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Synthesis of Novel Titanasiloxanes with Ring and Cage Structures Using Sterically Demanding Substituents

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Novel oligomeric titanasiloxanes have been synthesized in good yields by reaction of sterically demanding organosilanetriols with titanium alkoxides. The silanetriols $\mathrm{^tBu_2(Me_3Si)FlSi(OH)_3}$ (**5**), $\mathrm{(Me_3Si)FlSi(OH)_3}$ (**6**), and $\mathrm{MeFlSi(OH)_3}$ (**7**) and the titanium alkoxides $\mathrm{Ti(OEt)_4}$, $\mathrm{Ti(O^iPr)_4}$, and $\mathrm{Ti(O^iPr)_2(acac)_2}$ have been used as starting materials (Fl = fluorenyl). Quite different structures are obtained by only small modifications of the organic substituents of the substrates. Thus, the condensation reactions result in the formation of the polyhedral titanasiloxanes $\mathrm{[^tBu_2(Me_3Si)FlSi]_4O_{12}[TiOEt]_4}$ (**8**), $\mathrm{[(Me_3Si)FlSi]_2O_5[Ti(OEt)]_4[\mu_2\text{-}OEt]_6[\mu_4\text{-}O]}$ (**9**), $\mathrm{([^tBu_2(Me_3Si)FlSi]_3O_{10}[Ti(O^iPr)]_4[\mu_2\text{-}O^iPr]_2[\mu_3\text{-}O]Ti)_2O}$ (**10**), and $\mathrm{[MeFlSi]_2O_8[Ti(O^iPr)]_6[\mu_2\text{-}O^iPr]_4[\mu_3\text{-}O]_2[PhNH_2]_2}$ (**11**) and the cyclic titanasiloxane $\mathrm{[MeFlSi(O^iPr)]_2O_4[Ti(acac)_2]_2}$ (**12**). A 1:1 stoichiometry of the starting materials leads to **8** and **12** in quantitative yield, while **9**−**11** are isolated in minor quantities. If the appropriate substrate ratio is used, the latter compounds can also be obtained in high yields. All titanasiloxanes have been characterized by X-ray crystallography, NMR, IR, and elemental analysis.

Introduction

In recent years there has been considerable activity in the field of titanasiloxane chemistry. In view of the impressive catalytic use of $\mathrm{TiO_2/SiO_2}$ materials it is of interest to synthesize molecular model compounds, to gain a better insight into the formation of such materials and into the mechanisms involved in the catalytic processes.[1] Cyclic and spirocyclic titanasiloxanes are readily accessible by condensation of silanediols or their dilithium salts with titanium chlorides.[2] Polyhedral titanasiloxanes can be obtained by condensation of silanetriols with titanium alkoxides or chlorides.[2a,3]

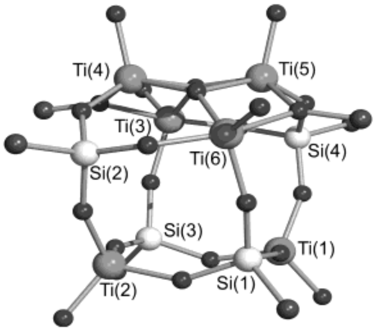

Figure 1. Ball-and-stick model of titanasiloxane **4**; the organic substituents are reduced to their ipso-carbon atoms.

We recently reported the synthesis of the cubic titanasiloxanes $\mathrm{[(Me_3Si)FlSi]_4O_{12}[TiO^tBu]_4}$ (**1**), $\mathrm{[Cp^*Si]_4O_{12}[TiO^tBu]_4}$ (**2**), and $\mathrm{[(Me_3Si)FlSi]_4O_{12}[TiO^iPr]_4}$ (**3**) and the polyhedral titanasiloxane $\mathrm{[(Me_3Si)FlSi]_4O_{12}[TiO^iPr]_6[\mu_2\text{-}O^iPr]_2[\mu_3\text{-}O]_2}$ (**4**).[4] The "roof-capped" structure of **4** is shown in Figure 1; the organic substituents are reduced to their ipso-carbon atoms for clarity.

The steric demand of the substituents in the employed starting materials and the reaction conditions have shown to be responsible for the observed structural variety. Thus, the product formation is strongly kinetically controlled. Furthermore, several substitution reactions have been reported, which proceed under preservation of the respective core structure. These results

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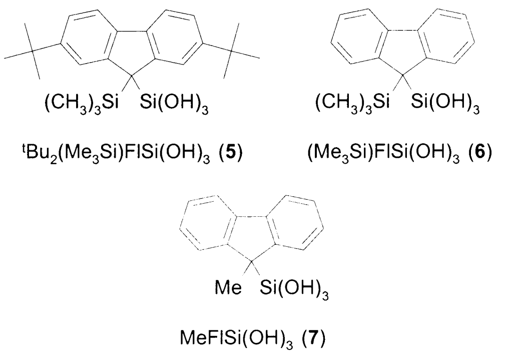
Scheme 1. Silanetriols Used for the Synthesis of Titanasiloxanes



$^tBu_2(Me_3Si)FlSi(OH)_3$ (**5**)

$(Me_3Si)FlSi(OH)_3$ (**6**)

$MeFlSi(OH)_3$ (**7**)

have prompted us to extend the investigation of co-condensation reactions of silanetriols and titanium alkoxides. We are particularly interested in investigating the influence of kinetic control on product formation by varying the steric demand of the reactants. In view of these requirements, fluorenyl groups seem to be ideal substituents for the silanetriol starting compounds. Modifications are possible in different positions of the fluorenyl substituents, so that the steric demand and the solubility can be varied. Different alkoxy groups are used as substituents for the titanium substrates. Here we report the high yield synthesis of titanasiloxanes with quite different and novel framework structures.

Results and Discussion

The silanetriols **5**−**7**, possessing differently substituted fluorenyl groups (see Scheme 1), and the titanium alkoxy compounds $Ti(OEt)_4$, $Ti(O^iPr)_4$, and $Ti(O^iPr)_2(acac)_2$ serve as starting materials in co-condensation reactions. The bulky (2,7-di-*tert*-butyl-9-(trimethylsilyl)fluorenyl)silanetriol, $^tBu_2(Me_3Si)FlSi(OH)_3$ (**5**), was synthesized in good yields by controlled hydrolysis of (2,7-di-*tert*-butyl-9-(trimethylsilyl)fluorenyl)trichlorosilane, $^tBu_2(Me_3Si)FlSiCl_3$, which was synthesized by the reaction of lithiated 2,7-di-*tert*-butyl-9-(trimethylsilyl)fluorene, $^tBu_2(Me_3Si)FlLi$, with $SiCl_4$ (see Experimental Section). The silanetriols (9-(trimethylsilyl)fluorenyl)silanetriol, $(Me_3Si)FlSi(OH)_3$ (**6**), and (9-methylfluorenyl)silanetriol, $MeFlSi(OH)_3$ (**7**), are known in the literature[5] and can be prepared in the same manner.

Synthesis and Structure of $[^tBu_2(Me_3Si)FlSi]_4O_{12}[TiOEt]_4$ (8). Reaction of $^tBu_2(Me_3Si)FlSi(OH)_3$ (**5**) with equimolar amounts of $Ti(OEt)_4$ in hexane at room temperature afforded the expected titanasilsesquioxane **8** (eq 1) in nearly quantitative yield.

$$4\ {}^tBu_2(Me_3Si)FlSi(OH)_3(\mathbf{5}) \xrightarrow{\text{hexane}} + 4\ Ti(OEt)_4 \quad [{}^tBu_2(Me_3Si)FlSi]_4O_{12}[TiOEt]_4\ (\mathbf{8}) + 12\ EtOH \qquad (1)$$

Compound **8** was obtained as a colorless solid, which is highly soluble in polar and nonpolar solvents. The identity of **8** was confirmed by multinuclear NMR spectroscopy and by X-ray crystallography. Suitable crystals were grown from a concentrated solution in hexane. The compound crystallizes in the monoclinic space group $P2_1/n$. The cubic core unit of the molecule is formed by four silicon and four titanium atoms, which occupy the corners in an alternating manner. The silicon atoms bear substituted fluorenyl groups, while the titanium atoms bear ethoxy groups as exocyclic substituents. All 12 Ti−Si edges of the cube are bridged by oxygen atoms in a μ_2 fashion. The six cube faces are composed of crown-like $Si_2Ti_2O_4$ rings. The structure of the molecule is dominated by a perfect wrapping with organic substituents. In Figure 2 the core structure of **8** is shown in the form of a ball-and-stick model; the organic substituents at silicon and titanium are represented only by their ipso-carbon atoms. Selected bond lengths and bond angles are given in Table 1.

A closer look at the framework of **8** reveals a rather strong distortion from the cubic geometry, compared with the deviation in other titanasilsesquioxanes.[3c−f,4] This distortion is found in the solid state and also in solution and can be explained by the high steric demand of the 2,7-di-*tert*-butyl-9-(trimethylsilyl)fluorenyl groups. In the solid state, the titanium and silicon atoms adopt distorted tetrahedral geometries with bond angles that differ significantly from 109.5° (see Table 1). The distortion of the cubic core is also indicated by a broad range of the Si−O−Ti bond angles and bond lengths. In the IR spectrum (measured as KBr pellet), the characteristic Ti−O−Si vibrations show a broad band at 977 cm^{-1}, with two shoulders at 1019 and 924 cm^{-1}. In solution, the cage distortion is documented by the NMR spectroscopic data. ^1H NMR and ^{13}C NMR spectra show several signals for the ethoxy and for the fluorenyl substituents (see Experimental Section). The ^{29}Si NMR spectrum displays several resonances for the silicon cage atoms, while the signals for the silicon atoms of the fluorenyl units cannot be resolved.

Synthesis and Structure of $[(Me_3Si)FlSi]_2O_5[Ti(OEt)]_4[\mu_2\text{-}OEt]_6[\mu_4\text{-}O]$ (9). Reaction of equimolar amounts of $(Me_3Si)FlSi(OH)_3$ (**6**) and $Ti(OEt)_4$ in hexane led to a mixture of products. The titanasiloxane **9** could be isolated in rather low yield by crystallization. It is important to note that the reaction in the appropriate stoichiometry (1 equiv of **6** and 2 equiv of $Ti(OEt)_4$) led in high yield exclusively to compound **9** (eq 2).

$$2\ (Me_3Si)FlSi(OH)_3\ (\mathbf{6}) \xrightarrow{\text{hexane}} + 4\ Ti(OEt)_4 \quad [(Me_3Si)FlSi]_2O_5[Ti(OEt)]_4[\mu_2\text{-}OEt]_6[\mu_4\text{-}O]\ (\mathbf{9}) + 6\ EtOH \qquad (2)$$

Compound **9** was obtained as a colorless solid, which is highly soluble in polar and nonpolar solvents. The identity of **9** was confirmed by multinuclear NMR spectroscopy and by X-ray crystallography. Suitable crystals were obtained from a concentrated solution in hexane. The compound crystallizes in the monoclinic space group $P2_1/c$. Compound **9** can be described as consisting of a rather symmetrical framework of two silicon and four titanium atoms, which is completely wrapped by organic groups, i.e., by fluorenyl substituents at silicon and by ethoxy substituents at titanium. The structure of **9** is represented by a ball-and-stick model in Figure 2; for clarity, the organic groups are represented only by their ipso-carbon atoms. Selected bond lengths and bond angles are given in Table 2.

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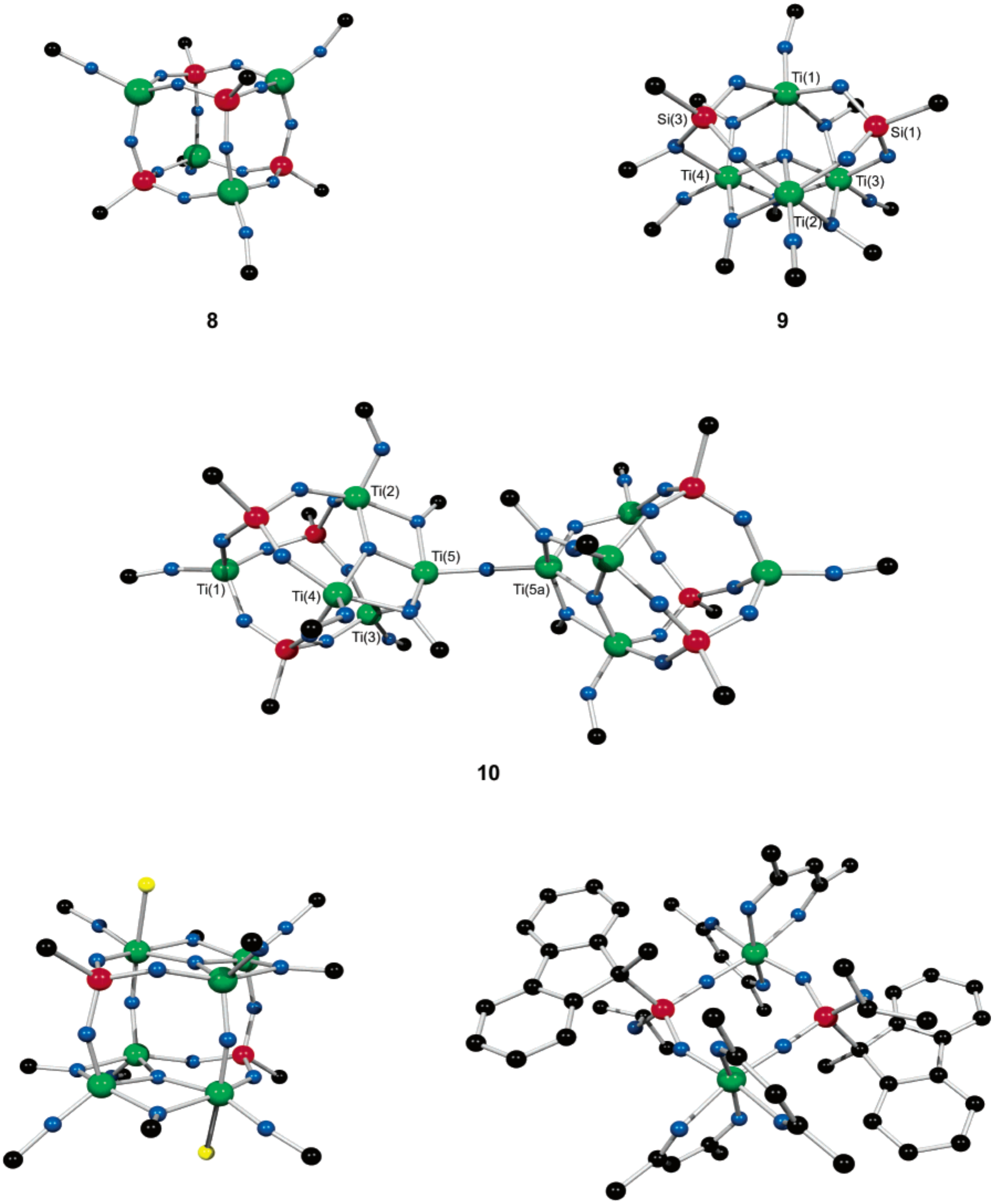

8 **9**

10

11 **12**

Figure 2. Ball-and-stick models of the titanasiloxanes **8**−**12** [Si (red), Ti (green), O (blue), N (yellow), C (black)]; the organic substituents of **8**−**11** are reduced to their ipso-carbon atoms.

Table 1. Selected Bond Lengths [Å] and Bond Angles [deg] of 8

d(Si−O)	1.615(6)−1.644(6)
∠(O−Si−O)/∠(O−Si−C)	107.0(3)−113.3(3)
d(Ti−O_{Si})	1.775(6)−1.820(5)
∠(O−Ti−O)	104.6(3)−114.1(3)
∠(Si−O−Ti)	141.9(4)−158.8(4)

The composition of **9** can be described as follows: (1) The central unit is built by a distorted tetrahedron of four titanium atoms, which are linked by a μ_4-oxygen atom; (2) those two faces of the Ti_4 tetrahedron, which are linked at the Ti(1)−Ti(2) edge, are capped by silicon atoms; (3) five of the six edges of the Ti_4 tetrahedron (except Ti(1)−Ti(2)) are bridged by μ_2-ethoxy groups; (4) Si(1) atom is connected with three titanium atoms by μ_2-oxygen units, whereas the Si(3) atom is connected with two titanium atoms by μ_2-oxygen atoms and with a third titanium atom by a μ_2-ethoxy group. The last interaction destroys the symmetric arrangement of the framework in **9** (Ti(1)−O−Ti(2) mirror plane). The Ti(1)−O−Ti(2) angle of 134° leads to a significant distortion of the central OTi_4 unit (see Table 2). As a consequence, the silicon-capped Ti_3 faces deviate from an ideal symmetric arrangement (equilateral triangles). The geometry at all titanium atoms is distorted octahedral, and that at the silicon atoms is distorted

Table 2. Selected Bond Lengths [Å] and Bond Angles [deg] of 9

d(Si−O)	1.608(4)−1.636(4)
∠(O−Si−O)/∠(O−Si−C)	103.2(2)−115.2(2)
∠(Si−O−Ti)	119.1(2)−129.4(2)
d(Ti−O$_{Si}$)	1.764(4)−1.888(4)
∠(O−Ti−O)	α,β:[a] 72.3(1)−107.1(2) γ:[a] 150.0(2)−175.8(2)
μ_2-OEt-fragment (Si−O$_{Et}$−Ti)	
d(Si−O)	1.695(4)
d(Ti−O)	2.226(4)
∠(Si−O$_{Et}$−Ti)	112.4(2)
μ_2-OEt-fragment (Ti−O$_{Et}$−Ti)	
d(Ti−O)	1.923(4)−2.162(4)
∠(Ti−O$_{Et}$−Ti)	103.1(2)−104.3(2)
μ_4-O-fragment	
d(Ti−O)	1.997(3)−2.075(3)
∠(Ti−O−Ti)	102.1(1)−105.3(2),
∠(Ti(1)−O−Ti(2))	134.1(2)

[a] See ref 6.

Table 3. Selected Bond Lengths [Å] and Bond Angles [deg] of 10

d(Si−O)	1.617(4)−1.637(4)
∠(O−Si−O)/∠(O−Si−C)	107.8(2)−112.8(2)
d(Ti−O$_{Si}$)	1.790(4)−1.849(4)
∠(O−Ti$_{tetrahedral}$−O)	106.4(2)−113.9(2)
∠(O−Ti$_{tri. bipyramidal}$−O)	α:[a] 71.9(2)−101.4(2) β:[a] 110.4(2)−135.3(2) γ:[a] 149.8(2)−162.7(2)
∠(Si−O−Ti)	136.8(2)−155.3(3)
μ_2-OiPr-fragment (Ti−O^{i}Pr−Ti)	
d(Ti−O)	1.943(4)−2.070(4)
∠(Ti−O^{i}Pr−Ti)	103.0(2)−103.3(2)
μ_3-O-fragment	
d(Ti−O)	1.943(4)−1.969(4)
∠(Ti−O−Ti)	106.7(2), 107.2(2), 145.4(2)
μ_2-O-bridge	
d(Ti−O)	1.81(1)
∠(Ti−O−Ti)	171.8(3)

[a] See ref 6.

tetrahedral. It is worth mentioning that the observed coordination of a silicon-bound alkoxy group to a titanium center (Si−(μ_2-OR)−Ti) is unique in titanasiloxane chemistry. The NMR data of **9** are in accord with the asymmetric structure. Thus, the ^{1}H NMR spectrum shows several signals for the alkoxy and also for the fluorenyl groups. The ^{29}Si NMR spectrum displays two signals for the framework silicon atoms and also for the trimethylsilyl groups of the fluorenyl substituents.

Synthesis and Structure of ([^{t}Bu$_2$(Me$_3$Si)FlSi]$_3$O$_{10}$-[Ti(O^{i}Pr)]$_4$[μ_2-O^{i}Pr]$_2$[μ_3-O]Ti)$_2$O (10). The reaction of ^{t}Bu$_2$(Me$_3$Si)FlSi(OH)$_3$ (**5**) and Ti(O^{i}Pr)$_4$ in a 1:1 stoichiometry led to a mixture of products. The titanasiloxane **10** could be isolated from this mixture in rather low yield by crystallization. The yield of **10** could be remarkably increased, when the appropriate stoichiometry of silanetriol **5**, titanium alkoxide, and water was used (eq 3).

$$\begin{aligned}&6\ {}^t\mathrm{Bu_2(Me_3Si)FlSi(OH)_3}\ (\mathbf{5})\\ &+ 10\ \mathrm{Ti(OEt)_4} + 5\ \mathrm{H_2O}\ \xrightarrow{\text{hexane}}\\ &[{}^t\mathrm{Bu_2(Me_3Si)FlSi]_3O_{10}[TiO^iPr)_4}[\mu_2\text{-}\mathrm{O^iPr}]_4\\ &[\mu_2\text{-}\mathrm{O^iPr}]_2[\mu_3\text{-}\mathrm{O}]\mathrm{Ti_2O}\ (\mathbf{10})\\ &+ 28\ {}^i\mathrm{PrOH}\end{aligned} \quad (3)$$

Compound **10** was obtained as a colorless solid, which is highly soluble in polar and nonpolar solvents. The identity of **10** was confirmed by multinuclear NMR spectroscopy and by X-ray crystallography. Crystals of **10** were obtained from a concentrated hexane solution at low temperature (−45 °C). Compound **10** crystallizes in the monoclinic space group *C*2/*c*. The molecule consists of two identical cage units, which are bridged by an oxygen atom in a μ_2 fashion, and it is completely enclosed by the organic moiety. The structure of the titanasiloxane core unit is shown in Figure 2, and selected bond lengths and bond angles are given in Table 3.

The cage units can be described on the basis of distorted titanasiloxane cubes possessing three silicon and five titanium atoms in corner positions. Two of the titanium atoms are four coordinated and three are five coordinated, while all silicon atoms are four coordinated. All silicon atoms are bound to substituted fluorenyl groups, while all titanium atoms, except the two cage bridging atoms, bear isopropoxy groups. Compared to the cubic titanasilsesquioxane **8**, one silicon atom of the cage is replaced by a titanium atom (Ti(5), see Figure 2). As a consequence, Ti(5) is connected to three titanium atoms by oxygen bridges. In detail, Ti(5) is linked with Ti(2) and Ti(4) by a μ_3-oxygen atom and by μ_2-isopropoxy bridges and with Ti(3) by a μ_2-oxygen bridge. In addition Ti(5) is μ_2-oxygen bridged to Ti(5a), the corresponding titanium atom of the second cube, with a Ti(5)−O−Ti(5a) angle of almost 180°. The sum of all bond angles at the μ_3-oxygen unit is close to 360°, which shows that the oxygen atom is placed almost in plane with the three titanium neighbors. The Ti−O and Si−O bond lengths are all in a typical range, comparable to those found in the compounds **8** and **9**. All three μ_3-oxygen-linked titanium atoms adopt a distorted trigonal bipyramidal geometry. The remarkable deviation from the ideal geometric shape is evident from the data given in Table 3. The remaining titanium atoms and all silicon atoms are distorted tetrahedrally coordinated, comparable to the bonding situation in **8**. The NMR data of **10** show two sets of signals for the isopropoxy groups, which can be assigned to the terminal and to the μ_2-bound substituents. The ^{29}Si NMR shows two resonances for the three framework silicon atoms; the signals for silicon atoms of the different fluorenyl groups cannot be resolved.

Synthesis and Structure of [MeFlSi]$_2$O$_8$-[Ti(O^{i}Pr)]$_6$[μ_2-O^{i}Pr]$_4$[μ_3-O]$_2$[PhNH$_2$]$_2$ (11). The reaction of MeFlSi(OH)$_3$ (**7**) and Ti(O^{i}Pr)$_4$ in a 1:1 stoichiometry and small amounts of aniline[7] led to a mixture of products. The titanasiloxane **11** was isolated in rather low yield by crystallization. The yield of **11** could be remarkably increased, when the appropriate stoichiometry of silanetriol **7**, titanium alkoxide, water, and aniline was used (eq 4).

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(6) Expected angles for an ideal polygon (octahedron: α, β = 90°, γ = 180°; trigonal bipyramid: α = 90°, β = 120°, γ = 180°; square pyramid: α, β = 90°, γ = 180°).

(7) Small amounts of aniline have remained from the synthesis of **7**.

$$2\ \mathrm{MeFlSi(OH)_3}\ (\mathbf{7}) + 6\ \mathrm{Ti(O^iPr)_4} + 2\ \mathrm{PhNH_2} + 4\ \mathrm{H_2O} \xrightarrow{\text{Hexane}} [(\mathrm{MeFlSi})_2\mathrm{O_8}[\mathrm{Ti(O^iPr)}]_6[\mu_2\text{-}\mathrm{O^iPr}]_4[\mu_3\text{-O}]_2[\mathrm{PhNH_2}]_2\ (\mathbf{11}) + 14\ {}^{i}\mathrm{PrOH} \quad (4)$$

Compound **11** was obtained as a colorless solid, which is highly soluble in polar and nonpolar solvents. The identity of **11** was confirmed by multinuclear NMR spectroscopy and by X-ray crystallography. Single crystals were obtained from a concentrated hexane solution at low temperature (−30 °C). Compound **11** crystallizes in the monoclinic space group $P2_1/n$. The structure of **11** can be described on the basis of a cubic core unit, possessing two silicon and six titanium atoms in corner positions. Aniline molecules and isopropoxy groups are bound to the titanium atoms, and 9-methylfluorenyl substituents are bound to the silicon atoms. The molecule is completely enclosed by the organic moiety. The core unit of the titanasiloxane is shown in Figure 2, and selected bond lengths and bond angles are given in Table 4.

The cubic core unit shows the two silicon atoms and the aniline-coordinated titanium atoms in diagonal positions. Four titanium atoms are five coordinated and two titanium atoms are six coordinated, while all silicon atoms are four coordinated. All faces of the cube possess one silicon and three titanium atoms in corner positions; two faces contain μ_3-oxygen- and μ_2-isopropoxy-linked titanium atoms. This kind of bonding pattern is also found in two faces of the cubes of compound **10**. The core structure of **11** is centrosymmetric. In contrast to all other titanasiloxanes described so far, two aniline molecules act as additional donors and allow the corresponding titanium atoms to adopt a distorted octahedral geometry. The Ti−N bond length is in the typical range for this kind of coordinative interaction.[8] The remaining four titanium corners of the cube show distorted square pyramidal symmetry. All silicon atoms are tetrahedrally coordinated. The NMR data of **11** are in accord with the solid state structure. Thus, signals for two equivalent fluorenyl groups and for five different alkoxy groups are observed.

Synthesis and Structure of [MeFlSi(O^{i}Pr)]$_2$O$_4$-[Ti(acac)$_2$]$_2$ (12). The reaction of MeFlSi(OH)$_3$ (**7**) and Ti(O^{i}Pr)$_2$(acac)$_2$ in a 1:1 stoichiometry led to the cyclic titanasiloxane **12** in good yields (eq 5).

$$2\ \mathrm{MeFlSi(OH)_3}\ (\mathbf{7}) + 2\ \mathrm{Ti(O^iPr)_2(acac)_2} \xrightarrow{\text{hexane}} [\mathrm{MeFlSi(O^iPr)}]_2\mathrm{O_4}[\mathrm{Ti(acac)_2}]_2\ (\mathbf{12}) + 2\ {}^{i}\mathrm{PrOH} + 2\mathrm{H_2O} \quad (5)$$

Table 4. Selected Bond Lengths [Å] and Bond Angles [deg] of 11

d(Si−O)	1.614(2)−1.641(2)
∠(O−Si−O)/∠(O−Si−C)	106.94(1)−111.82(1)
d(Ti−O$_{\mathrm{Si}}$)	1.767(2)−1.868(2)
d(Ti−N)	2.380(3)
∠(O−Ti$_{\mathrm{sq.pyramidal}}$−O)	α,[a] β:[a] 72.83(8)−113.0(1)
	γ:[a] 133.6(1), 156.32(9)
∠(O−Ti$_{\mathrm{octahedral}}$-O)/	α, β:[a] 71.92(7)−100.2(1)
∠(O−Ti$_{\mathrm{octahedral}}$−N)	γ:[a] 159.1(1)−173.5(1)
μ_2-OiPr-fragment (Ti−O^{i}Pr−Ti)	
d(Ti−O)	1.956(2)−2.078(2)
∠(Ti−O^{i}Pr−Ti)	102.09(8), 103.10(8)
μ_3-O-fragment	
d(Ti−O)	1.923(2)−2.030(2)
∠(Ti−O−Ti)	108.22(9), 107.13(8), 144.4(1)

[a] See ref 6.

Table 5. Selected Bond Lengths [Å] and Bond Angles [deg] of 12

d(Si−O)	1.621(3)−1.628(3)
∠(O−Si−O)/∠(O−Si−C)	108.2(2)−111.3(2)
d(Ti−O$_{\mathrm{Si}}$)	1.806(3), 1.816(3)
d(Ti−O$_{\mathrm{acac}}$)	1.965(3), 1.975(3)
	2.066(3), 2.073(3)
∠(O−Ti$_{\mathrm{octahedral}}$-O)	α, β:[a] 80.3(1)−100.1(1)
	γ:[a] 166.7(1)−169.5(1)
∠(Si−O−Ti)	150.7(2), 177.5(2)

[a] See ref 6.

Compound **12** was obtained as a colorless solid, which is highly soluble in polar and nonpolar solvents. The identity of **12** was confirmed by multinuclear NMR spectroscopy and by X-ray crystallography. Single crystals were grown from a concentrated solution in dichloromethane. Titanasiloxane **12** crystallizes in the triclinic space group $P\bar{1}$. Its structure is shown in Figure 2, and selected bond lengths and bond angles are given in Table 5.

The centrosymmetric structure of **12** can be described as an eight-membered Si$_2$O$_4$Ti$_2$ ring. The silicon atoms are tetrahedrally coordinated by two μ_2-oxygen atoms belonging to the ring, one isopropoxy group, and one fluorenyl group. Each of the two titanium atoms is distorted octahedrally coordinated by two μ_2-oxygen atoms belonging to the ring and by four oxygen atoms belonging to the two acetylacetonato substituents. Due to the steric requirements of an octahedral environment of the titanium atoms, two rather large Si−O−Ti angles in the range of 180° are observed in the Si$_2$O$_4$Ti$_2$ unit. The remaining two Si−O−Ti angles (151°) are comparable with those observed in the Si$_2$O$_4$Ti$_2$ ring units of **8**. The Ti−O$_{\mathrm{Si}}$ bond lengths are in the same range as found for all other titanasiloxanes discussed here. Concerning the Ti−O$_{\mathrm{acac}}$ bond lengths it has to be mentioned that those two bonds, which are located trans to the Ti−O$_{\mathrm{Si}}$ bonds, are significantly longer than the remaining two Ti−O$_{\mathrm{acac}}$ bonds. The NMR data can be assigned in accord with the described solid state structure of **12**.

Conclusions

In this work and in a recent publication[4] we have shown that substituent variations in the system Ti(OR)$_4$/R′Si(OH)$_3$ allow the isolation of oligomeric titanasiloxanes with quite different framework structures. More or less bulky cyclopentadienyl groups (R′ = Cp$^{\mathrm{R}}$) at silicon and alkoxy and acetylacetonato groups OR at titanium (see Scheme 1) have been chosen to modify the steric requirements. With a given substrate ratio of 1:1,

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(8) Duan, Z.; Naiini, A. A.; Lee, J.-H.; Verkade, J. G. *Inorg. Chem.* **1995**, *34*, 5477.

the expected compounds with a cubic core structure $[R'Si]_4O_{12}[TiOR]_4$ possessing terminal R′ and OR and bridging $Si-(\mu_2O)-Ti$ units have been isolated in high yields only in a few cases (compounds $[(Me_3Si)FlSi]_4O_{12}[TiO^tBu]_4$ (**1**), $[Cp^*Si]_4O_{12}[TiO^tBu]_4$ (**2**), $[(Me_3Si)FlSi]_4O_{12}[TiO^iPr]_4$ (**3**),[4] and $[^tBu_2(Me_3Si)FlSi]_4O_{12}[TiOEt]_4$ (**8**)). Quite often a mixture of products has been obtained, from which only the crystalline species, which were formed in rather low yield, could be unambiguously characterized (compounds $[(Me_3Si)FlSi]_4O_{12}[TiO^iPr]_6[\mu_2\text{-}O^iPr]_2[\mu_3\text{-}O]_2$ (**4**),[4] $[(Me_3Si)FlSi]_2O_5[Ti(OEt)]_4[\mu_2\text{-}OEt]_6[\mu_4\text{-}O]$ (**9**), $([^tBu_2(Me_3Si)FlSi]_3O_{10}[Ti(O^iPr)]_4[\mu_2\text{-}O^iPr]_2[\mu_3\text{-}O]Ti)_2O$ (**10**), and $[MeFlSi]_2O_8[Ti(O^iPr)]_6[\mu_2\text{-}O^iPr]_4[\mu_3\text{-}O]_2[PhNH_2]_2$ (**11**)). Those compounds were obtained in nearly quantitative yield, when the appropriate substrate ratio was used (including the addition of further substrates such as water or aniline). The more complex polyhedral structures of **4** and **9**−**11** show, in addition to the structural features of the cubic core compounds, $(\mu_3\text{-}O)-Ti_3$, $(\mu_4\text{-}O)-Ti_4$, $Ti-(\mu_2\text{-}OR)-Ti$, and $Si-(\mu_2\text{-}OR)-Ti$ units. Silicon atoms always are four coordinated, whereas titanium atoms show coordination numbers from four to six. The presence of Ti−O−Ti units indicates competing Ti−OH condensation reactions; Ti−OH species are built from the hydrolysis of Ti−OR units; the necessary water molecules arise from silanol condensation reactions and from the reaction of silanol groups with liberated alcohol molecules. Another high-yield product from a 1:1 substrate ratio is the eight-membered ring system **12**, containing six-coordinated Ti centers; the acetylacetonato substituents are not involved in exchange reactions and thus prevent the formation of a polyhedral structure. Earlier experiments[4] with the system $Ti(OR)_4/R'Si(OH)_3$ have shown that the product formation depends also on solvent and reaction temperature. From all these results it can be concluded that further variations of substrates and reaction conditions will lead to novel types of titanasiloxanes. The system $Ti(OR)_4/R'Si(OH)_3$ seems to be best suited to perform reactions under kinetic control. The investigation of parameters that influence the formation of titanasiloxanes is important for a better understanding of hydrolysis and condensation reactions during sol/gel processing of TiO_2/SiO_2 solids.

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. The compounds $^tBu_2(Me_3Si)FlH$,[9] $(Me_3Si)FlSi(OH)_3$ (**6**),[5] $MeFlSi(OH)_3$ (**7**),[5] and $Ti(O^iPr)_2(acac)_2$[10] were prepared according to the literature. $Ti(OEt)_4$ and $Ti(O^iPr)_4$ (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 (^1H 500.1 MHz; $^{13}C\{^1H\}$ 125.8 MHz; $^{29}Si\{^1H\}$ 99.4 MHz; $^{15}N\{^1H\}$ 36.1 MHz). Chemical shifts are reported in ppm and were referenced to $SiMe_4$ ($MeNO_2$ for $^{15}N\{^1H\}$) as external 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.

$[^tBu_2(Me_3Si)FlSiCl_3]$. To a solution of 2.9 g of $^tBu_2(Me_3Si)FlH$ (8.3 mmol) in 30 mL of THF was added dropwise 5.4 mL of n-BuLi (1.6 mol/L in hexane, 8.3 mmol) at 0 °C. The mixture was stirred for 4 h and was allowed to warm to room temperature. The resulting deep red solution was added slowly at room temperature to a solution of 2.54 g of $SiCl_4$ (15.0 mmol) in 30 mL of THF. After stirring the mixture for 15 h, all volatile compounds were removed in vacuo. The remaining solid was suspended in 60 mL of hexane and filtered. The filtrate was concentrated in vacuo, and the product was isolated at −60 °C as colorless crystals (3.13 g 6.5 mmol; 78%). Mp: 143 °C. ^1H NMR ($CDCl_3$): δ −0.09 (s, 9H, $Si(CH_3)_3$), 1.38 (s, 18H, CCH_3), 7.45 (q, 2H, $^3J_{H-H} = 8.1$ Hz, $^4J_{H-H} = 1.7$ Hz, aromat-*H*), 7.78 (d, 2H, $^3J_{H-H} = 8.1$ Hz, aromat-*H*), 7.86 (d, 2H, $^4J_{H-H} = 1.7$ Hz, aromat-*H*). ^{13}C NMR ($CDCl_3$): δ −1.6 ($Si(CH_3)_3$), 31.6 (CCH_3), 35.0 (CCH_3), 47.8 (allyl-*C*), 119.4, 122.7, 123.5 (aromat-*C*), 138.5, 141.1, 149.5 (quart. aromat-*C*). ^{29}Si NMR ($CDCl_3$): δ 2.8, 6.5. IR (KBr): $\tilde{\nu}$ 454 (w), 509 (vs), 570 (vs), 585 (vs), 609 (m), 688 (w), 755 (m), 814 (s), 850 (vs), 911 (s), 942 (m), 1127 (m), 1253 (vs), 1362 (m), 1402 (m), 1474 (s), 1604 (m), 2867 (sh), 2901 (sh), 2963 (vs), 3068 (w). MS (EI): m/z (I_{rel}) 484 (31) [M^+], 376 (73) [$M^+ - (SiMe_3) - Cl$], 73 (100) [$(SiMe_3)^+$]. Anal. Calcd for $C_{24}H_{33}Cl_3Si_2$: C 59.54; H 6.87. Found: C 59.40; H 6.83.

$[^tBu_2(Me_3Si)FlSi(OH)_3]$ (5). A solution of 2.04 g of $^tBu_2(Me_3Si)FlSiCl_3$ (4.21 mmol) in 30 mL of Et_2O was added very slowly to a solution of 1.18 g of aniline (12.63 mmol) and 0.23 g of H_2O (12.63 mmol) in 30 mL of Et_2O at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The precipitated anilinium hydrochloride was filtered off, and all volatiles were removed in vacuo. After washing the remaining solid with small amounts of cold hexane, the product was isolated as a white solid (1.61 g, 3.75 mmol, 89%). Mp: 137 °C. ^1H NMR ($CDCl_3$): δ −0.20 (s, 9H, $Si(CH_3)_3$), 1.29 (s, 18H, CCH_3), 3.64 (s, 3H, $Si(OH)_3$), 7.27 (q, 2H, $^3J_{H-H} = 8.1$ Hz, $^4J_{H-H} = 1.4$ Hz, aromat-*H*), 7.62 (d, 2H, $^4J_{H-H} = 1.4$ Hz, aromat-*H*), 7.64 (d, 2H, $^3J_{H-H} = 8.1$ Hz, aromat-*H*). ^{13}C NMR ($CDCl_3$): δ −2.2 ($Si(CH_3)_3$), 31.7 (CCH_3), 34.8 (CCH_3), 42.7 (allyl-*C*), 118.9, 121.8, 121.9 (aromat-*C*), 137.5, 144.8, 148.7 (quart. aromat-*C*). ^{29}Si NMR ($CDCl_3$): δ 5.3 ($SiMe_3$), −45.7 ($Si(OH)_3$). IR (KBr): $\tilde{\nu}$ 469 (m), 670 (m), 731 (sh), 754 (sh), 816 (vs), 842 (vs), 927 (vs), 1025 (s), 1104 (w), 1128 (w), 1257 (vs), 1362 (m), 1404 (m), 1474 (s), 1604 (m), 2869 (m), 2902 (sh), 2960 (vs), 3387 (br), 3555 (br). MS (EI): m/z (I_{rel}) 428 (17) [M^+], 413 (31) [$M^+ - CH_3$], 372 (31) [$M^+ - C(CH_3)_3$], 73 (100) [$(SiMe_3)^+$]. Anal. Calcd for $C_{24}H_{36}O_3Si_2$: C 67.23; H 8.46. Found: C 67.14; H 8.64.

$[^tBu_2(Me_3Si)FlSi]_4O_{12}[TiOEt]_4$ (8). At room temperature 0.26 g (1.14 mmol) of $Ti(OEt)_4$ was added slowly to a suspension of 0.5 g (1.14 mmol) of $^tBu_2(Me_3Si)FlSi(OH)_3$ (**5**) in 30 mL of hexane using a syringe. A clear solution was formed immediately, and the mixture was stirred for 15 h. After removal of all volatile compounds in vacuo, a slightly yellow solid remained. Single crystals were obtained from hexane (0.54 g, 0.26 mmol, 94%). For NMR and elemental analysis the crystals were treated in vacuo for several hours. Mp: > 250 °C. ^1H NMR ($CDCl_3$): δ −0.29, −0.28, −0.27 (s, 36H, $Si(CH_3)_3$), 0.84−0.88 (m, 12H, CH_2CH_3), 1.23, 1.24, 1.25 (s, 72H, CCH_3), 3.81−3.88 (m, 8H, CH_2CH_3), 7.26 (s, 8H, aromat-*H*), 7.63−7.66 (m, 16H, aromat-*H*). ^{13}C NMR ($CDCl_3$): δ −2.1, −2.0, −1.9 ($Si(CH_3)_3$), 18.6, 18.7 (CH_2CH_3), 31.6, 31.7, 31.8 (CCH_3), 34.7 (CCH_3), 41.2 (allyl-*C*), 74.0 (CH_2CH_3), 118.3, 121.3, 121.9 (aromat-*C*), 137.6, 145.2, 148.0, 148.1 (quart. aromat-*C*). ^{29}Si NMR ($CDCl_3$): δ 5.0 ($SiMe_3$), −77.4, −77.5, −77.6 (SiO_3). IR (KBr): $\tilde{\nu}$ 445 (s), 458 (s), 641 (w), 731 (m), 814 (m), 842 (s), 924 (sh), 977 (vs), 1019 (sh), 1101 (w), 1129 (w), 1257 (m), 1362 (w), 1407 (w), 1475 (w), 2870 (m), 2902 (sh), 2962 (s). Anal. Calcd for $C_{104}H_{152}O_{16}Si_8Ti_4$: C 60.21; H 7.38. Found: C 60.40; H 7.50.

$[(Me_3Si)FlSi]_2O_5[Ti(OEt)]_4[\mu_2\text{-}OEt]_6[\mu_4\text{-}O]$ (9). At room temperature 1.01 g (4.42 mmol) of $Ti(OEt)_4$ in 20 mL of hexane

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[9] Carpino, L. A.; Wu, A. C. PCT Int. Appl. WO9108190, 1991.

[10] Bradley, D. C.; Holloway, C. E. *J. Chem. Soc. (A)* **1969**, 282.

Table 6. Description of the X-ray Data Collection and Structural Analysis of Compounds 8−12

	8	**9**	**10**	**11**	**12**
empirical formula	$C_{104}H_{152}O_{16}Si_8Ti_4\cdot{}^1/_2\,H_2O$	$C_{52}H_{84}O_{16}Si_4Ti_4\cdot{}^1/_2\,C_6H_{14}$	$C_{180}H_{282}O_{35}Si_{12}Ti_{10}$	$C_{70}H_{106}N_2O_{20}Si_2Ti_6\cdot C_6H_{14}$	$C_{54}H_{64}O_{14}Si_2Ti_2\cdot 2CH_2Cl_2$
fw, g/mol	2082.58	1312.24	3822.14	1725.32	1258.88
temp, K	100	163	100	173	173
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$C2/c$	$P2_1/n$	$P\bar{1}$
lattice params					
a, Å	15.7610(3)	22.8832(11)	31.698(3)	12.1779(6)	11.050(2)
b, Å	37.4720(11)	12.0932(6)	31.066(3)	24.5692(12)	11.422(3)
c, Å	22.80000(6)	24.0331(12)	27.167(2)	14.8205(7)	13.323(3)
α, deg					74.97(2)
β, deg	102.503(1)	93.208(1)	98.499(7)	99.9080(10)	77.74(2)
γ, deg					70.85(2)
V, Å^3	13146.2(6)	6640.3(6)	26465(4)	4368.2(4)	1519.1(6)
Z	4	4	4	2	1
diffractometer	Nonius KappaCCD	Siemens SMART CCD	Nonius KappaCCD	Siemens SMART CCD	Siemens P2$_1$
cryst size, mm^{-3}	0.18 × 0.21 × 0.36	0.10 × 0.20 × 0.35	0.20 × 0.20 × 0.25	0.20 × 0.30 × 0.40	0.1 × 0.2 × 0.4
$d_{\text{calc,}}$ g/cm^3	1.052	1.313	0.959	1.312	1.376
F(000)	4432	2772	8120	1820	656
μ(Mo Kα), mm^{-1}	0.357	0.596	0.388	0.614	0.539
abs corr	multiscan	multiscan	none	multiscan	none
min./max. transmn	0.88/0.94	0.82/0.94		0.79/0.89	
2θ range, deg	6−49	4−54	6−50	4−54	3−57
no. of reflns collected	48 549	61 819	151 485	41 191	8110
no. of unique reflns	18094 [R_{int} = 0.07]	14314 [R_{int} = 0.2011]	23172 [R_{int} = 0.0758]	9435 [R_{int} = 0.0350]	7721 [R_{int} = 0.0667]
no. obsd data [$I > 2\sigma(I)$]	9485	5535	14957	7267	4323
no. of params refined	1223	750	1097	497	359
final R1[a] [$I > 2\sigma(I)$]/ wR2[b]	0.102, 0.3193	0.0741, 0.1800	0.0816, 0.2693	0.0488, 0.1469	0.0765, 0.2063
largest peak in final diff map, e/Å^3	0.946	0.726	1.185	1.039	0.695
no. of disordered carbon atoms	4	9	7	2	0
isotripically refined non H atoms	none	disordered atoms	disordered atoms	disordered atoms	none

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

was added slowly to a suspension of 0.70 g (2.21 mmol) of (Me$_3$Si)FlSi(OH)$_3$ (**6**) in 20 mL of hexane. A clear solution was formed immediately, and the mixture was stirred for 15 h. After removal of all volatile compounds in vacuo the remaining slightly orange solid was crystallized from a solution in hexane (1.34 g, 1.06 mmol, 96%). For NMR and elemental analysis the crystals were treated in vacuo for several hours. Mp: >250 °C. ^{1}H NMR (CDCl$_3$): δ −0.10, −0.09 (2s, 9H, Si(CH_3)$_3$), 1.78 (t, $^3J_{H-H}$ = 5.8−7.0, 3H, CH$_2$CH_3), 1.15−1.35 (m, 27H, CH_2-CH$_3$), 3.34 (q, 2H, CH_2CH$_3$), 4.26−4.52 (m, 18H, CH_2CH$_3$), 7.26 (m, 8H, aromat-*H*), 7.82, 7.96 (2d, $^3J_{H-H}$ = 7.8, 7.7, 4H, aromat-*H*). ^{13}C NMR (CDCl$_3$): δ −2.7, −2.8 (Si(*C*H$_3$)$_3$), 14.1 (CH$_2$*C*H$_3$), 43.2 (allyl-*C*), 73.7 (*C*H$_2$CH$_3$), 119.2, 124.0, 125.6, 129.1 (aromat-*C*), 140.2, 146.7 (quart. aromat-*C*). ^{29}Si NMR (CDCl$_3$): δ 3.8, 3.7 (*Si*Me$_3$), −60.4, −61.4 (*Si*O$_3$). IR (KBr): $\tilde{\nu}$ 508 (s), 592 (m), 740 (s), 846 (vs), 887 (vs), 925 (s), 952 (s), 1044 (m), 1075 (m), 1102 (s), 1248 (s), 1262 (s), 1364 (w), 1432 (m), 1445 (m), 2838 (m), 2878 (m), 2926 (m), 2968 (s), 3059 (m). Anal. Calcd for $C_{52}H_{84}O_{16}Si_4Ti_4$: C 49.21; H 6.67. Found: C 48.50; H 6.65 (even additional amounts of catalyst (V$_2$O$_5$) cannot complete the oxidation process).

([^{t}Bu$_2$(Me$_3$Si)FlSi]$_3$O$_{10}$[TiO^{i}Pr]$_4$[μ_2-O^{i}Pr]$_2$[μ_3-O]Ti)$_2$O (10). To a suspension of 0.46 g (1.07 mmol) of ^{t}Bu$_2$(Me$_3$Si)FlSi(OH)$_3$ (**5**) and 16.1 mg (0.89 mmol) of H$_2$O in 30 mL of hexane was added slowly 0.51 g (1.79 mmol) of Ti(O^{i}Pr)$_4$. A clear solution was formed immediately. The mixture was stirred overnight. After removal of all volatile compounds in vacuo, the remaining slightly yellow solid was crystallized from hexane at −60 °C (0.54 g, 0.14 mmol, 84%). For NMR and elemental analysis the crystals were treated in vacuo for several hours. Mp: > 250 °C. ^{1}H NMR (CDCl$_3$): δ −0.29, −0.28 (s, 54H, Si(CH_3)$_3$), 0.76 (d, br, 48H, ^3J = 5.7 Hz, CH(CH_3)$_2$), 0.81 (d, 24H, ^3J = 6.3 Hz, CH(CH_3)$_2$), 1.21, 1.23, 1.25 (s, 108H, CCH_3), 4.20 (sep, br, 8H, ^3J = 5.7 Hz, CH(CH$_3$)$_2$), 4.30 (sep, 4H, ^3J = 6.3 Hz, CH(CH$_3$)$_2$), 7.23−7.28 (m, 12H, aromat-*H*), 7.63−7.68 (m, 24H, aromat-*H*). ^{13}C NMR (CDCl$_3$): δ −1.9 (Si(*C*H$_3$)$_3$), 25.2 (CH$_2$*C*H$_3$), 31.7, (C*C*H$_3$), 34.7 (*C*CH$_3$), 41.2 (allyl-*C*), 80.6 (*C*H(CH$_3$)$_2$), 118.3, 121.3, 121.9 (aromat-*C*), 137.7, 145.1, 148.0 (quart. aromat-*C*). ^{29}Si NMR (CDCl$_3$): δ 5.0 (*Si*Me$_3$), −65.2, −77.6 (*Si*O$_3$). IR (KBr): $\tilde{\nu}$ = 445 (s), 459(s), 638 (w), 731 (m), 813 (m), 842 (s), 972 (vs), 1052 (s), 1101 (w), 1130 (w), 1257 (m), 1363 (w), 1407 (w), 1475 (w), 2869 (m), 2902 (sh), 2965 (s). Anal. Calcd for $C_{180}H_{282}O_{35}Si_{12}Ti_{10}$: C 56.57; H 7.44. Found: C 57.04; H 7.44.

[MeFlSi]$_2$O$_8$[Ti(O^{i}Pr)]$_6$[μ_2-O^{i}Pr]$_4$[μ_3-O]$_2$[PhNH$_2$]$_2$ (11). To a suspension of 0.4 g (1.55 mmol) of MeFlSi(OH)$_3$ (**7**), 0.14 g (1.55 mmol) of aniline, and 0.11 g (6.19 mmol) of H$_2$O in 10 mL of hexane was added dropwise 2.64 g (9.29 mmol) of Ti(O^{i}Pr)$_4$ in 10 mL of hexane. A clear mixture was obtained and stirred for 15 h. After removal of all volatile compounds in vacuo, a yellow-orange solid was obtained. Crystallization from hexane at −30 °C afforded compound **11** as colorless crystals (1.64 g, 1.39 mmol, 90%). For NMR and elemental analysis the crystals were treated in vacuo for several hours. Mp: > 250 °C. ^{1}H NMR (CDCl$_3$): δ 1.07, 1.17, 1.22, 1.26, 1.27 (5d, $^3J_{H-H}$ = 6.1−6.3, 12H, CH(CH_3)$_2$), 1.63 (s, 6H, CH_3), 3.55 (s, br, 4H, PhNH_2), 4.61 (sep, 6H, CH(CH$_3$)$_2$), 4.69 (sep, 4H, CH(CH$_3$)$_2$), 6.64 (d, $^3J_{H-H}$ = 7.8, 4H, *Ph*NH$_2$), 6.76 (t, $^3J_{H-H}$ = 7.4, 2H, *Ph*NH$_2$), 7.13 (t, $^3J_{H-H}$ = 7.8, 4H, *Ph*NH$_2$), 7.22 (m, 8H, Fl-aromat-*H*), 7.71 (dd, $^3J_{H-H}$ = 6.3, 5.6, 4H, Fl-aromat-*H*), 7.74 (dd, $^3J_{H-H}$ = 6.2, 5.6, 4H, Fl-aromat-*H*). ^{13}C NMR (CDCl$_3$): δ 19.7 (*C*H$_3$), 23.4, 23.5 25.5, 25.6, 25.9 (CH(*C*H$_3$)$_2$), 42.6 (Fl-allyl-*C*), 75.6, 79.5, 79.6 (*C*H(CH$_3$)$_2$), 115.8, 119.1, 129.2, 145.7 (*Ph*-NH$_2$), 119.3, 124.5, 125.0, 125.8, (Fl-aromat-

C), 140.1, 151.0 (quart. Fl-aromat-*C*). ^{29}Si NMR ($CDCl_3$): δ −70.0. ^{15}N NMR ($CDCl_3$): δ −141.4 ($\omega_{1/2} = 11060$ Hz). IR (KBr): $\tilde{\nu}$ 486 (s), 612 (s), 772 (s), 852 (m), 929 (vs), 1002 (m), 1127 (s), 1162 (m), 1363 (m), 1378 (m), 1445 (m), 1604 (m), 2862 (m), 2925 (m), 2967 (s), 3062 (w), 3301 (w), 3381 (w). Anal. Calcd for $C_{70}H_{106}N_2O_{20}Si_2Ti_6$ (1173.97): C 51.30; H 6.52; N 1.71. Found: C 51.27; H 6.54; N 1.47.

[MeFlSi(O^{i}Pr)]$_2$O$_4$[Ti(acac)$_2$]$_2$ (12). To a suspension of 0.4 g (1.55 mmol) of MeFlSi(OH)$_3$ (**7**) in 10 mL of hexane was added dropwise a solution of 0.57 g (1.55 mmol) of Ti(O^{i}Pr)$_2$(acac)$_2$ in 10 mL of hexane. After stirring the mixture overnight it was refluxed for 5 h. All volatiles were removed in vacuo, and the remaining colorless solid was crystallized from dichloromethane (0.81 g, 0.74 mmol, 96%). For NMR and elemental analysis the crystals were treated in vacuo for several hours. Mp: 105 °C. ^{1}H NMR ($CDCl_3$): δ 0.40 (d, $^3J_{H-H} = 6.1$, 12H, CH(C*H*$_3$)$_2$), 2.01, 2.03 (2s, 6H, *acac*), 2.14 (s, 6H, C*H*$_3$), 3.38 (m, 2H, C*H*(CH$_3$)$_2$), 7.22 (m, 8H, aromat-*H*), 7.72, 8.15 (2d, $^3J_{H-H} = 6.6$, 6.7, 4H, aromat-*H*). ^{13}C NMR ($CDCl_3$): δ 19.5 (*C*H$_3$), 24.5, 25.2 (*acac*), 27.2 (CH(*C*H$_3$)$_2$), 44.7 (*allyl-C*), 65.1 (*C*H(CH$_3$)$_2$), 104.1 (*acac*), 118.9, 124.7, 125.8, 125.9, (aromat-*C*), 140.2, 151.9 (quart. aromat-*C*), 186.2, 192.3 (*acac*). ^{29}Si NMR ($CDCl_3$): δ −73.5. IR (KBr): $\tilde{\nu}$ 508 (m), 731 (m), 744 (m), 802 (m), 821 (m), 955 (vs), 993 (sh), 1014 (vs), 1040 (sh), 1097 (m), 1109 (m), 1261 (m), 1280 (m), 1361 (s), 1379 (sh), 1524 (vs), 1530 (vs), 1578 (s), 1606 (s), 2856 (m), 2918 (m), 2961 (m), 3034 (w), 3050 (w). MS (EI): m/z (I_{rel}) 908 (2) [(M − Fl(Me))$^+$], 647 (14) [($Si_2O_6Ti_2$(acac)$_4$)$^+$], 178 (26) [Fl(Me)$^+$], 85 (31) [($C_4H_5O_2$)$^+$], 41 (100) [(C_3H_4)$^+$]. Anal. Calcd for $C_{54}H_{64}O_{14}Si_2Ti_2 \cdot CH_2Cl_2$ (1173.97): C 56.27; H 5.67. Found: C 56.63; H 6.14.

X-ray Structures. All measurements were carried out using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by using direct methods and were refined by using full-matrix least squares against F^2 with anisotropic thermal parameters for all non-hydrogen atoms with the exception of some disordered atoms (located in the organic moiety of the compounds and in solvent molecules, respectively), which are listed in Table 6. H atoms were included at calculated positions using a riding model. Programs used were from Siemens SHELXTL PLUS and SHELX-97.

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Supporting Information Available: Tables of structure crystal data, positional and thermal parameters, selected bond lengths and angles, and ORTEP plots of **8**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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