Silsesquioxane Chemistry, 4.☆
Silsesquioxane Complexes of Titanium(III) and Titanium(IV)

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Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday

Abstract

Reaction of the incompletely condensed silsesquioxane derivative $Cy_7Si_7O_9(OH)_3$ (1) with $Ti(OEt)_4$ affords the dimeric titanasilsesquioxane $[(Cy_7Si_7O_{12})Ti(\mu\text{-}OEt)(EtOH)]_2$ (13) in 81% yield. The known titanasilsesquioxane $[Cy_7Si_7O_{11}(OSiMe_3)]_2Ti$ (18) has been prepared through a modified procedure starting from titanium tetraalkoxides. Novel oxotitanium silsesquioxane derivatives are obtained from reactions of titanocene dihalides with $Cy_7Si_7O_9(OH)_2(OSiMe_3)$ (14). Cp_2TiCl_2 yields dinuclear $(\mu\text{-}O)[\{Cy_7Si_7O_{11}(OSiMe_3)\}TiCp]_2$ (19), while with $Cp_2^*TiCl_2$ the trinuclear titanacycle $Cp_2^*Ti_3O_3[Cy_7Si_7O_{11}(OSiMe_3)]_2$ (20) is obtained. In addition, a new synthetic route to model compounds for titanium catalysts immobilized on silica has been developed. Disilylated $Cy_7Si_7O_9(OH)(OSiMe_3)_2$ (15) cleanly reacts with the 'tucked-in' fulvene complex $Cp^*Ti(C_5Me_4CH_2)$ to give the titanium(III) silsesquioxane $Cp_2^*Ti[Cy_7Si_7O_{10}(OSiMe_3)_2]$ (21). In a similar manner treatment of $Cp^*Ti(C_5Me_4CH_2)$ with $Cy_7Si_7O_9(OH)_2(OSiMe_3)$ (14) affords the mono(pentamethylcyclopentadienyl) complex $Cp^*Ti[Cy_7Si_7O_{11}(OSiMe_3)][Cy_7Si_7O_{10}(OH)(OSiMe_3)]$ (22) which is an advanced model compound for a catalytically active titanium center on a silica surface. The molecular structures of these titanium silsesquioxane derivatives have been determined by X-ray diffraction analyses. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silsesquioxanes; Titanium; Titanasilsesquioxanes; μ-Oxo complexes; Crystals structure

1. Introduction

In catalysis, many industrially and commercially important processes are catalyzed by transition metal complexes immobilized on silica surfaces [2–8]. However, due to the heterogeneous nature of the catalysts the catalytic species are often difficult to characterize and mechanisms of the catalyzed organic transformations and the nature of the metal-silica interactions remain unclear. In these cases metallasiloxanes could serve as molecular model compounds [9]. Especially metal complexes derived from 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. In material science certain metallasiloxanes are of interest as molecular precursors for metal-containing inorganic polymers [10,11] and other new materials. [12–17] Finally, 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].

Especially useful for the preparation of metallasilsesquioxanes are incompletely condensed silsesquioxanes. The most prominent representative of this class of organosilicon compounds is the trisilanol derivative $Cy_7Si_7O_9(OH)_3$ (1), which was first reported by Brown and Vogt [19,20] and more recently investigated in great detail by Feher and co-workers [21]. The established synthetic route to this useful material involves controlled hydrolysis of trichloro(cyclohexyl)silane, $CySiCl_3$, in an acetone–water mixture [21b].


1: R = cyclohexyl
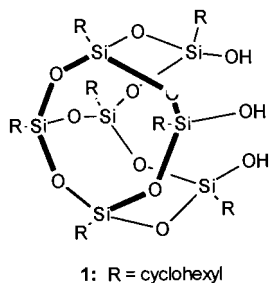
Trisilanol **1** has been the starting point for the preparation of numerous metallasilsesquioxanes containing main group elements as well as early transition metals and lanthanides [21a]. Apparently the most thoroughly investigated class of complexes in this area are Ti complexes because of their promising catalytic applications [21a]. The first Ti derivatives were made by Feher et al. and include Ti(III) [22] and Ti(IV) silsesquioxanes [23]. The former have been prepared by reacting **1** with either Ti[N(SiMe$_3$)$_2$]$_3$ or TiCl$_3$(NMe$_2$)$_2$. Initial product in these reactions is the blue dimeric complex [Cy$_7$Si$_7$O$_{12}$Ti]$_2$ (**2**). Treatment of **2** with pyridine affords the bis-adduct [Cy$_7$Si$_7$O$_{12}$Ti(py)]$_2$ (**3**) in almost quantitative yield [22]. Corner-capping of the silsesquoxane framework with a TiCp unit can also be readily achieved yielding monomeric Cy$_7$Si$_7$O$_{12}$TiCp (**4**) [23]. Other titanasilsesquioxanes have been designed as model compounds for titanosilicates, which are industrially important as oxidation catalysts [24]. Examples of such realistic models include (MeC$_5$H$_4$)$_4$Ti$_4$-(Si^{i}Bu)$_4$O$_{12}$ (**5**) [25], [2,6-^{i}Pr$_2$C$_6$H$_3$NH$_3$][(RSiO$_3$)$_3$-Ti$_4$Cl$_4$(μ$_3$-O)] [**6**, R = 2,6-^{i}Pr$_2$C$_6$H$_3$N(SiMe$_3$)] [26], [Cy$_7$Si$_7$O$_{12}$MgTiCl$_3$]$_n$ (**7**, n = 1,2) [27], and [R$_7$Si$_7$O$_{12}$-TiO^{i}Pr]$_n$ (**8a**: R = c-C$_5$H$_9$; **8b**: c-C$_6$H$_{11}$; n = 1,2) [28]. Most recently it has become widely accepted that various titanium silsesquioxanes are veritable catalysts themselves, e.g. in olefin polymerizations and epoxidation reactions [29]. Treatment of Cy$_7$Si$_7$O$_{12}$Ti(O^{i}Pr) (**8b**) with methanol affords the six-coordinate titanasilsesquioxane dimer [Cy$_7$Si$_7$O$_{12}$Ti(μ-OMe)(MeOH)]$_2$ (**9**) which was structurally characterized [28]. Related complexes, although monomeric, have also been isolated from reactions of **2** with Ti(CH$_2$Ph)$_4$, Ti(NMe$_2$)$_4$ or Ti(OSiMe$_3$)$_4$ yielding Cy$_7$Si$_7$O$_{12}$TiCH$_2$Ph (**10**), Cy$_7$Si$_7$O$_{12}$TiNMe$_2$ (**11**), and Cy$_7$Si$_7$O$_{12}$TiOSiMe$_3$ (**12**) [30,31].

In the first part of this paper we report our results on reactions of **1** with titanium tetraalkoxides. While this work was in progress, several titanasilsesquioxane alkoxides, including [R$_7$Si$_7$O$_{12}$TiO^{i}Pr]$_n$ (**8a**: R = c-C$_5$H$_9$; **8b**: c-C$_6$H$_{11}$; n = 1,2) and [Cy$_7$Si$_7$O$_{12}$Ti(μ-OMe)-(MeOH)]$_2$ (**9**) have been published by Crocker and co-workers [30]. Thus we will focus here only on those results which complement the previous findings. In addition, we report in this paper the preparation and structural characterization of the first titanocene deriva-

tives containing silsesquioxane ligands, including a novel preparative route to soluble model compounds for catalytically active titanium centers on silica surfaces.

2. Results and discussion

The hitherto unknown ethoxide derivative **13** was prepared according to Eq. (1) by treatment of **1** with an equimolar amount of titanium tetraethoxide. Compound **13** is isolated in 81% yield as a moisture-sensitive, colorless crystalline solid which is thermally quite robust (m.p. 263–265°C). It is readily soluble in various organic solvents such as toluene, diethylether, or THF. An X-ray crystal structure determination (Table 1, Fig. 1) revealed the presence of a dimeric compound with bridging alkoxide ligands and coordinated ethanol molecules in analogy with the structure of the corresponding methoxide derivative [Cy$_7$Si$_7$O$_{12}$Ti(μ-OMe)(MeOH)]$_2$ (**9**) [30].

13
R = cyclohexyl
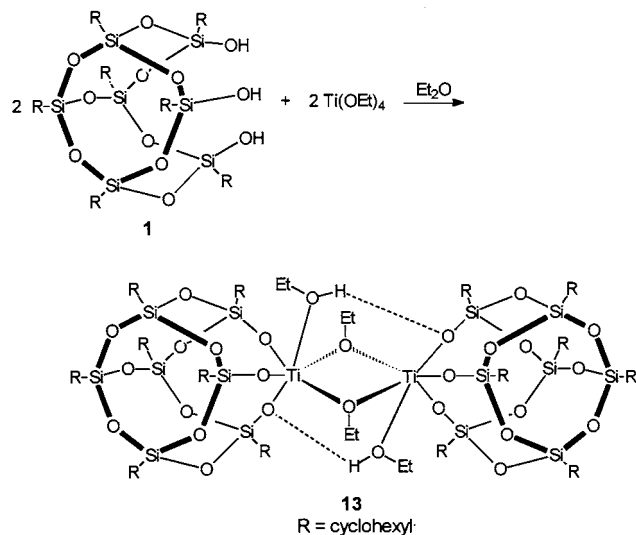
(1)

In the dimeric molecule **13** the Ti atoms are hexacoordinated with the silsesquioxane cages acting as tridentate ligands. The complex comprises two bridging ethoxide ligands as well as two terminal ethanol molecules coordinated to titanium. Hydrogen bridges connect the OH group of each ethanol ligand with a silsesquioxane oxygen which is coordinated to the opposite titanium center. As expected, most bond lengths and angles in **13** are virtually identical with the corresponding values in the methoxide derivative **9**. The molecule comprises three different types of Ti–O bonds with the average Ti–O(cage) distances being the shortest ones (184.8(3) pm, cf. 183.7(7) pm in **9**). An average value of 202.2(3) pm is found for the Ti–O distances to the brigding ethoxide ligands (**9**: 200.4(7) pm) while the coordinated ethanol ligands constitute the longest Ti–O

bonds in **13** (average 222.2(4) pm, cf. 221.0(7) pm in **9**). With 169(4)° the hydrogen bond in **13** is significantly closer to linearity than that in **9** (147.6°).

According to studies by Feher et al. [21b] the functionality of trisilanol **1** can be modified through silylation via treatment with various stoichiometric amounts of Me_3SiCl/NEt_3. The resulting silylated products $Cy_7Si_7O_9(OH)_2(OSiMe_3)$ (**14**), $Cy_7Si_7O_9(OH)(OSiMe_3)_2$ (**15**), and $Cy_7Si_7O_9(OSiMe_3)_3$ (**16**) can be isolated as

pure materials and represent a useful set of differently functionalized silsesquioxane reagents. It was shown by Crocker et al. that treatment of **14** with one equivalent of $Ti(O^iPr)_4$ smoothly produced monomeric $Cy_7Si_7O_{11}(OSiMe_3)[Ti(O^iPr)_2]$ (**17**) as the sole product. A homoleptic bis(silsesquioxane) titanium complex, $[Cy_7Si_7O_{11}(OSiMe_3)]_2Ti$ (**18**), can be prepared by reacting **14** with tetrabenzyltitanium, $Ti(CH_2Ph)_4$ [30]. Parallel to this work it was found in our lab that compound

Table 1
Summary of crystal structure determination data

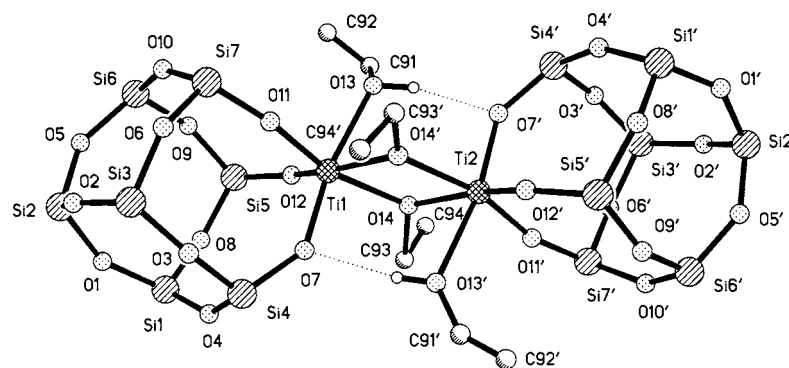| Compound	13	20	21	22
Empirical formula	$C_{92}H_{176}O_{28}Si_{14}Ti_2 \cdot C_4H_{10}O$	$C_{110}H_{202}O_{27}Si_{16}Ti_3$	$C_{68}H_{125}O_{12}Si_9Ti \cdot 0.5C_7H_8$	$C_{100}H_{188}O_{24}Si_{16}Ti \cdot 1.5C_7H_8$
M_r	2293.51	2549.86	1481.46	2410.04
Habit, colour	Colourless prism	Red plate	Green prism	Pale yellow prism
Crystal dimensions (mm³)	$0.70 \times 0.35 \times 0.10$	$0.42 \times 0.42 \times 0.14$	$0.88 \times 0.41 \times 0.36$	$0.45 \times 0.35 \times 0.30$
Crystal system	$P\bar{1}$	$Pna2_1$	$P2_1/n$	$P\bar{1}$
Unit cell constants				
a (Å)	16.56692)	61.621(1)	13.087(1)	12.0428(3)
b (Å)	16.927(2)	15.617(1)	26.163(1)	22.461(2)
c (Å)	23.938(4)	15.312(2)	24.449(2)	25.540(2)
α (°)	108.485(8)	90	90	106.667(3)
β (°)	93.259(8)	90	97.616(3)	99.602(3)
γ (°)	102.641(6)	90	90	100.045(3)
V (Å³)	6153	14736	8297.58	6342.2
Z	2	4	4	2
$D_{x(calc)}$ (Mg m⁻³)1.238	1.149	1.189	1.262	
μ (mm⁻¹) 0.33		0.35	0.29	0.28
$F(000)$	2468	5472	3208	2602
Temperature (°C)	−100	−130	−100	−120
$2\theta_{max}$	53.1	51.7	56.7	53.4
Number of reflexes				
Measured	35426	65890	54689	31546
Independent	24050	24158	20363	24118
R_{int}	0.045	0.115	0.053	0.034
Refined parameters	1324	1311	844	1382
$wR(F^2$, alle Reflections)	0.281	0.345	0.136	0.194
$R(F, >4\sigma(F))$	0.187	0.119	0.054	0.080
S	1.06	1.06	1.02	1.04
Max. $\Delta\rho$ (e Å⁻³)	1.19	1.05	0.99	1.11

Fig. 1. Structure of **13** in the crystal. Selected interatomic distances (pm) and bond angles (°) (average values, cyclohexyl substituents omitted for clarity): Ti–O(cage) 184.8(3), Ti–O(μ-OEt) 202.2(3), Ti–O(EtOH) 222.2(4), O–H(EtOH) 86.7, O⋯H(hydrogen bridge) 200.4(5), O–Ti–O(μ-OEt) 72.2(1), Ti–O–Ti(μ-OEt) 107.8(1), O–H⋯O 169(4).

**18** is also readily accessible through reactions of Ti(OEt)$_4$ or Ti(O^{i}Pr)$_4$ with **14** according to Eq. (2). Both reactions afford white crystalline **18** in almost quantitative yields (96–97%) and do not require reagents which are not commercially available. An X-ray diffraction study recently published by Crocker et al. revealed that the central titanium atom in **18** is tetrahedrally coordinated by the two dianionic silsesquioxane cages [30].

14

18
R = cyclohexyl
L = OEt, OiPr

(2)
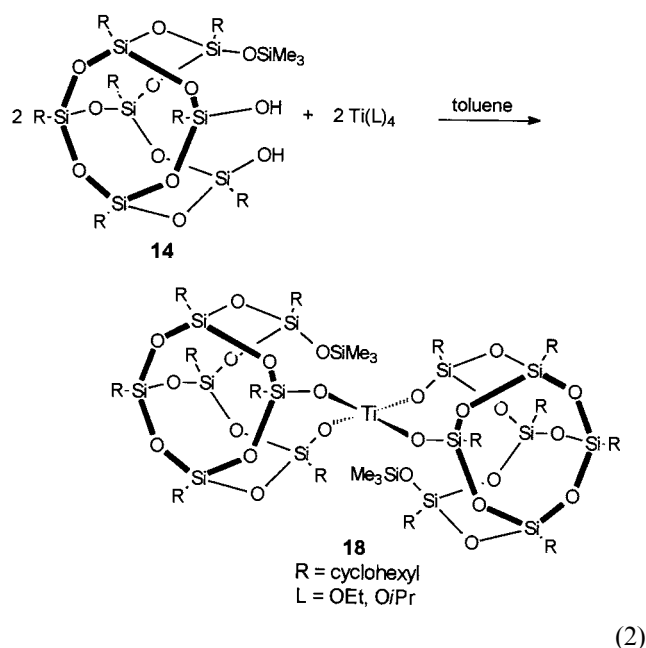
In addition to the titanium alkoxide reactions we report here for the first time the preparation and characterization of several titanocene derivatives containing silsesquioxane ligands. Thus far it has turned out that reactions of **1** or its monosilylated derivative **14** with titanocene dihalides 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 be 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 **14** with Cp$_2$TiCl$_2$ in toluene solution in the presence of triethylamine. In this case the μ-oxo dititanium complex (μ-O)[Cy$_7$Si$_7$O$_{11}$-(OSiMe$_3$)Ti]$_2$ (**19**) has been isolated in ca. 70% yield in the form of orange crystals Eq. (3).

The molecular structure of **19** has been established by an X-ray diffraction analysis. Serious disorder problems involving several cyclohexyl substituents of the silsesquioxane cages prevented complete refinement of this structure. Thus a detailed discussion of bond lengths and angles is not possible. However, the overall

connectivities within the molecule as depicted schematically in Eq. (3) are unambiguous and clearly show the presence of a dinuclear metallasilsesquioxane with a central Ti–O–Ti unit. During the course of the reaction one Cp ligand per Ti atom is eliminated upon protonolysis to give the observed mono(cyclopentadienyl) titanium(IV) derivative.

14

19
R = cyclohexyl

(3)
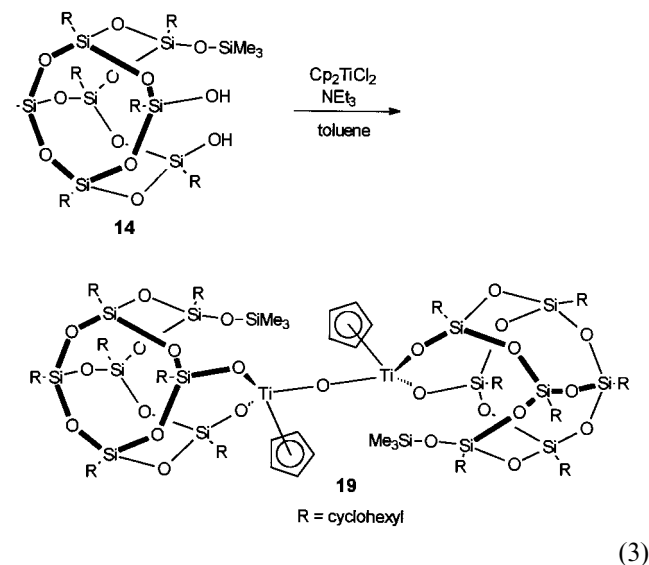
Apparently at least two different products are formed when **14** is reacted with the corresponding pentamethylcyclopentadienyl titanium complex Cp$_2^*$TiCl$_2$ in the presence of triethylamine. While a yellow component has not yet been identified, it was possible to isolate and fully characterize the red crystalline trinuclear 1,3,5-trititana-2,4,6-trioxane derivative Cp$_2^*$Ti$_3$O$_3$-[Cy$_7$Si$_7$O$_{11}$(OSiMe$_3$)]$_2$ (**20**) (Eq. (4)). The molecular structure of **20** has been elucidated by an X-ray structural analysis (Fig. 2). The central structural motif of **20** is an unsymmetrically substituted six-membered Ti$_3$O$_3$ 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$_3$O$_4$ ring systems within the silsesquioxane frameworks. This results in an unusual bis(spirocyclic) inorganic ring system in the molecular structure of **20**. There is significant variation in the Ti–O bond lengths within the six-membered ring. With 195.3(7) and 192.6(8) pm the longest bonds are found for the oxygen atoms directly connected to the Cp$_2^*$Ti unit. This corresponds to a small O–Ti–O angle of 95.1(3)°. The remaining Ti–O distances within the Ti$_3$O$_3$ ring are significantly shorter and fall in the range between 173.0(7) and 183.7(7) pm. The average inner-ring O–Ti–O angle at Ti(2) and Ti(3) is 107.3(4)°. For the Ti–O distances to the silsesquioxane oxygen atoms an average value of 182.4(8) pm was determined. This can be favorably compared to corresponding Ti–O(cage) bonds lengths of 183.7(7) pm in **9** and 178.6(6)–182.8(11) pm in **18** [30].
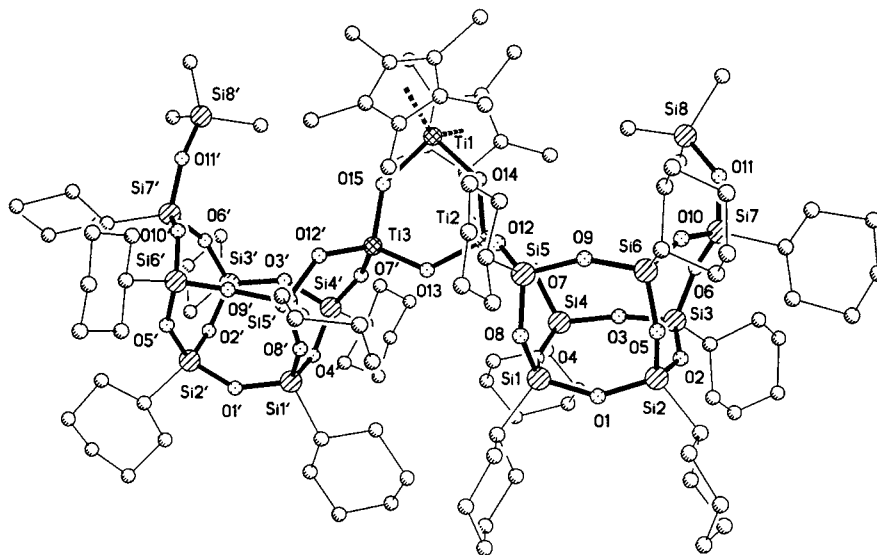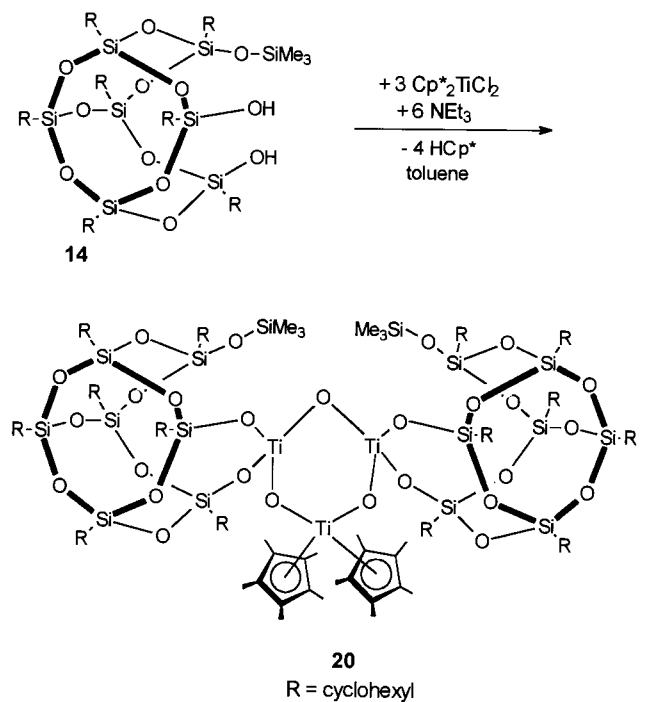
Fig. 2. Structure of **20** in the crystal. Selected interatomic distances (pm) and bond angles (°): Ti(1)–O(14) 195.3(7), Ti(2)–O(14) 173.0(7), Ti(2)–O(13) 180.1(8), Ti(3)–O(13) 183.7(7), Ti(3)–O(15) 177.1(8), Ti(1)–O(15) 192.6(8), Ti–O(cage) 182.4(8) (av.), Ti–C 242.7(13), O(14)–Ti(1)–O(15) 95.1(3), Ti(1)–O(14)–Ti(2) 140.5(4), O(14)–Ti(2)–O(13) 107.3(3), Ti(2)–O(13)–Ti(3) 130.9(4), O(13)–Ti(3)–O(15) 107.2(4), Ti(3)–O(15)–Ti(1) 139.0(4), Si–O–Si(OSiMe$_3$) 145.5(8) (av.).


14

20

R = cyclohexyl

(4)

Several compounds containing six-membered Ti$_3$O$_3$ ring systems have previously been reported in the literature [32]. Most of them contain isolated metallacycles but the ring system can also be part of a more complex titanium–oxygen cage structure. Typical examples in-

clude among others the complexes [Cp*TiCl(μ-O)]$_3$, [Cp*TiBr(μ-O)]$_3$, and [Cp*TiMe(μ-O)]$_3$ as well as the alkylidyne-capped cage compounds [Cp*Ti(μ-O)]$_3$(μ$_3$-CR) (R = H, Me) [32]. For comparison, the Ti–O bond lengths in [Cp*TiCl(μ-O)]$_3$ range from 181.2(5) to 183.3(5) pm, averaging 182.3(5) pm [32a].

In a more straightforward manner a bis(pentamethyl-cyclopentadienyl)titanium(III) silsesquioxane complex became available according to the preparative route outlined in Eq. (5). This synthesis has been developed as a new preparative route leading to model compounds for titanium catalysts immobilized on silica surfaces. It involves addition of the silsesquioxane precursors across the Ti–C bond of the 'tucked in' fulvene titanium complex Cp*Ti(C$_5$Me$_4$CH$_2$) [33]. The main advantage of this procedure is that it is a salt-free route by which bis(pentamethylcyclopentadienyl)titanium complexes can be obtained without the need of separating any by-products. The method had first been successfully employed by Teuben et al. who prepared various new Cp$_2^*$Ti derivatives by reacting Cp*Ti(C$_5$Me$_4$CH$_2$) with protic reagents such as alcohols, thiols etc. [33]. It was now found that the fulvene complex Cp*Ti(C$_5$Me$_4$CH$_2$) is also the reagent of choice to make novel titanium silsesquioxanes. For example, treatment of Cp*Ti(C$_5$Me$_4$CH$_2$) with one equivalent of the monosilylated silsesquioxane precursor **15** resulted in clean formation of the titanium(III) silsesquioxane complex **21**.

$$(5)$$
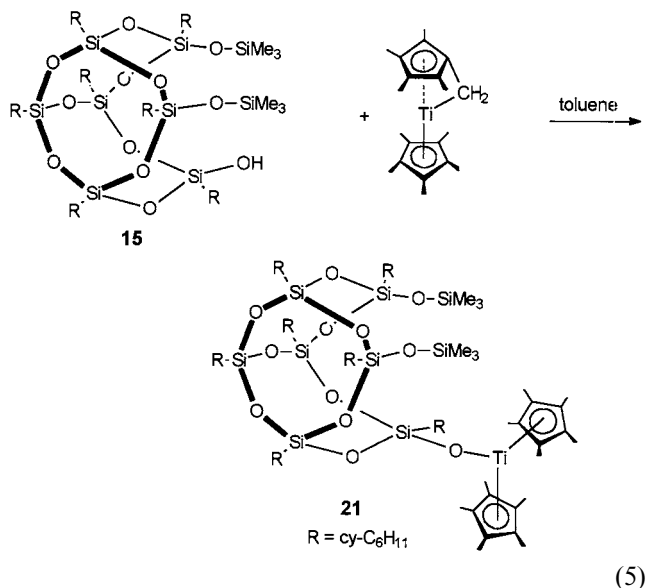
Simple crystallization from the concentrated reaction mixture afforded **21** in the form of air-sensitive, dark green crystals. The low isolated yield (16%) can be traced back to the very high solubility of **21** even in non-polar organic solvents which makes it somewhat difficult to recover the material from concentrated solutions in toluene or hexane. The novel titanium(III) silanolate derivative **21** has been fully characterized and its molecular structure has been elucidated by an X-ray diffraction study. As shown in Fig. 3 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. The Ti–O bond length in **21** is 192.7(2) pm. The ^{1}H-NMR spectrum of **21** was

in accordance with the presence of a decamethyltitanocene(III) derivative. A very broad signal ($v_{1/2} \cong 1000$ Hz) at δ 14.6 ppm could be unambiguously assigned to the pentamethylcyclopentadienyl protons. This value is in good agreement with those reported by Teuben et al. for a series of Cp$_2$TiX complexes (X = Cl, Br, I, BH$_4$, NMe$_2$, O$'$Bu, O$_2$CH) which fall in the range of 14.1–18.4 ppm. Line widths at half maximum were reported for these complexes to vary between 620 and 5000 Hz [33].

The new synthetic route using the fulvene precursor Cp*Ti(C$_5$Me$_4$CH$_2$) was also successfully employed in the preparation of a compound which can be regarded as one of the most advanced molecular models for a catalytically active titanium center on a silica surface. When Cp*Ti(C$_5$Me$_4$CH$_2$) was reacted with the monosilylated silsesquioxane precursor **14** in refluxing toluene a color change from deep purple to amber was observed. Crystallization afforded a bright yellow material which was subsequently shown to be the novel mono(pentamethylcyclopentadienyl) titanium(IV)silsesquioxane complex **22** (69% yield). Its formation is illustrated schematically in Eq. (6).

$$(6)$$
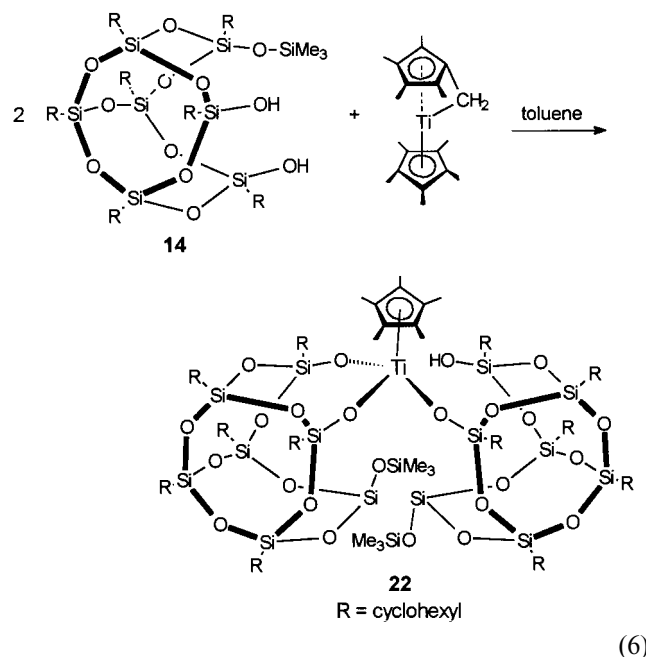
The surprising outcome of this reaction is the exclusive formation of a Cp*Ti^{IV} complex in which two silsesquioxanes are bonded in different ways to a single titanium center. In the course of the reaction one equivalent of pentamethylcyclopentadiene is eliminated (GC control). The presence of a novel titanasilsesquioxane was confirmed by an X-ray diffraction analysis (Fig. 4).

Fig. 4 clearly shows that compound **22** is an advanced and highly 'realistic' molecular model for a titanium catalyst immobilized on a silica surface. A mono(pentamethylclopentadienyl) titanium unit resides
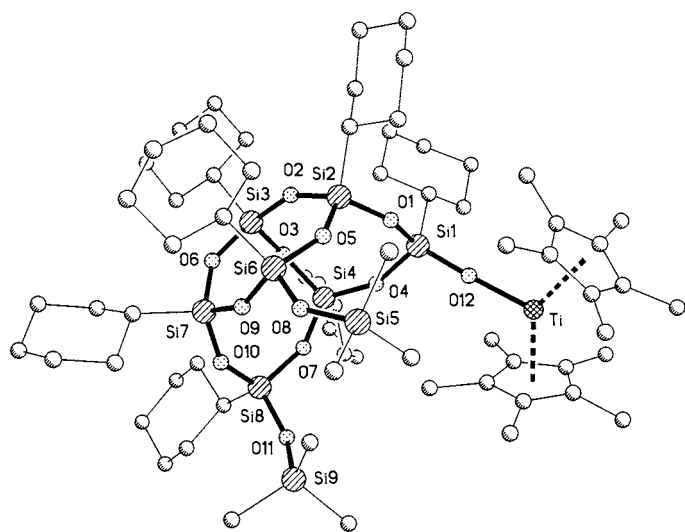

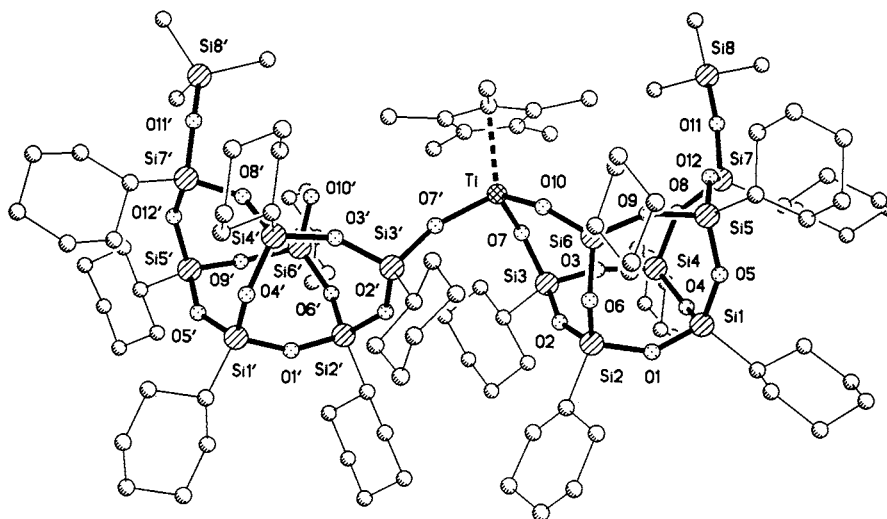
Fig. 3. Structure of **21** in the crystal. Selected interatomic distances (pm) and bond angles (°): Ti–O(12) 192.7(2), Si(1)–O(12) 159.5(2), Ti–C 241.1(3) (av.), Ti–O(12)–Si(1) 177.8(1), Si(6)–O(8)–Si(5) 146.1(1), Si(8)–O(11)–Si(9) 147.7(1).

Fig. 4. Structure of **22** in the crystal. Selected interatomic distances (pm) and bond angles (°): Ti–O7 178.9(3), Ti–O7′ 179.4(3), Ti–O10 180.5(3), Ti–C 231.7(5), Si3–O7 157.5(3), Si3′–O7′ 157.1(3), Si6–O10 158.0(3), O7–Ti–O7′ 104.3(2), O7–Ti–O10 103.9(2), O7′–Ti–O10 105.3(2), Ti–O7–Si3 148.9(2), Ti–O7′–Si3′ 162.9(2), Ti–O10–Si6 154.8(2).

on a 'model silica surface' formed by one chelating and one monodentate silsesquioxane ligand. With an average of 179.6(3) pm the three Ti–O bond lengths are practically identical. A highly unusual feature of **22** which makes this compound a particular 'realistic' model system is a silanol function in close proximity to the titanium center. Very weak hydrogen bonding interaction of this silanol group with a cage oxygen atom (C8′) apparently prevents the molecule from intermolecular protonation of the remaining Cp* ligand, thus 'taming' the reactivity of the Si–OH function. It should be noted that $^{47/49}$Ti-NMR measurements (22.56 MHz, concentrated solutions in C_6D_6, 25°C, external standard: $TiCl_4$ in C_6D_6) were attempted with all new compounds reported in this paper. All compounds except **20** could be dissolved in amounts of ca. 500 mg in 2.5 ml of C_6D_6. However, for none of the samples a signal could be detected. This negative result is in line with findings by Berger et al. who reported that of various compounds with a Ti–O bond only $Ti(O^iPr)_4$ gave a detectable $^{47/49}$Ti-NMR signal [34].

3. Conclusions

A main conclusion to be drawn from this work is the finding that various types of titanocene derivatives containing silsesquioxne ligands are accessible, albeit not always in a straightforward manner. Simple metathetical reactions involving titanocene dichlorides preferably lead to the formation of μ-oxo titanium silsesquioxanes. The 'tucked-in' fulvene complex $Cp*Ti(C_5Me_4CH_2)$ has been found to be a highly useful

precursor for the synthesis of new soluble model compounds for silica-immobilized titanium catalysts. The addition of silanol functions across the Ti–C bond of the fulvene complex should be more generally applicable to the preparation of other related titanasiloxanes.

4. Experimental

4.1. General information

4.2. Preparation of $[(Cy_7Si_7O_{12})Ti(\mu\text{-}OEt)(EtOH)]_2$ **(13)**

Neat $Ti(OEt)_4$ (0.90 ml = 0.98 g, 4.3 mmol) was added via syringe to a suspension of **1** in diethylether (80 ml). The resulting clear solution was stirred for 24 h at room temperature (r.t.). Concentration in vacuo to one half of the original volume caused a white powder of **13** to precipitate, which was isolated by filtration (1.68 g). Further concentration to a total volume of ca. 20 ml and cooling to −20°C afforded a second crop of crystalline material to give a combined yield of 3.61 g (81%), m.p. 263–265°C. No characteristic fragments were detected in the CI MS spectrum. IR (KBr, cm⁻¹): 3430 (vw, vbr), 2922 (vs), 2851 (vs), 2792 (vw), 1636 (vw), 1461 (vs), 1448 (vs), 1381 (w), 1355 (w), 1347 (w), 1327 (w), 1292 (w), 1269 (s), 1196 (vs), 1129 (vs, br), 1016 (vs, br), 939 (s), 891 (vs), 849 (s), 825 (m), 809 (w), 758 (w), 742 (m), 644 (vw), 508 (vs, br), 471 (vs). ^{1}H-NMR (C_6D_6, 25°C): δ 4.73, 4.45 (br, 6H), 2.13 (m, br, 27H), 1.79 (m, br, 28H), 1.64 (m, br, 46H), 1.31 (m, br, 46H), 1.06 (m, br, 16H). ^{13}C-NMR (C_6D_6, 25°C): δ 28.0, 27.9, 27.8, 27.5, 27.4, 27.3 (s, CH_2), 24.3, 23.9 (m, 3:4, CH), 18.4 (m, μ-ethoxide-CH_3). ^{29}Si-NMR (C_6D_6, 25°C): δ −67.2, −67.5, −68.3. Anal. Calc. for $C_{92}H_{176}O_{28}Si_{14}Ti_2$ (MW 2219.35): C, 49.8; H, 8.0. Found: C, 49.4; H, 7.6%.

4.3. Modified preparation of $[Cy_7Si_7O_{11}(OSiMe_3)]_2Ti$ **(18)**

Neat $Ti(OEt)_4$ (0.30 ml = 0.33 g, 1.38 mmol) or $Ti(O^iPr)_4$ (0.40 ml = 0.38 g, 1.35 mmol), respectively, were added via syringe to a stirred solution of **14** (3.08 g, 2.94 mmol) in diethylether (80 ml). The mixture was stirred for 72 h at r.t. and concentrated in vacuo to a total volume of ca. 20 ml. Cooling to 2°C for 12 h yielded a first crop of colorless crystals. A second portion was obtained by repeating the crystallization procedure after concentrating the mother liquid to a small volume (ca. 5 ml) to give a total yield of 2.92 g (96%, based on $Ti(OEt)_4$) or 2.81 g (97%, based on $Ti(O^iPr)_4$), respectively. M.p. 369.3–371.0°C. MS: (EI, 65 eV, 300°C): 2133 (M⁺, 100%), 2052 (M⁺−C_6H_{11}, 30%), 1090 ($C_{45}H_{86}O_{12}Si_8Ti$, 5%). IR (KBr, cm⁻¹): 2923 (vs), 2850 (vs), 1636 (vw), 1448 (s), 1355 (vw), 1347 (vw), 1327 (vw), 1268 (m), 1251 (m), 1197 (s), 1111 (vs, br), 1038 (s), 999 (m), 922 (vs), 893 (vs), 848 (s), 826 (m), 756 (m), 704 (vw), 637 (w), 510 (m), 464 (m). ^{1}H-NMR (C_6D_6, 25°C): δ 2.16 (m, br, 28H, Cy–CH_2), 1.77 (m, br, 70H, Cy–CH_2), 1.24 (m, br, 56H, Cy–CH_2, Cy–CH), 0.51 (s, 18H, OSiMe₃). ^{13}C-NMR (C_6D_6, 25°C): δ 28.2–27.3 (m, Cy–CH_2), 25.7–23.9 (m, Cy–CH), 2.5 (s, OSiMe₃). ^{29}Si-NMR (C_6D_6, 25°C): δ 10.4 (OSiMe₃); −66.4, −66.8, −66.9, −68.3, −69.3, −69.5, −69.8 (equal intensity). Anal. Calc. for $C_{90}H_{172}O_{24}Si_{16}Ti$ (2135.59): C, 50.6; H, 8.1. Found: C, 50.6; H, 8.1%.

4.4. Preparation of $(\mu\text{-}O)[\{Cy_7Si_7O_{11}(OSiMe_3)\}TiCp]_2$ **(19)**

A solution of Cp_2TiCl_2 (0.48 g, 1.93 mmol) in toluene (40 ml) was mixed with a solution of **14** (2.00 g, 1.91 mmol) in toluene (50 ml), triethylamine (0.60 ml = 0.44 g, 4.33 mmol) was added via syringe, and the reaction mixture was stirred at r.t. Within 1 h a color change from brick–red to orange–yellow was observed. Stirring was continued for 3 days, whereupon the precipitation of a powdery yellow precipitate was observed. This material (0.46 g) was removed by filtration. The clear red filtrate was concentrated in vacuo to a total volume of 20 ml. Slow cooling to −20°C afforded 1.65 g (74%) **19** in the form of orange block-like crystals. M.p. 325°C (dec.). IR (KBr, cm⁻¹): 3435 (w), 2922 (vs), 2849 (vs), 1625 (vw), 1448 (s), 1346 (vw), 1326 (vw), 1262 (s), 1196 (s), 1108 (vs), 1014 (vs), 944 (m), 895 (s), 847 (s), 804 (vs), 755 (m), 694 (w), 661 (w), 643 (w), 617 (vw), 575 (w), 516 (s), 499 (m), 455 (s), 414 (m). ^{1}H-NMR (C_6D_6, 25°C): δ 6.06 (s, 10H, Cp), 2.18 (m, br, 31H, Cy–CH_2), 1.74 (m, br, 68H, Cy–CH_2), 1.33 (m,br, 41H, Cy–CH_2), 1.03 (m, br, 14H, Cy–CH), 0.14 (s, 18H, OSiMe₃). ^{13}C-NMR (C_6D_6, 25°C): δ 117.1 (Cp–CH), 28.5–27.3 (m, Cy–CH_2), 26.2, 26.1, 25.5, 24.2, 24.1 (1:2:2:1:1, s, Cy–CH), 9.3 (s, OSiMe₃). ^{29}Si-NMR (C_6D_6, 25°C): δ 8.0 (OSiMe₃); −66.3, −66.8, −66.9, −67.3, −69.2 (intensity 1:2:1:1:2). Anal. Calc. for $C_{100}H_{182}O_{25}Si_{16}Ti_2$ (2329.66): C, 51,6; H, 7,9. Found: C, 51,9; H, 7,4%.

4.5. Preparation of $Cp_2^*Ti_3O_3[Cy_7Si_7O_{11}(OSiMe_3)]_2$ **(20)**

A solution of $Cp_2^*TiCl_2$ (1.12 g, 2.88 mmol) in toluene (40 ml) was mixed with a solution of **14** (2.01 g, 1.92 mmol) in toluene (50 ml), and triethylamine (0.60 ml = 0.44 g, 4.33 mmol) was added via syringe. After stirring for 14 days at r.t. a powdery yellow precipitate was removed by filtration and the clear filtrate was concentrated in vacuo to one-half of the original volume. After standing for several days at 20°C, 0.93 g of (38%) **20** was isolated as well-formed dark red crystals. M.p. ca. 260°C (dec.). Further concentration of the supernatant solution followed, cooling afforded only yellow amorphous material which could not be fully characterized. IR (KBr, cm⁻¹): 3432 (m), 2923 (vs), 2850 (s), 1629 (vw), 1448 (w), 1380 (vw), 1262 (w), 1197 (m), 1104 (vs, br), 987 (s), 917 (w), 895 (w), 846 (m), 824 (w), 809 (vw), 753 (w), 697 (m, br), 648 (w), 619 (w), 573 (w), 516 (m), 501 (m), 458 (m), 421 (w), 410 (w). ^{1}H-NMR (CDCl₃, 25°C): δ 2.09 (s, 30H, Cp*–CH_3), 1.75 (m, br, 60H, Cy–CH_2), 1.25 (m, br, 74H, Cy–CH_2), 0.80 (m, br, 20H, Cy–CH_2, Cy–CH), 0.15 (s, 18H, OSiMe₃). Anal. Calc. for $C_{110}H_{202}O_{27}Si_{16}Ti_3$ (2549.86): C, 51.8; H, 8.0. Found: C, 53.0; H, 8.1%.

4.6. Preparation of Cp*₂Ti[Cy₇Si₇O₁₀(OSiMe₃)₂] (21)

A solution of **15** (1.00 g, 0.89 mmol) and Cp*Ti(C₅Me₄CH₂) (0.28 g, 0.89 mmol) in toluene (50 ml) was stirred for 24 h at r.t. and heated to reflux for another 2 h. The resulting green solution was concentrated in vacuo to ca. 25 ml and cooled to −20°C to give 0.21 g (16%) of **21** as dark green air-sensitive crystals. M.p. 294°C. IR (KBr, cm⁻¹): 3435 (w), 2918 (vs), 2850 (vs), 2793 (vw), 1627 (vw), 1448 (s), 1380 (vw), 1355 (vw), 1347 (vw), 1327 (vw), 1293 (vw), 1269 (s), 1197 (vs, br), 1115 (vs), 1039 (vs), 1027 (vs), 999 (vs), 939 (vs), 893 (vs), 849 (s), 826 (m), 746 (s, br), 701 (w, sh), 630 (vw), 577 (w), 509 (vs), 468 (s), 407 (s). ^{1}H-NMR (CDCl₃, 25°C): δ 14.6 (br, $v_{1/2} \cong 1000$ Hz, C₅Me_5), 2.2–0.4 (m br, 95H, Cy–CH₂, Cy–CH, OSiMe₃). A ^{13}C-NMR spectrum could not be recorded because of strong broadening of the signals due to the presence of paramagnetic Ti³⁺. Anal. Calc. for C₆₈H₁₂₅O₁₂Si₉Ti (1435.38): C, 56,9; H, 8.8. Found: C, 56.0; H, 8.7%.

4.7. Preparation of Cp*Ti[Cy₇Si₇O₁₁(OSiMe₃)]-[Cy₇Si₇O₁₀(OH)(OSiMe₃)] (22)

A brown–green solution containing **14** (1,04g, 0,99 mmol) and Cp*Ti(C₅Me₄CH₂) (0,33g, 1,04 mmol) in toluene (50 ml) was stirred for 24 h at r.t. and heated under reflux for another 2 h, whereby a color change to amber was observed. The resulting solution was concentrated in vacuo to ca. 20 ml and slowly cooled to −20°C to give 0.78 g (69%) of **22** in the form of bright yellow crystals. M.p. 248–252°C. IR (KBr, cm⁻¹): 2923 (vs), 2850 (s), 1448 (w), 1255 (vw), 1261 (w), 1197 (w), 1109 (vs), 1039 (s), 1027 (m), 940 (s), 896 (m), 847 (m), 825 (w), 755 (vw), 694 (vw), 619 (vw), 516 (w), 502 (w), 456 8w), 418 (w). ^{1}H-NMR (CDCl₃, 25°C): δ 2.97 (s, 1H, Si–OH), 2.43 (s, 15H, C₅Me_5), 2.17 (m, br, 32H, Cy–CH₂), 1.77 (m, br, 69H, Cy–CH₂), 1.36 (m, br, 39H, Cy–CH₂), 1.07 (m, br, 14H, Cy–CH), 0.36 (s, 9H, OTMS), 0.33 (s, 9H, OTMS). ^{13}C-NMR (C₆D₆, 25°C): δ 127.4 (C₅Me_5), 28.8-27.3 (m, Cy–CH₂), 26.5–23.9 (m, Cy–CH), 12.9 (C₅Me_5), 2.5 (OSiMe₃), 2.3 (OSiMe₃). ^{29}Si-NMR (C₆D₆, 25°C): δ 9.6, 7.9 (OSiMe₃); −66.3 to −69.1 (m). Anal. Calc. for C₁₀₀H₁₈₇O₂₄Si₁₆Ti (2270.82): C, 52,9; H, 8.3. Found: C, 53.4; H, 8.3%.

4.8. Crystal structure determinations (cf. Table 1)

All measurements were performed on a Brucker CCD system with Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) and graphite monochromator. Selected crystals of **13**, **29**, **21**, and **22** were coated with mineral oil, mounted on a glass fibre and transferred to the cold nitrogen stream (Siemens LT-2 attachment). Full hemispheres of the reciprocal space were scanned by ω in three sets of frames of 0.3°. As an absorption correction the SAD-ABS routine was applied. The crystal structures were solved by direct methods (SHELXS-86 for **13**, SHELXS-97 for **20**, **21**, and **22**). For structure refinement the program SHELXL 97 was used [37,38]. For **20** the absolute structures could be determined with $x = 0.10(5)$.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 142020 for compound (**13**), CCDC no. 142018 for compound (**20**), CCDC no. 142017 for compound (**21**), and CCDC no. 142019 for compound (**22**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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