**), depending on the choice of temperature and solvent. Substitution reactions with Ph_3SiOH, Me_2NOH, or acetylacetone at the titanium centers proceed selectively under conservation of the respective TiOSi core structures, whereas substitution reactions at the silicon centers performed with ethanol, HCl, and water are connected with core degradation. Both the novel titanasiloxanes and their titanium-functionalized derivatives have been characterized by IR and NMR spectroscopy as well as by single-crystal X-ray diffraction studies. Thermolysis of **3** leads to quantitative formation of 9-(Me_3Si)Fluorene and 2-methylpropene.

Introduction

Titanasiloxanes containing the Si−O−Ti moiety have attracted considerable interest in recent years for several reasons.[1] Synthetic titanasilicates are widely used as heterogeneous catalysts in industrial processes. They catalyze olefin epoxidation[2] and also other oxidation reactions of diverse substrates, such as alkanes, arenes, and amines.[3] In view of the impressive catalytic utility of these materials, it was of interest to synthesize soluble molecular titanasiloxanes as models for titanasilicates and for titanium complexes supported on silica surfaces. Titanasiloxanes are also considered as precursors for silicone polymers containing metal centers in the polymer backbone.[4] Especially promising compounds are the polyhedral titanasiloxanes. Their attraction stems from the appealing combination of an inorganic core and an organic periphery with potentially useful functionalities. They serve as model systems for titanium-doped zeolites.[5] Among these, compounds with a cubic core structure are of particular interest. Starting from three-functional, incompletely condensed oligosilsesquioxanes, Feher et al. synthesized cubic titanasilsesquioxanes in corner-capping reactions;[6] these compounds have a metal−silicon content of 1:7. Roesky et al. used the co-condensation of silanetriols with titanium(IV)-alkoxides for the synthesis of mainly cubic titanasiloxanes with a metal−silicon content of 4:4.[7] Although there are many silanetriols known in the literature,[8] only (arylamino)silanetriols of the type [Aryl(Me_3Si)-N]$Si(OH)_3$, (Aryl, e.g., 2,4,6-Me_3-phenyl)[7] have been extensively used in co-condensation reactions.

We are particularly interested in polyhedral, cubic titanasiloxanes possessing eight potential leaving groups at the corners of the cubic core. Substitution reactions at the core atoms allow the preparation of novel dendrimer-type compounds[9] and of SiOTi-based hybrid materials.[10] Furthermore, substitution reactions under elimination of the organic periphery can afford tailor-made Ti−O−Si phases, in which the cubic precursors act as secondary building blocks (SBU). In such cubic titanasiloxanes, attack of electrophiles or nucleophiles can effect either substitution reactions at the corner atoms or core opening by Ti−O−Si bond splitting. Core-

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Scheme 1

$$4\cdot\text{9-(Me}_3\text{Si)Fluorenyl-Si(OH)}_3\ \mathbf{1} + 4\ \text{Ti(O}^t\text{Bu)}_4 \xrightarrow[\text{hexane, rt}]{} [\text{9-(Me}_3\text{Si)Fluorenyl-Si}]_4\text{O}_{12}[\text{TiO}^t\text{Bu}]_4\ \mathbf{3} + 4\ {}^t\text{BuOH}$$

$$4\cdot\text{Cp*Si(OH)}_3\ \mathbf{2} + 4\ \text{Ti(O}^t\text{Bu)}_4 \xrightarrow[\text{hexane, rt}]{} [\text{Cp*Si}]_4\text{O}_{12}[\text{TiO}^t\text{Bu}]_4\ \mathbf{4} + 4\ {}^t\text{BuOH}$$

$$4\cdot\text{9-(Me}_3\text{Si)Fluorenyl-Si(OH)}_3\ \mathbf{1} + 4\ \text{Ti(O}^i\text{Pr)}_4 \xrightarrow[\substack{\text{hexane, -78 °C}\\ \text{or THF, rt}}]{} [\text{9-(Me}_3\text{Si)Fluorenyl-Si}]_4\text{O}_{12}[\text{TiO}^i\text{Pr}]_4\ \mathbf{5} + 4\ {}^i\text{PrOH}$$

opening finally results in a mixture of oligomeric products. Thus, reaction conditions have to be found where substitution reactions under conservation of the core structure are favored. Useful substitution reactions on such systems must proceed in nearly quantitative yields, because otherwise complex mixtures of deficiently substituted compounds would be formed.

In titanium(IV) chemistry, alkoxy groups have been shown to be good leaving groups. In silicon(IV) chemistry, the potential of cyclopentadienyl ligands as good leaving groups is well documented.[11] Accordingly, our approach is the preparation of polyhedral titanasiloxanes with alkoxy groups at the titanium and with Cp^R groups at the silicon centers. Changes in the alkoxy groups as well as in the Cp^R ligands allow the fine-tuning of steric properties, thus influencing structure and reactivity of the correspondingly substituted titanasiloxane.

There are reports concerning the reactivity of Si−O−Ti bonds of cyclic, nonpolyhedral titanasiloxanes,[12] indicating a strong sensitivity toward hydrolytic ring cleavage. A substitution reaction under conservation of the core structure of a cubic silsesquioxane was performed by Maschmeyer et al.[13] The ^{i}PrO group at the Ti moiety of the model compound $cHex_7Si_7O_{12}Ti(O^iPr)$ was substituted by the MeO group. The above compounds were also shown to be exellent homogeneous catalysts for olefin epoxidation with *tert*-butylhydroperoxide (TBHP).[14] Only recently has a detailed catalytic study been performed with the cubic titanasilsesquioxane $[2,6\text{-}^iPr_2C_6H_3)(Me_3Si)NSi]_4O_{12}[TiOEt]_4$,[15] which also catalyzes the epoxidation of cyclohexene. In this study the EtO groups of the above compound were selectively substituted by OO^tBu, ^tBuO, and $^tBuCH_2O$ groups.

With this contribution we describe the synthesis of the first polyhedral titanasiloxanes bearing Cp^R ligands at their silicon centers[16] and report on selective core-functionalization reactions which lead to further novel titanasiloxanes.

Results and Discussion

Synthesis of Polyhedral Titanasiloxanes. Two Cp^R-functionalized silanetriols and two tetraalkoxy titanium compounds serve as starting materials for the synthesis of three-dimensional titanasiloxanes. The silanetriols $9\text{-}(Me_3Si)Fluorenyl\text{-}Si(OH)_3$[17] (**1**) and $Cp^*Si(OH)_3$[18] (**2**) have been prepared in good yields by controlled hydrolysis of the corresponding chlorosilanes. At room temperature, compound **1** shows long-term stability in the solid state and in solution, whereas compound **2** decomposes slowly.[19] Compound **2** can be stored at temperatures lower than 0 °C without decomposition.

Co-condensation of equimolar amounts of the silanetriols **1** or **2** and of $Ti(O^tBu)_4$ in hexane at room temperature afforded the cubic titanasiloxanes **3** and **4** in nearly quantitative yields (Scheme 1); the cubic titanasiloxane **5** is formed as the main product by co-condensation of equimolar amounts of **1** and of $Ti(O^iPr)_4$ in THF at room temperature or in hexane at −78 °C. The compounds **3**−**5** are obtained as colorless solids, which are highly soluble in polar and unpolar organic solvents. The identity of these compounds has been confirmed by multinuclear NMR and IR spectroscopy, by elemental analysis, and by single-crystal X-ray diffraction. In the NMR spectra, the ^1H and ^{13}C chemical shifts are observed within the range expected for η^1-Cp^R and for O^iPr and O^tBu groups. The ^{29}Si NMR spectra exhibit a single resonance for the four SiO_3 units at about $\delta = -78$ ppm, indicating a high symmetry in solution. These resonances are observed about 30 ppm upfield from those of the corresponding silanetriols. IR spectra of the titanasiloxanes are dominated by the Si−O−Ti stretching frequencies observed at 900−1000 cm^{-1}. Further spectral data are detailed in the Experimental Section. Single crystals of **3**, **4**, and **5**, suitable for an X-ray crystal structure determination, were grown from concentrated solutions in hexane. Selected bond lengths and bond angles of **3**, **4**, and **5** are given in Table 1. The solid state structures differ only slightly with regard to the inorganic core. As an example, the structure of **4** is shown in Figure 1. The core structure can be defined by four silicon and four titanium atoms

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(19) Cp*H was detected as a decomposition product.

Table 1. Selected Bond Lengths [Å] and Bond Angles [deg] of 3, 4, and 5

	3	**4**	**5**
d(Si−O)	1.6226(19)−1.6319(19)	1.623(3)−1.640(3)	1.618(3)−1.636(3)
∠(O−Si−O)	108.03(9)−109.69(10)	107.50(16)−109.46(17)	108.21(13)−109.42(14)
d(Ti−O)	1.7891(17)−1.8155(17) *endocyclic*	1.797(3)−1.823(3) *endocyclic*	1.783(3)−1.814(2) *endocyclic*
	1.7456(18)−1.7584(18) *exocyclic*	1.756(3)−1.771(3) *exocyclic*	1.745(2)−1.754(2) *exocyclic*
∠(Si−O−Ti)	137.13(11)−163.68(11)	136.92(18)−158.31(19)	138.32(15)−165.09(16)
∠(O−Ti−O)	106.55(8)−109.13(9)	105.72(15)−112.22(15)	106.27(11)−109.13(11)
$d(O_3\mathrm{Si}{-}\mathrm{C}_{\mathrm{CpR}})$	1.856(2)−1.870(3)	1.873(4)−1.881(4)	1.855(3)−1.876(4)
$d(Me_3\mathrm{Si}{-}\mathrm{C}_{\mathrm{CpR}})$	1.912(3)−1.928(3)		1.906(4)−1.924(4)

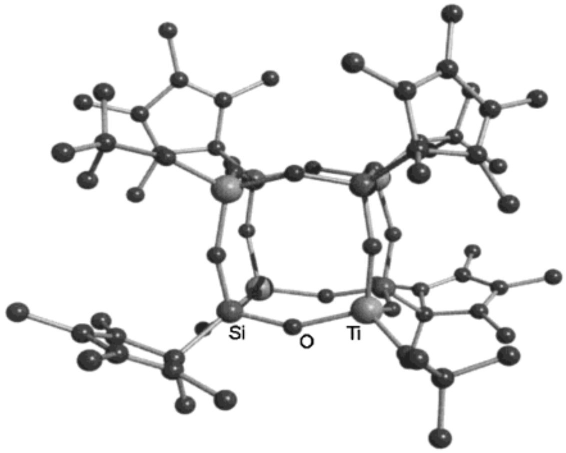

Figure 1. Structure of compound **4**. For clarity one of the four *tert*-butoxy groups is represented only by an oxygen atom.

occupying alternate corners of a cube. Each of the 12 Si−Ti edges is bridged by an oxygen atom in a μ^2 fashion. There are six $Si_2Ti_2O_4$ eight-membered rings that define the faces of the cube, and each of these rings adopts a pseudo C_4 crown conformation. The titanium and silicon atoms adopt distorted tetrahedral geometries. Although the cage structures of **3**, **4**, and **5** appear to be highly symmetric also in the solid state, closer inspection reveals that they show no symmetry at all. A strong distortion of the cubes is indicated by the broad range of the Ti−O−Si angles. The distortion of the Ti−O−Si angles in **3** and **5** is stronger than that in **4**. This observation can be explained by the greater steric demand of the 9-($SiMe_3$)fluorenyl group compared to that of the Cp* ligand. The average endocyclic (framework) Ti−O bond is slightly longer than the average exocyclic Ti−O bond. The distortion of the cages is caused presumably by packing effects in the solid state. The $Ti_4Si_4O_{12}$ polyhedrons are completely enclosed by hydrophobic Cp^R and alkoxy groups, thus leading to a high solubility of these compounds even in nonpolar solvents such as hexane.

Surprisingly, the co-condensation of equimolar amounts of **1** and of $Ti(O^iPr)_4$ in hexane at room temperature led to the formation of a mixture of products containing mainly the polyhedral titanasiloxane **6** and in addition compound **5** and some polysiloxanes. The ratio of the three components depends on the reaction conditions described in the Experimental Section. When the reactants were mixed according to the right stoichiometry for the formation of compound **6** (4 **1**, 6 $Ti(O^iPr)_4$, 2 H_2O), this species was obtained in quantitative yield and in analytically pure form (Scheme 2). The identity of **6** has been confirmed by multinuclear NMR and IR spectroscopy, by elemental analysis, and by an X-ray crystal structure determination. The NMR chemical shifts can be assigned in accordance with the solid state structure (see Experimental Section). The IR spectrum is dominated by the typical Si−O−Ti stretching frequencies around 960 cm^{-1}. Single crystals were obtained from a concentrated solution in hexane. The structure of **6** resembles a cubelike polyhedron with an additional “roof”. Figure 2 offers side views, which show how the addition of this “roof” leads to a distortion of the cage. The “roof” is created by insertion of a Ti(4)−(μ_3-O)$_2$−Ti(5) fragment into the cube face formed by Si(2), Ti(3), Si(4), and Ti(6). In Figure 3, a top view of the upper part of the molecule shows the interconnection between the Ti(3), Ti(4), Ti(5), and Ti(6) atoms via μ_3-O and μ_2-

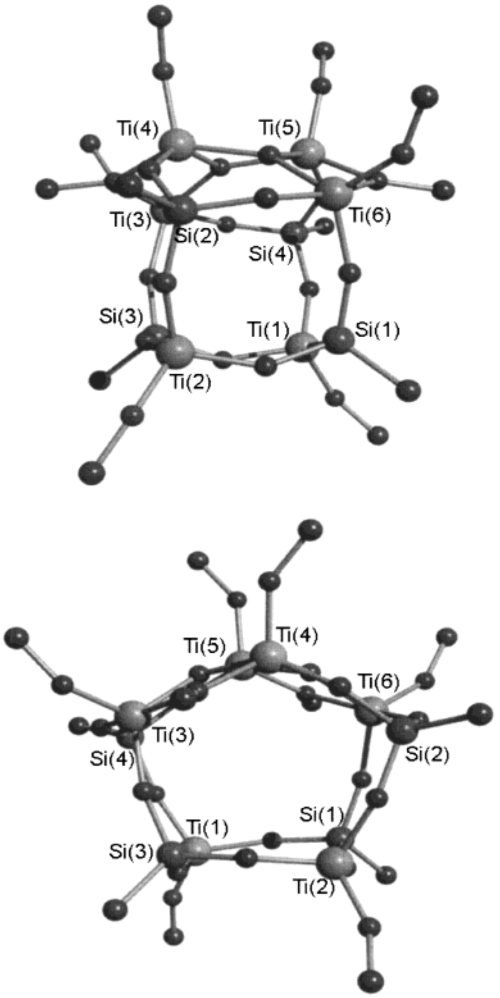

Figure 2. Side views of the framework of compound **6**. For clarity, 9-(Me_3Si)Fluorenyl groups and *iso*-propyl groups are represented only by the ipso carbon.

Scheme 2

$$4 \cdot \mathbf{1} + 4\,\mathrm{Ti(O^iPr)_4} \xrightarrow[\text{hexane, rt}]{} [\text{9-(Me}_3\text{Si)FluorenylSi}]_4\mathrm{O_{12}[TiO^iPr]_6[\mu_2\text{-}O^iPr]_2[\mu_3\text{-}O]_2}\ \mathbf{6} + 4\ {}^i\mathrm{PrOH} + \text{polysiloxanes}$$

$$4 \cdot \mathbf{1} + 6\,\mathrm{Ti(O^iPr)_4} + 2\,\mathrm{H_2O} \xrightarrow[\text{hexane, rt}]{} \mathbf{6} + 16\ {}^i\mathrm{PrOH}$$

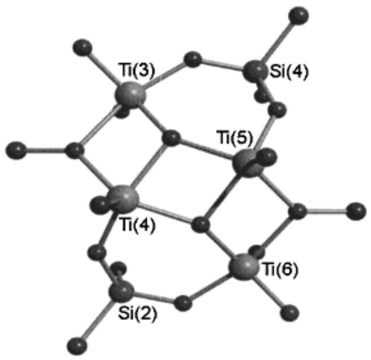

Figure 3. Top view of the upper half of **6**.

Table 2. Selected Bond Lengths [Å] and Bond Angles [deg] of 6

$d(\mathrm{Ti{-}O_{Si}})$	1.794(2)−1.866(2) *endocyclic* 1.751(2)−1.774(2) *exocyclic*
∠(O−Ti−O)	94.47(9)−111.25(10)
d(Si−O)	1.611(2)−1.641(2)
∠(O−Si−O)	107.42(12)−111.05(12)
∠(Si−O−Ti)	134.46(13)−160.82(14)
μ_2-O^{i}Pr-Fragment	
d(Ti−O)	1.930(2), 1.936(2) 2.104(2), 2.096(2)
∠(Ti−O^{i}Pr-Ti)	102.63(9), 102.87(9)
μ_3-O-Fragment	
d(Ti−O)	1.962(2), 1.956(2) 2.003(2), 2.009(2) 1.905(2), 1.911(2)
∠(Ti−O−Ti)	144.49(11), 144.36(11) 107.43(10), 107.09(10) 102.56(10), 102.55(10)

O^{i}Pr linkages. A comparison of the different Ti−O bond lengths in the OTi$_3$ and ^{i}PrOTi$_2$ units with the sum of the covalent radii of oxygen and titanium suggests that the μ_3-O fragments are connected to the titanium atoms formally by two covalent and one coordinative bond, whereas the μ_2-O^{i}Pr fragments are connected by one covalent and one coordinative bond. A nearly planar coordination is observed for the μ_3-O units (sum of the bond angles 354.5° and 354.0°). Compound **6** is the unique case of a titanasiloxane containing three differently coordinated Ti centers. While Ti(1) and Ti(2) are tetrahedrally coordinated, Ti(3) and Ti(6) are trigonal bipyramidally coordinated and Ti(4) and Ti(5) are square pyramidally coordinated. The μ_n-O ($n = 2$, 3) and μ_2-OR linkages of Ti atoms found in **6** are also common structural features in titanium oxo clusters.[20] Further structural parameters are given in Table 2.

The formation of the titanasiloxane **6**, possessing structural elements such as μ_3-O units and Ti−O−Ti linkages, requires side reactions in the co-condensation process of the silanetriol **1** with Ti(O^{i}Pr)$_4$. Thus, autocondensation of silanetriol molecules under formation of polysiloxanes and water has to take place. Partial hydrolysis of Ti−O^{i}Pr bonds by the liberated water followed by condensation reactions results in the connection of Ti−O−Ti units by μ_3-O or by μ_2-OR bridges. Interestingly, the described side-reactions can be avoided by offering the reactants (including water) in the right stoichometry for the formation of **6**.

Our investigations have shown that small modifications of the alkoxy ligands of the titaniumalkoxide and the solvent lead to structural changes in the Ti−O−Si framework of the resulting titanasiloxanes. Thus, cocondensation of **1** with Ti(O^{t}Bu)$_4$ leads to the expected cubic Ti$_4$Si$_4$O$_{12}$ polyhedron **3**, whereas the products of the co-condensation of **1** with Ti(O^{i}Pr)$_4$ depend on the reaction parameters. The reaction of **2** with Ti(O^{t}Bu)$_4$ afforded the expected cubic compound; the reaction of **2** with Ti(O^{i}Pr)$_4$ led to a mixture of oligomeric products that could not be clearly identified.[17]

Substitution Chemistry of Polyhedral Titanasiloxanes. Reactivity studies have been performed with the titanasiloxanes **3**−**6**. Due to the sensitivity of the TiOSi core units toward acid- or base-catalyzed oligomerizations, the choice of reactants for selective core functionalizations is strictly limited. Thus, reactions of the above compounds with ethanol or methanol resulted in ring cleavage, followed by polycondensation. Despite these problems, we have found conditions for selective substitution reactions at the titanium centers, which proceed under conservation of the core structure of the respective titanasiloxane. First hints for selective substitution reactions resulted from experiments with [9-(Me$_3$Si)Fluorenyl-Si]$_4$O$_{12}$[TiO^{t}Bu]$_4$ (**3**) and [Cp*Si]$_4$-O$_{12}$[TiO^{t}Bu]$_4$ (**4**) as catalysts for the epoxidation of cyclohexene with TBHP.[17] During the catalytic cycle, O^{t}Bu groups have to be substituted by OO^{t}Bu groups. The measured turnover numbers indicated that all four Ti centers are involved in the catalytic process. The catalysts could be regained quantitatively, a proof for the core stability during many catalytic cycles.

The reaction of **3** or **5** with 4 equiv of Ph$_3$SiOH in THF proceeded readily at room temperature and afforded the colorless substitution product **7** almost quantitatively, whereby the corresponding alcohols were liberated (Scheme 3). Compound **7** has been characterized by multinuclear NMR and IR spectroscopy, by elemental analysis, and by an X-ray crystal structure determination. The ^{29}Si NMR spectrum exhibits sharp resonances for the SiMe$_3$ ($\delta = 4.74$ ppm), the SiPh$_3$ ($\delta = -12.37$ ppm), and the SiO$_3$ group ($\delta = -78.21$ ppm), indicating a high symmetry of the cage compound in solution. The ^{1}H NMR and ^{13}C NMR chemical shifts can also be assigned in accordance with a symmetric structure. The IR spectrum is dominated by the Si−O−Ti stretching frequency observed at 917 cm^{-1}. Further spectroscopic data are given in the Experimental Section. Suitable single crystals of **7** were grown from a concentrated solution in hexane, and the crystal structure was determined. The Ti$_4$Si$_4$O$_{12}$ polyhedron of **7** is completely

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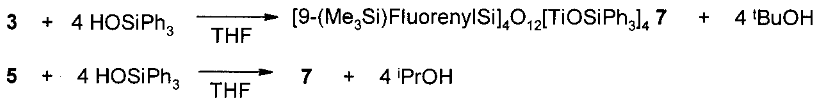
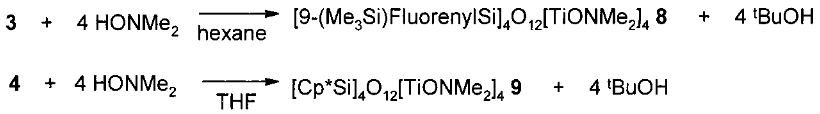
Scheme 3



$$\mathbf{3} + 4\,\mathrm{HOSiPh_3} \xrightarrow[\mathrm{THF}]{} [9\text{-}(\mathrm{Me_3Si})\mathrm{FluorenylSi}]_4\mathrm{O_{12}}[\mathrm{TiOSiPh_3}]_4\ \mathbf{7} + 4\ {}^t\mathrm{BuOH}$$

$$\mathbf{5} + 4\,\mathrm{HOSiPh_3} \xrightarrow[\mathrm{THF}]{} \mathbf{7} + 4\ {}^i\mathrm{PrOH}$$

Scheme 4



$$\mathbf{3} + 4\,\mathrm{HONMe_2} \xrightarrow[\mathrm{hexane}]{} [9\text{-}(\mathrm{Me_3Si})\mathrm{FluorenylSi}]_4\mathrm{O_{12}}[\mathrm{TiONMe_2}]_4\ \mathbf{8} + 4\ {}^t\mathrm{BuOH}$$

$$\mathbf{4} + 4\,\mathrm{HONMe_2} \xrightarrow[\mathrm{THF}]{} [\mathrm{Cp^*Si}]_4\mathrm{O_{12}}[\mathrm{TiONMe_2}]_4\ \mathbf{9} + 4\ {}^t\mathrm{BuOH}$$

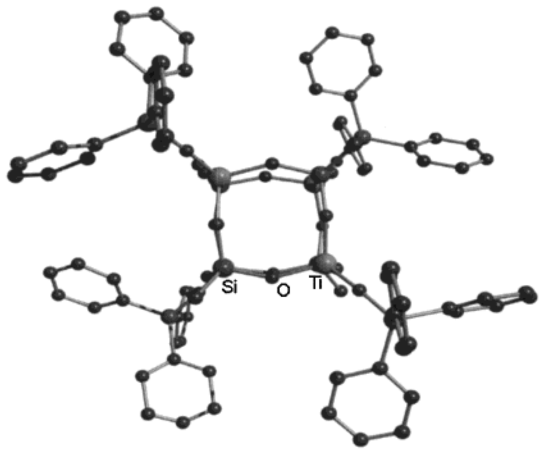


Figure 4. Drawing of the structure of compound **7**. For clarity, 9-(Me_3Si)Fluorenyl groups are represented by the ipso carbon atoms.

Table 3. Selected Bond Lengths [Å] and Bond Angles [deg] of 7

d(Si−O)	1.626(2)−1.638(2) *endocyclic* 1.643(1)−1.655(1) *exocyclic*
∠(O−Si−O)	107.73(6)−109.20(6)
d(Ti−O)	1.784(1)−1.814(1) *endocyclic* 1.789(1)−1.796(1) *exocyclic*
∠(Si−O−Ti)	135.59(7)−158.93(8) *endocyclic* 160.72(9)−172.60(9) *exocyclic*
∠(O−Ti−O)	104.67(5)−114.61(6)
d(Si_O−C_{Fl})	1.855(2)−1.860(2)

enclosed by hydrophobic 9-($SiMe_3$)Fluorenyl and $OSiPh_3$ groups, which show a propeller-like conformation. All bond lengths and angles fall in the expected ranges and are comparable to those observed for the parent compounds **3** and **5**. Figure 4 shows the cubic core structure of **7** and the arrangement of the pendant $OSiPh_3$ groups on the titanium moieties. Structural parameters are given in Table 3.

Treatment of **3** and **4** with 4 equiv of Me_2NOH afforded the compounds **8** and **9**, respectively, in high yields, whereby *tert*-butyl alcohol was liberated (Scheme 4). The colorless products have been characterized by multinuclear NMR and IR spectroscopy, by elemental analysis, and by X-ray crystal structure determination. The ^{29}Si NMR spectra exhibit one sharp resonance for the four SiO_3 units (δ −77.3 ppm, **8**, and δ −73.9 ppm, **9**), and the ^1H NMR and ^{13}C NMR spectra display only one resonance for the Me_2NO ligands, indicating a high symmetry of the compounds in solution. The IR spectra show typical Si−O−Ti stretching frequencies around 950 cm^{-1}. Further spectroscopic data are given in the Experimental Section. Single crystals suitable for an X-ray crystal structure investigation were grown from concentrated solutions in dichloromethane/hexane (**8**) or in diethyl ether (**9**). The solid state structures of **8** and **9** are comparable with regard to their $Ti_4Si_4O_{12}$ cage and their Ti−O−NMe_2 moieties. As an example, a representation of the structure of **8** is shown in Figure 5. The titanium centers of the $Ti_4Si_4O_{12}$ polyhedra are coordinated with dimethylhydroxylamido ligands ($ONMe_2$) in a bidentate fashion, whereby Ti−O bonds and additional Ti−N β-donor bonds are formed. This situation leads to an overall 5-fold coordination at titanium. The average N−Ti bond lengths are 2.10 Å (**8**) and 2.12 Å (**9**) ($\sum r_{vdW}$: 3.05 Å). The average Ti−O−N angles are 77.50° (**8**) and 78.05° (**9**). All framework Ti−O−Si bond lengths and angles fall in the expected ranges and are comparable with the values found in the parent compounds **3** and **4**. Further structural parameters of compounds **8** and **9** are given in Table 4.

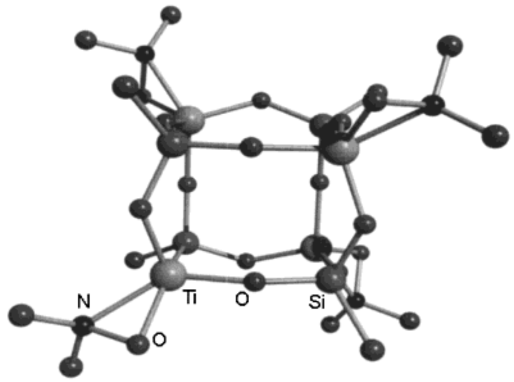


Figure 5. Drawing of the structure of compound **8**. For clarity, 9-(Me_3Si)Fluorenyl groups are represented by the ipso carbon atoms.

A few *N*,*N*-dialkylhydroxylamido compounds of titanium are known in the literature.[21] The solid state structure of the homoleptic $Ti(ONMe_2)_4$ was confirmed by an X-ray structure investigation. In this symmetric molecule, the nitrogen atoms serve as β-donors, leading to an eight-coordinate environment on titanium, achieving an intramolecular saturation of the coordination sphere.

The reaction of **4** and **6** with 4 equiv of acetylacetone afforded the compounds **10** and **11**, respectively, whereby the corresponding alcohols were liberated (Scheme 5). The identity of the colorless products has been confirmed by multinuclear NMR and IR spectroscopy, by elemental analysis, and by X-ray crystal structure determination. The ^1H NMR and ^{13}C NMR chemical shifts can be assigned in accordance with the solid state structure. The ^{29}Si NMR spectrum exhibits a sharp

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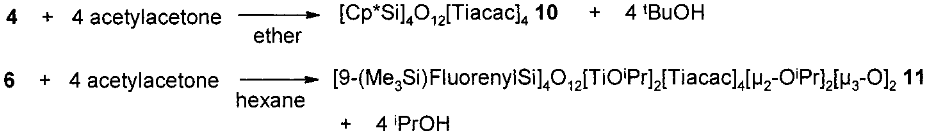
Table 4. Selected Bond Lengths [Å] and Bond Angles [deg] of 8 and 9

	8	**9**
d(Si−O)	1.617(1)−1.637(1)	1.618(3)−1.648(3)
∠(O−Si−O)	108.65(6)−110.53(6)	106.09(13)−111.16(15)
d(Ti−O)	1.815(1)−1.827(1) *endocyclic* 1.878(1) *exocyclic*	1.807(2)−1.835(2) *endocyclic* 1.872(2)−1.882(3) *exocyclic*
d(Ti−N)	2.103(1)	2.108(3)−2.124(3)
∠(N−O−Ti)	77.50(8)	77.83(19)−78.26(17)
∠(Si−O−Ti)	132.61(8)−160.32(8)	130.18(14)−178.6(2)
∠(O−Ti−O)	97.31(5)−121.79(5)	99.26(12)−116.24(11)
d(Si$_O$−C$_{CpR}$)	1.871(1)	1.885(3)−1.889(3)

Scheme 5



$$\mathbf{4} + 4\ \text{acetylacetone} \xrightarrow[\text{ether}]{} [\text{Cp*Si}]_4\text{O}_{12}[\text{Tiacac}]_4\ \mathbf{10} + 4\ {}^t\text{BuOH}$$

$$\mathbf{6} + 4\ \text{acetylacetone} \xrightarrow[\text{hexane}]{} [\text{9-(Me}_3\text{Si)FluorenylSi}]_4\text{O}_{12}[\text{TiO}^i\text{Pr}]_2[\text{Tiacac}]_4[\mu_2\text{-O}^i\text{Pr}]_2[\mu_3\text{-O}]_2\ \mathbf{11} + 4\ {}^i\text{PrOH}$$

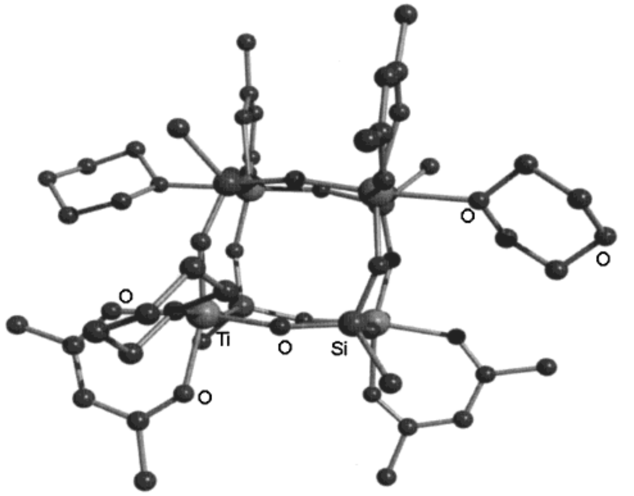


Figure 6. Drawing of the structure of compound **10**·4 dioxane. For clarity, Cp* groups are represented by the ipso carbon atom.

Table 5. Selected Bond Lengths [Å] and Bond Angles [deg] of 10·4 dioxane

d(Ti−O$_{Si}$)	1.781(3)−1.833(3)
d(Ti−O$_{acac}$)	2.038(3)−2.065(3)
d(Ti−O$_{dioxane}$)	2.237(3)−2.317(3)
∠(O$_{Si}$−Ti−O$_{Si}$)	99.25(11)−102.34(11)
∠(O$_{acac}$−Ti−O$_{acac}$)	80.15(10)−81.25(11)
d(Si−O)	1.603(3)−1.634(2)
∠(O−Si−O)	107.82(14)−111.48(14)
∠(Si−O−Ti)	148.06(16)−162.93(16)
d(Si−C$_{Cp*}$)	1.884(4)−1.900(4)

resonance for **10** (SiO$_3$ $\delta = -80.43$ ppm) and two different resonances ($\delta = -61.87, -65.72$ ppm) for **11**. IR spectra of both compounds are dominated by the Si−O−Ti stretching frequencies observed at 900−1000 cm^{-1}. Single crystals of [**10**·4 dioxane] could be obtained from recrystallization from an diethyl ether/dioxane mixture. Suitable single crystals of **11** were grown from a concentrated solution in diethyl ether. Crystal structures of both compounds were determined. Four acetylacetonato ligands are bound to the titanium atoms of **10** (Figure 6) in addition to four dioxane molecules from the solvent. This bonding situation leads to a six-coordinate environment at the metal. The average Ti−O$_{acac}$ bond length (2.05 Å) is shorter than the average Ti−O$_{dioxane}$ bond length (2.27 Å). The average Ti−O bond length in the framework is 1.81 Å. The framework Ti−O−Si angles range from 148.06° to 162.95°, indicating a distortion of the cage. Further structural parameters are given in Table 5.

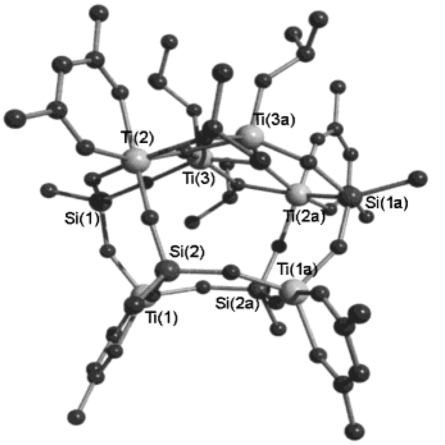


Figure 7. Drawing of the structure of compound **11**. For clarity, 9-(Me$_3$Si)Fluorenyl and *iso*-propyl groups are represented by the ipso carbon atoms.

The core structure of **11** (Figure 7 gives a side view) is comparable to that of the parent compound **6**, resembling a cubelike polyhedron with an additional "roof", created by insertion of the Ti(3)−(μ_3-O)$_2$−Ti(3a) fragment into the cube face formed by Si(1), Ti(2), Si(1a), and Ti(2a). Four titanium atoms [Ti(1), Ti(1a), Ti(2), and Ti(2a)] possess acetylacetonato substituents, whereas two titanium atoms [Ti(3), Ti(3a)] are still fixed to isopropoxy groups. This bonding situation leads to a five-coordination at Ti(1) and Ti(1a) (with trigonal bipyramidal geometry), to a six-coordination at Ti(2) and Ti(2a) (with octahedral geometry), and to five-coordination at Ti(3) and Ti(3a) (with square pyramidal geometry). A top view of the upper part of the molecule is presented in Figure 8. Selected structural parameters are given in Table 6.

We have demonstrated that the polyhedral titanasiloxanes **3**−**6** can be functionalized selectively at their titanium centers without decomposition of the Si−O−Ti core structure. The choice of reagents is crucial. The best results are achieved with substrates that lead to an increase of the coordination number (chelating ligands).

In our experiments exploring the reactivity of the Cp^R substituents at the silicon centers in the compounds **3**

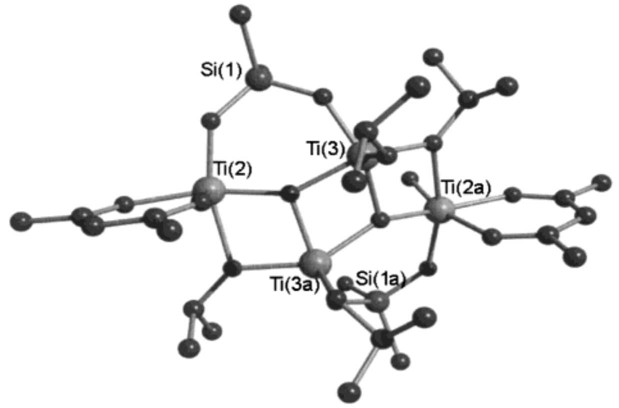


Figure 8. Upper half of **11**.

Table 6. Selected Bond Lengths [Å] and Bond Angles [deg] of 11

d(Ti−O_{Si})	1.790(1)−1.844(1) *endocyclic* 1.817(1) *exocyclic*
d(Ti−O_{acac})	1.960(1)−2.107(1)
∠(O_{Si}−Ti−O_{Si})	95.88(5)−113.00(5)
∠(O_{acac}−Ti−O_{acac})	80.10(5)−80.96(5)
d(Si−O)	1.613(1)−1.633(1)
∠(O−Si−O)	107.75(6)−111.87(6)
∠(Si−O−Ti)	134.74(7)−164.98(7)
μ_2-O-fragment	
d(Ti−O)	1.942(1)−2.133(1)
∠(Ti−O^iPr−Ti)	100.54(5)
μ_3-O-fragment	
d(Ti−O)	1.896(1)−1.968(1)
∠(Ti−O−Ti)	103.24(5)−147.17(6)

(9-(Me3Si)Fluorenyl-substituted) and **4** (Cp*-substituted), we have indeed observed the substitution of the Cp^R ligands, but in most cases so far only with concomitant degradation of the Si−O−Ti core.

In studies performed with compound **4** we found that the Cp*−Si bonds are easily cleaved by treatment with stoichometric amounts of ethanol, water, or HCl to afford Cp*H. In addition these reactions afforded gels that form insoluble solids after removal of the solvent. Interestingly, the formation of the protonated ligand Cp^RH has not been observed in comparable reactions performed with **3** possessing (Me_3Si)Fluorenyl groups at the silicon centers. The slow formation of insoluble solids indicates ring opening followed by oligomerization reactions.

Interestingly, quantitative cleaving reactions have also been observed under thermal treatment. Thus heating of **3** (300 °C) led to the formation of 2-methylpropene (from the *tert*-butyl group) and to the liberation of the protonated (Me_3Si)Fluorenyl ligand. Similarly, heating (200 °C) of **4** afforded Cp* radicals, which disproportionate to give Cp*H and tetramethylfulvene, a well-known process in gase phase decomposition of Cp*-silanes.[22]

In these heterolytic and homolytic cleavage reactions, we have not fully identified the structure of the remaining inorganic Ti−O−Si materials so far; detailed studies are in progress, exploring whether the stripping of the organic periphery in the described polyhedral titanasiloxanes affords novel Si−O−Ti materials not accessible by the sol−gel process.

Conclusions

With this contribution we have presented the synthesis of novel polyhedral titanasiloxanes bearing Cp^R substituents at silicon and alkoxy substituents at titanium. The observed reaction pathways are dominated by the steric requirements of the substituents at silicon and at titanium and even by solvent and temperature. We have shown that titanium centers of polyhedral titanasiloxanes can be selectively functionalized. This procedure might be used to attach polymerizable organic groups (e.g., allyl groups) to polyhedral titanasiloxanes. Such side chain functionalized titanasiloxanes might serve as structurally well-defined nanosized building blocks for the preparation of inorganic−organic hybrid materials.[23] Functionalization of titanasiloxanes at titanium moieties with chelating ligands increases the overall stability of the compounds by steric shielding of the titanium centers. These modifications might alter the reactivity of the Cp^R titanasiloxanes in favor of Cp−Si bond splitting under conservation of the original core structure. We are currently pursuing studies concerning this aspect and have obtained first results supporting this assumption.

Experimental Section

General Comments. All manipulations were carried out under a purified argon atmosphere using standard vacuum techniques. The solvents were purified by conventional means and distilled immediately prior to use. Compounds **1** and **2** were prepared according to the literature.[17] Titanium(IV) ethoxide, titanium(IV) isopropoxide, and titanium(IV) *tert*-butoxide (Fluka) were used as received. The melting point determinations were performed using a Büchi 510 melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld. NMR spectra were recorded using a Bruker Avance DRX 500 spectrometer (^{1}H 500.1 MHz, $^{13}C\{^1H\}$ 125.8 MHz, $^{29}Si\{^1H\}$ 99.4 MHz). Chemical shifts are reported in ppm and were referenced to the solvent resonances as internal standard. IR data were collected using a Bruker Vektor 22-FT spectrometer over the range 4000−400 cm^{-1}. The samples were measured as KBr pellets.

$[Me_3SiFlSi]_4O_{12}[TiO^tBu]_4$ (3). At room temperature 0.80 g (2.34 mmol) $Ti(OtBu)_4$ was added dropwise over 10 min to a suspension of 0.74 g (2.34 mmol) of **1** in hexane (18 mL) using a syringe. The reaction mixture was stirred for 15 h. A clear solution was formed immediately, followed by the slow formation of a colorless precipitate. After removal of volatile compounds in vacuo a yellow-orange solid remained, which was dried in vacuo. Single crystals suitable for an X-ray crystal structure determination were grown from a concentrated solution in hexane (0.97 g, 0.56 mmol, 95%), mp >250 °C. ^{1}H NMR ($CDCl_3$): δ −0.20 (s, 36H, *Me*), 0.96 (s, 36H, *tBu*), 7.21, 7.31 (2t, $^3J_{H-H} = 7.2$, 8H, *aromat-H*), 7.63, 7.83 (2d, $^3J_{H-H} =$ 7.7, 7.6, 8H, *aromat-H*). ^{13}C NMR ($CDCl_3$): δ −2.1 (*Me*), 32.2 ($C(CH_3)_3$), 42.0 (*allyl-C*), 86.2 ($C(CH_3)_3$), 119.4, 124.2, 124.5, 124.8, 125.4 (*aromat-C*), 140.3, 145.6 (*vinyl-C*). ^{29}Si NMR ($CDCl_3$): δ 5.0 (*Si*Me_3), −78.2 (*Si*O_3). IR (KBr): 444 (m), 492 (m), 738 (s), 842 (s), 854 (s), 965 (vs), 1072 (m), 1248 (m), 1262 (m), 1364 (m), 1432 (m), 1445 (m), 2893 (m), 2922 (m), 2967 (m), 3054 (w). MS (ESI, in THF) m/z (I_{rel}): 1737 (100) [M^+], 1679 (10) [$(M - tBu)^+$], 1664 (8) [$(M - SiMe_3)^+$]. Anal. Calcd

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Table 7. Composition of the Product Mixture (%)

reaction	**5**	**6**	polysiloxane
a	81.5	18	0.5
b	66	33	1
c	19	76	5
d		100	

for $C_{80}H_{104}O_{16}Si_8Ti_4$ (1737.92): C, 55.29; H, 6.03. Found: C, 54.04; H, 5.86 (due to the formation of SiC, the carbon content is low).

$[Cp^*Si]_4O_{12}[TiO^tBu]_4$ (4). At room temperature 1.14 g (3.36 mmol) of $Ti(O^tBu)_4$ was added dropwise over 10 min to a suspension of 0.72 g (3.36 mmol) of **2** in 18 mL of hexane using a syringe. The mixture was stirred for 15 h. A clear solution was formed immediately, and a colorless precipitate was formed after 15 h. After removal of volatile compounds in vacuo the remaining slightly yellow solid was rinsed two times with a minimum of cooled hexane and dried in vacuo. Single crystals suitable for an X-ray crystal structure determination were grown from a concentrated solution in hexane (1.12 g, 0.84 mmol, 82%), mp ~180 °C (dec). ^{1}H NMR ($CDCl_3$): δ 1.14 (s, 12H, *Me*), 1.27 (s, 36H, *tBu*), 1.80, 1.91 (2s, 24H, *Me*). ^{13}C NMR ($CDCl_3$): δ 11.5, 11.6, 15.2 (*Me*), 31.4 (C(*C*H$_3$)$_3$), 51.6 (*allyl-C*), 84.8 (*C*(CH$_3$)$_3$), 134.8, 137.1 (*vinyl-C*). ^{29}Si NMR ($CDCl_3$): δ −77.5. IR (KBr): 451 (s), 474 (s), 799 (s), 960 (vs), 1068 (s), 1237 (w), 1364 (m), 1455 (w), 2864 (m), 2924 (m), 2974 (m). MS (ESI, in THF) m/z (I_{rel}): 1329 (3) [M$^+$], 1060 (10) [(M − 2Cp*)$^+$]. Anal. Calcd for $C_{56}H_{96}O_{16}Si_4Ti_4$ (1329.23): C, 50.60; H, 7.28. Found: C, 50.96; H, 7.28.

$[Me_3SiFlSi]_4O_{12}[TiO^iPr]_4$ (5) and $[Me_3SiFlSi]_4O_{12}[TiO^iPr]_6[\mu_2\text{-}^iPrO]_2[\mu_3\text{-}O]_2$ (6). (a) At room temperature, an equimolar amount of $Ti(O^iPr)_4$ was added dropwise over 10 min to a solution of **1** in THF (8 mL per mmol). The mixture was stirred for 15 h. (See workup procedure and Table 7.)

(b) A suspension of **1** in hexane (6 mL per mmol) was cooled to −78 °C, and a solution of an equimolar amount $Ti(O^iPr)_4$ in hexane (6 mL per mmol) was added dropwise over 10 min. The mixture was stirred for 15 h and was allowed to warm to room temperature. A clear solution was obtained. (See workup procedure and Table 7.)

(c) At room temperature, an equimolar amount of $Ti(OiPr)_4$ was added dropwise over 10 min to a suspension of **1** in hexane (8 mL per mmol). The mixture was stirred for 15 h. A clear solution was obtained. (See workup procedure and Table 7.)

(d) At room temperature 3 equiv of $Ti(OiPr)_4$ was added dropwise over 10 min to a suspension of 2 equiv of **1** and 1 equiv of H_2O in hexane (8 mL per mmol) using a syringe. A clear solution was formed immediately and was stirred for 15 h.

Workup Procedure for a−d. After removal of all volatile compounds in vacuo a yellow-orange solid was obtained. Fractional crystallization from hexane at −30 °C afforded the compounds **5** and **6** as colorless crystals. The NMR and IR spectra of the product mixture indicate a polysiloxane as the third component.

$[Me_3SiFlSi]_4O_{12}[TiO^iPr]_4$ (5). Mp > 250 °C. ^{1}H NMR ($CDCl_3$): δ −0.21 (s, 36H, Si*Me*$_3$), 0.87 (d, $^3J_{H-H}$ = 3.8, 24H, CH(C*H*$_3$)$_2$), 4.17 (m, 4H, C*H*(CH$_3$)$_2$), 7.30 (m, 16H, *aromat-H*), 7.64, 7.82 (2d, $^3J_{H-H}$ = 7.6, 8H, *aromat-H*). ^{29}Si NMR ($CDCl_3$): δ 5.2 (*Si*Me$_3$), −78.0 (*Si*O$_3$). IR (KBr): 447 (m), 492 (m), 740 (s), 855 (s), 968 (vs), 1055 (m), 1103 (m), 1172 (m), 1248 (m), 1262 (m), 1432 (m), 1445 (m), 2880 (m), 2924 (m), 2969 (m), 3057 (w). Anal. Calcd for $C_{76}H_{96}O_{16}Si_8Ti_4$ (1681.81): C, 54.28; H, 5.75. Found: C, 54.12; H, 5.69.

$[Me_3SiFlSi]_4O_{12}[TiO^iPr]_6[\mu_2\text{-}^iPrO]_2[\mu_3\text{-}O]_2$ (6). Mp > 250 °C. ^{1}H NMR ($CDCl_3$): δ −0.19, −0.16 (2s, 18H, *Me*), 0.56, 0.78, 0.80, 0.84, 0.87, 0.91, 0.96, 1.09 (8d, $^3J_{H-H}$ = 5.8−7.0, 6H, CH(C*H*$_3$)$_2$), 3.98 (sept, 4H, C*H*(CH$_3$)$_2$), 4.39, 4.52 (2sept, 2H, C*H*(CH$_3$)$_2$), 7.12, 7.29 (2t, $^3J_{H-H}$ = 7.5, 7.4, 2H, *aromat-H*), 7.63, 7.76 (2d, $^3J_{H-H}$ = 7.7, 2H, *aromat-H*), 7.21, 7.36 (2m, 6H, *aromat-H*), 7.80−7.90 (m, 12H, *aromat-H*). ^{13}C NMR ($CDCl_3$): δ −1.8, −1.7 (Si*Me*$_3$), 22.0, 24.6, 25.0, 25.5, 25.6, 25.65, 25.7 (CH(*C*H$_3$)$_2$), 42.9, 43.3 (*allyl-C*), 76.2, 80.2, 81.1, 81.9 (*C*H(CH$_3$)$_2$), 119.1, 119.2, 119.4, 123.8, 123.9, 124.0, 125.2, 125.3, 125.4 (*aromat-C*), 140.1, 140.2, 140.4, 146.1, 146.3, 146.4, 146.7 (*vinyl-C*). ^{29}Si NMR ($CDCl_3$): δ 5.2, 4.4 (*Si*Me$_3$), −69.2, −80.4 (*Si*O$_3$). IR (KBr): 465 (m), 635 (m), 739 (s), 855 (s), 826 (s), 934 (vs), 955 (vs), 991 (vs), 1054 (s), 1112 (m), 1132 (m), 1172 (m), 1248 (m), 1262 (m), 1365 (w), 1379 (w), 1432 (m), 1445 (m), 2838 (w), 2878 (w), 2927 (m), 2970 (m), 3067 (w). Anal. Calcd for $C_{88}H_{124}O_{22}Si_8Ti_6$ (2132.09): C, 51.60; H, 6.11. Found: C, 51.35; H, 6.13.

Polysiloxane. ^{29}Si NMR ($CDCl_3$): δ −83.3 (*Si*O$_3$). IR (KBr): 1102 (vs).

$[Me_3SiFlSi]_4O_{12}[TiOSiPh_3]_4$ (7). (a) At 0 °C 0.17 g (0.60 mmol) $HOSiPh_3$ in 5 mL of THF was added dropwise over 10 min to a solution of 0.25 g (0.15 mmol) of **3** in 20 mL of THF under vigorous stirring. The mixture was stirred for a further 16 h. After removal of volatile compounds in vacuo a colorless solid was obtained. Single crystals suitable for an X-ray crystal structure determination were grown from a concentrated solution in hexane (0.36 g, 0.14 mmol, 93%).

(b) At 0 °C 0.38 g (1.38 mmol) of $HOSiPh_3$ in 10 mL of THF was added dropwise over 10 min to a solution of 0.58 g (0.35 mmol) of **4** in 40 mL of THF under vigorous stirring. The mixture was stirred for a further 16 h, then volatile compounds were removed in vacuo. A colorless solid was obtained. Single crystals suitable for an X-ray crystal structure determination were grown from a concentrated solution in hexane (0.86 g, 0.34 mmol, 97%), mp <250 °C. ^{1}H NMR ($CDCl_3$): δ −0.60 (1s, 36 H, *Me*), 6.79, 6.97 (2t, $^3J_{H-H}$ = 7.2, 16H, *aromat-H*), 7.33 (m, 60 H, *aromat-H*), 7.48, 7.62 (2d, $^3J_{H-H}$ = 7.1, 6.8, 16 H, *aromat-H*). ^{13}C NMR ($CDCl_3$): δ −2.0 (*Me*), 40.9 (*allyl-C*), 119.6, 124.2, 124.4, 125.6, 127.9, 129.8, 130.1, 135.1 (*aromat-C*), 139.8, 144.1 (*vinyl-C*). ^{29}Si NMR ($CDCl_3$): δ 4.74 (−SiMe$_3$), −12.37 (−SiPh$_3$), −78.21(−SiO$_3$). IR (KBr): 514 (s), 697 (m), 712 (m), 739 (w), 836 (sh), 855 (sh), 917 (vs), 998 (w), 1028 (w), 1119 (w), 1171 (vs), 1187 (w), 1262 (s), 1428 (s), 2924 (m), 2961 (m), 3023 (w), 3067 (m). Anal. Calcd for $C_{136}H_{128}Si_{12}O_{16}Ti_4$ (2547.09): C, 63.44; H, 5.16. Found: C, 63.48; H, 5.46.

$[Me_3SiFlSi]_4O_{12}[TiONMe_2]_4$ (8). At 0 °C 38 μL (0.55 mmol) of Me_2NOH was added dropwise over 10 min to a solution of 0.24 g (0.14 mmol) of **3** in 20 mL of hexane under vigorous stirring. The mixture was stirred at room temperature for a further 3 days. After removal of volatile compounds in vacuo a colorless solid was obtained. Single crystals suitable for an X-ray crystal structure determination were grown from a CH_2Cl_2/hexane mixture (0.22 g, 0.13 mmol, 93%), mp <250 °C. ^{1}H NMR ($CDCl_3$): δ −0.25 (s, 36H, *Me*), 2.37 (s, 24H, *Me*), 7.22, 7.31 (2t, $^3J_{H-H}$ = 7.2, 8H, *aromat-H*), 7.65, 7.80 (2d, $^3J_{H-H}$ = 7.7, 7.6, 8H, *aromat-H*). ^{13}C NMR ($CDCl_3$): δ −1.8 (*Me*), 42.84 (*allyl-C*), 49.2 (Me), 119.0, 124.0, 125.4, 125.7 (*aromat-C*), 140.0, 146.5 (*vinyl-C*). ^{29}Si NMR ($CDCl_3$): δ 5.0 (−SiMe$_3$), −77.3 (−SiO$_3$). IR (KBr): 539 (w), 598 (w), 654 (s), 689 (w), 722 (sh), 739 (s), 838 (s), 889 (s), 962 (vs), 1048 (vs), 1172 (sh), 1248 (s), 1308 (w), 1434 (s), 1608 (m), 2928 (m), 2956 (m), 3060 (m). Anal. Calcd for $C_{72}H_{92}N_4O_{16}Si_8Ti_4$ (1685.76): C, 51.31; H, 5.51; N, 3.32. Found: C, 51.13; H, 5.51; N, 3.24.

$[Cp^*Si]_4O_{12}[TiONMe_2]_4$ (9). At −78 °C 0.04 g (0.66 mmol) of Me_2NOH in 10 mL of THF was added dropwise over 10 min to a solution of 0.22 g (0.17 mmol) of **5** in 10 mL of THF. The colorless solution was allowed to warm to room temperature and was stirred for 15 h. After removal of volatile compounds in vacuo a colorless solid was obtained. Single crystals suitable for an X-ray crystal structure determination were grown from a concentrated solution in ether (0.21 g, 0.16 mmol, 98%), mp > 250 °C. ^{1}H NMR ($CDCl_3$): δ 1.15 (s, 12H, *Cp*-Me*), 1.73, 1.89 (2s, 24H, *Cp*-Me*), 2.88 (s, 24H, ON*Me*$_2$). ^{13}C NMR ($CDCl_3$): δ 11.4, 12.0, 15.5 (Cp*-*Me*), 49.8 (ON*Me*$_2$), 51.4 (*allyl-C*), 134.1, 138.2 (*vinyl-C*). ^{29}Si NMR ($CDCl_3$): δ −73.9. IR (KBr): 443 (m), 456 (m), 658 (m), 798 (m), 956 (vs), 1038 (vs), 1262 (m), 1448 (m), 2862 (m), 2921 (m), 2964 (m). MS (ESI, in

THF) m/z (I_{rel}): 1315 (100) [$(M + K)^+$], 1300 (76) [$(M + Na)^+$]. Anal. Calcd for $C_{48}H_{84}N_4O_{16}Si_4Ti_4$ (1277.07): C, 45.14; H, 6.63. Found: C, 43.68; H, 6.75 (due to the formation of SiC, the carbon content is low).

[Cp*Si]$_4$O$_{12}$[Tiacac]$_4$ (10). At 0 °C 0.11 g (1.08 mmol) of acetylacetone was added dropwise over 10 min to a solution of 0.36 g (0.27 mmol) of **5** in 40 mL of ether under vigorous stirring. A yellow solution was formed. The mixture was stirred for a further 16 h. After removal of volatile compounds in vacuo a colorless solid was obtained. Single crystals of [**10**·4dioxane] suitable for an X-ray crystal structure determination were grown from an ether/dioxane mixture (0.45 g, 0.25 mmol, 93%), mp <250 °C. ^{1}H NMR (CDCl$_3$): δ 1.03 (s, 12H, *Me*), 1.87, 1.94, 1.96 (3s, 72H, *Me*), 3.67−3.70 (b, 8H, *dioxane*) 5.57 (s, 4H, *acac*). ^{13}C NMR (CDCl$_3$): δ 11.1, 11.5, 14.5 (*Me*), 24.6, 25.0 (*acac*), 51.4 (*allyl-C*), 68.3 (*dioxane*), 103.9 (*acac*), 132.2, 139.7 (*vinyl-C*), 190.2, 191.9 (*acac*). ^{29}Si NMR (CDCl$_3$): δ −80.43. IR (KBr): 430 (s), 530 (m), 657 (m), 665 (m), 875 (sh), 975 (vs), 1057 (sh), 1281 (m), 1365 (s), 1439 (m), 1526 (s), 1596 (s), 2857 (s), 2918 (s). Anal. Calcd for $C_{60}H_{88}O_{20}Si_4Ti_4$ (1433.21): C, 50.28; H, 6.19. Found: C, 53.25; H, 6.35 (elemental analyses not successful due to tenacious retainment of fractional amounts of solvent).

[Me$_3$SiFlSi]$_4$O$_{12}$[TiO^{i}Pr]$_2$[Tiacac]$_4$[μ_2-^{i}PrO]$_2$[μ_3-O]$_2$ (11). At 0 °C 145 μL (1.41 mmol) of acetylacetone was added dropwise over 10 min to a solution of 0.50 g (0.24 mmol) of **6** in 30 mL of hexane under vigorous stirring. The mixture was stirred for a further 16 h. After removal of volatile compounds a colorless solid was obtained. Single crystals suitable for an X-ray crystal structure determination were grown at −30 °C from a concentrated solution in ether (0.45 g, 0.20 mmol, 83%), mp <250 °C. ^{1}H NMR (CDCl$_3$): δ −0.45 to −0.13 (m, 36H, *Me*), 0.90, 0.87, 0.83, 0.69 (d, $^3J_{H-H} = 3.8$, 12H, CH(C*H*$_3$)$_2$), 1.77−2.30 (m, 24 H, Me), 3.82 (m, 4H, C*H*(CH$_3$)$_2$), 7.13−7.24, (m, 16H, *aromat-H*), 7.65−7.90 (m, 16H, *aromat-H*). ^{13}C NMR (CDCl$_3$): δ −2.2 (b, Si*Me*$_3$), 25.2, 25.7, 26.1(CH(*C*H$_3$)$_2$), 43.0 (*allyl-C*), 65.9 (*C*H(CH$_3$)$_2$, 118.7, 123.3, 124.9, 125.8 (*aromat-C*), 139.9, 147.3 (*vinyl-C*), 190.4 (*acac*). ^{29}Si NMR (CDCl$_3$): δ 5.01, 4.73, 4.06, −61.87, −65.72. IR (KBr): 447 (m), 499 (w), 689 (w), 541 (w), 663 (m), 739 (m), 800 (s), 948 (m), 1021 (vs), 1102 (sh), 1172 (sh), 1262 (s), 1360 (s), 1433 (m), 1526 (s), 1594 (s), 2963 (m). Anal. Calcd for $C_{96}H_{124}Si_8O_{26}Ti_6$ (2206.00): C, 52.27; H, 5.67. Found: C, 49.91; H, 5.67 (due to the formation of SiC, the carbon content is low).

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Supporting Information Available: Tables of structure crystal data, positional and thermal parameters, and selected bond lengths and angles of **3**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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