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Dihydroxyoligosilanes as novel ligands in coordination chemistry—first synthesis of 2,5-dioxa-3,4-disilatitanacyclopentanes

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Abstract

The reaction of two equivalents of $(Me_3Si)_2RSi{-}K \times 3THF$ (**1** R = $SiMe_3$, **2** R = Ph) with $Cl_2MeSi{-}SiMeCl_2$, followed by hydrolysis in the presence of $NH_4(NH_2COO)$ leads to the formation of the dihydroxyoligosilanes MeR(HO)Si–Si(OH)RMe [**4** R = $Si(SiMe_3)_3$, **6** R = $Si(SiMe_3)_2Ph$] as diastereomeric mixtures. Addition of two equivalents of *n*-BuLi to the diastereomerically pure ligands (*meso*)-**4/6** and (*rac*)-**4/6**, respectively, and subsequent treatment with Cp_2TiCl_2 yields the (*Z*) and (*E*) arranged five-membered rings $(MeRSi{-}O)_2TiCp_2$ [**7** R = $Si(SiMe_3)_3$, **8** R = $Si(SiMe_3)_2Ph$], respectively. The crystal structures of the ligand (*rac*)-**6** as well as of the titanacycles (*E*)-**8** and (*Z*)-**7** are reported.

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Keywords: Silicon; Titanium; Titanacycles; Dihydroxydisilanes; Hexasilanes

1. Introduction

The chemistry of transition metal siloxide complexes containing Si–O–M linkages has continued to attract considerable attention in the field of material science [1] and catalysis [2], particularly over the last 20 years. The synthesis, reactivity, and bonding of such complexes in a wide variety of supporting ligand environments continues to be explored. In this regard numerous silanediols, disilanols and silanetriols have been described in the literature [3], which could be used as building blocks for the preparation of novel titanium containing heterocubanes and titanasiloxanes [3b,4]. For example, Feher et al. reported the synthesis of incompletely condensed polyhedral oligosilasesquioxanes (POSS) bearing three free Si–OH groups [5]. This class of polydentate ligands has been extensively exploited as a source for the generation of a wide variety of metallasiloxanes with different coordination geometries [6].

Our interest in this area lies mainly in the development of well defined new transition metal complexes using novel bidentate ligands on the basis of oligosilanes which possess two silanol functionalities. Of special interest are compounds in which the hydroxy groups are fixed at different silicon atoms along the oligosilane chain. Due to their high condensation tendency only some of those derivatives, namely α,ω-dihydroxyoligosilanes, have been prepared and for a few of those compounds the X-ray crystal structures were reported [7]. The coordination chemistry of these compounds that might be of interest as ligands for the construction of chelate complexes with different ring sizes is relatively unknown [8]. In context with studies concerning the electronic influence of the silicon backbone on the structure and reactivity of polyhydroxyoligosilanes, we report herein the synthesis of dihydroxyoligosilanes of the type MeR(HO)Si–Si(OH)RMe [R = $Si(SiMe_3)_3$, $Si(SiMe_3)_2Ph$]. With the aim of exploring the complex chemistry of these disiloxide ligands, some novel dioxadisilatitanacyclopentanes have been synthesized and structurally characterized.

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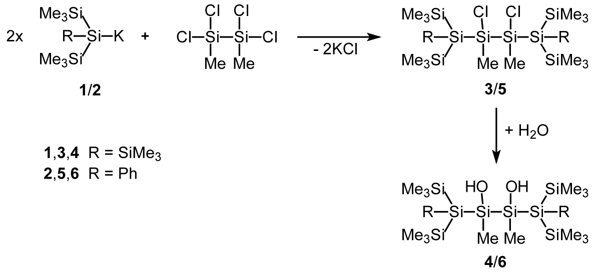
2. Results and discussion

2.1. Synthesis of the ligands MeR(HO)Si–Si(OH)RMe

As mentioned above, simple 1,2-dihydroxydisilanes are proven to be unstable due to their high condensation tendency. Therefore, the aim was to synthesize 1,2-dihydroxydisilanes, in which each of this two Si–OH units are surrounded by sterically demanding substituents, preventing condensation reactions. Our strategy for preparing this class of compounds involved the selective 1,2-linkage of two equivalents of bulky silylpotassium derivatives with $Cl_2MeSi{-}SiMeCl_2$, followed by hydrolyses of the two retained Si–Cl units.

In fact, the hexasilanes **3**–**6** were synthesized according to the procedure outlined in Scheme 1. $(Me_3Si)_3Si{-}K \times 3THF$ was reacted with $Cl_2MeSi{-}SiMeCl_2$ in pentane at −78 °C to yield the dichlorohexasilane **3** exclusively. Finally, without isolation **3** was hydrolyzed in an aqueous solution of $NH_4(NH_2COO)$ to give the 1,2-dihydroxyhexasilane **4** consistent with a 1:1 mixture of (*rac*)-**4** and (*meso*)-**4** as determined by ^{1}H-NMR analysis. After column chromatographic separation of the mixture, (*rac*)-**4** and (*meso*)-**4** could be obtained in an overall yield of 39 and 41%. By analogy with the preparation and separation of **4**, the phenyl substituted 1,2-dihydroxyhexasilanes (*rac*)-**6** and (*meso*)-**6** (2:1 mixture) were isolated in an overall yield of 53 and 27%.



Scheme 1. Synthesis of the dihydroxyhexasilanes **3**–**6**.

The hexasilanes **3**–**6** are air-stable colourless solids and the proposed structures are in full agreement with the straightforward NMR spectra as well as the IR and the MS data. In the ^{1}H-NMR spectra as well as in the ^{13}C-NMR spectra of **4** only one signal was found for the $SiMe_3$ groups, and also the ^{29}Si-NMR spectra show only one signal for the $SiMe_3$ silicon atoms. In comparison to this NMR spectra of **6** exhibit two signals for the diastereotopic $SiMe_3$ groups, respectively.

In addition, the molecular structure of (*rac*)-**6** has been derived from X-ray diffraction data. Single crystals suitable for an X-ray structure analysis were grown from nitromethane at room temperature. The central silicon atoms show a slightly distorted tetrahedral configuration with Si–Si–Si bond angles being 110.24(9) and 112.75(9)°. The Si–Si bond lengths lie unremarkably within the range of 2.355–2.360 Å. The Si–O bond lengths amount to 1.673(5) Å (Si3–O1) and 1.682(4) Å (Si4–O2) which are longer than the corresponding Si–O distance of approximately 1.66 Å in 1.2-dihydroxytetramethyldisilane [7b]. The results of the X-ray analysis give a good idea on the steric congestion in the molecules and reveal that the two hydroxy groups are fully enclosed by the two $(Me_3Si)_2PhSi$ substituents. The conformation of (*rac*)-**6** is predominantly determined by the steric repulsion of the two bulky $(Me_3Si)_2PhSi$ substituents, while the two hydroxy groups are playing a minor role (Fig. 1). The arrangement gives a roughly eclipsed conformation of the silicon backbone at the two

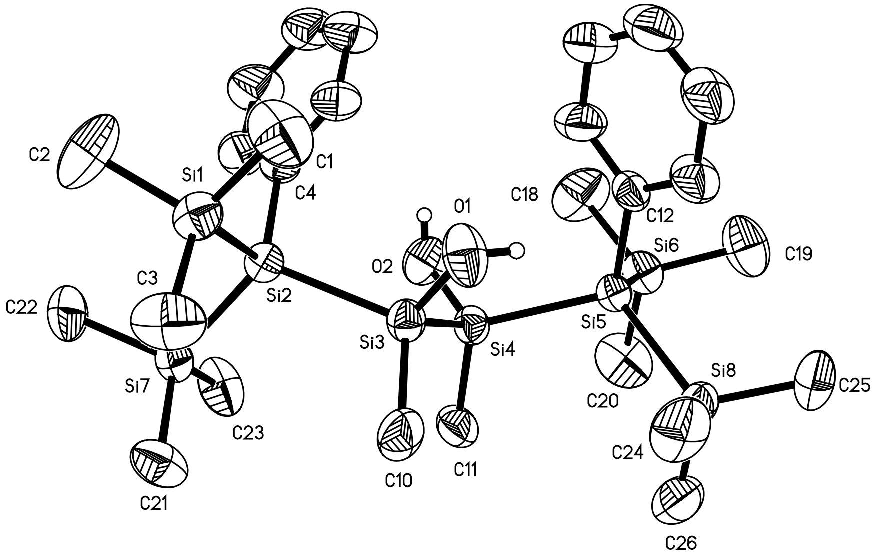


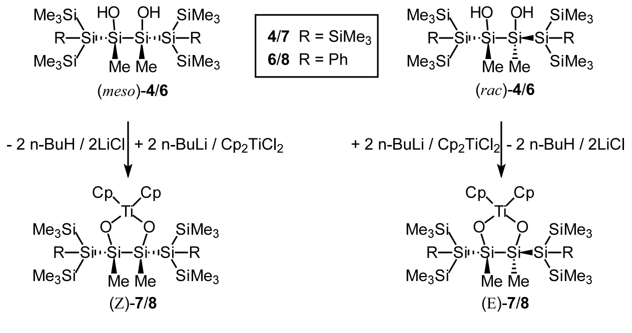
Fig. 1. Molecular structure of (*rac*)-**6** in the crystal (ORTEP, 30% probability level, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Si3–O1 1.673(5), Si4–O2 1.682(4), Si3–Si4 2.365(2), Si2–Si3 2.358(2), Si4–Si5 2.359(2), Si3–C10 1.845(6), Si4–C11 1.828(6), Si5–C12 1.885(6), Si2–C4 1.891(6), Si2–Si3–Si4 110.24(9), Si5–Si4–Si3 112.75(9), O1–Si3–Si4 110.83(18), O2–Si4–Si3 110.2(2), C10–Si3–Si4 110.4(3), C11–Si4–Si3 109.0(2), O1–Si3–Si4–O2 99.2(3), Si2–Si3–Si4–O2 20.8(2), C10–Si3–Si4–C11 25.8(4), O1–Si3–Si4–Si5 22.3(3), Si2–Si3–Si4–Si5 142.24(9).

central silicon atoms; the dihedral angles were found to be 142.24(9)° (Si2–Si3–Si4–Si5) and 99.2(3)° (O1–Si3–Si4–O2). Thus, it is not unexpected that (*rac*)-**6** realizes neither intermolecular hydrogen bonds in the solid state as observed for the 1.2-dihydroxytetra-methyldisilane reported by Kelling et al. [7b].

2.2. *Synthesis and characterization of the dioxadisilatitanacyclopentanes 7 and 8*

The dioxadisilatitanacyclopentanes **7** and **8** were synthesized according to the procedure outlined in Scheme 2. Deprotonation of the diastereomerically pure 3.4-dihydroxyhexasilanes **4/6** by equimolar amounts of *n*-BuLi in heptane solutions selectively afforded white powders of the corresponding dilithium salts. Reactions of toluene solutions of the dilithium salts with titanocenedichloride in toluene at −78 °C proceed selectively, providing the corresponding complexes **7/8** in excellent yields (Scheme 2). **7/8** are soluble in common organic solvents (heptane, pentane, THF and ether) and form red–orange crystals which are stable on air but decompose slowly in solution.

The proposed structures of the titanacycles **7/8** were confirmed by NMR and MS data and were in full agreement with the results of an X-ray crystal structure analysis. The NMR (^{1}H, ^{13}C, ^{19}Si) spectra of **7/8** are rather straightforward and show roughly the same features as observed for the corresponding ligands **4** and **6**. The ^{1}H-NMR spectra of (*E*)-**7**/(*E*)-**8** show one singlet and of (*Z*)-**7**/(*Z*)-**8** show two singlets for the protons of the cyclopentadienyl groups. For the complexes, the ^{29}Si-NMR spectra display three resonances for **7** and four resonances for **8**, due to the two diastereotopic $SiMe_3$ groups. The ^{29}Si-NMR spectroscopy proves to be a very useful tool for the characterization of the complexes, as the differences in chemical shift are large enough to distinguish between bonded and unbonded ligands. For example, the signals for the cyclic silicon atoms are significantly shifted to lower field [(*Z*)-**7** $\delta = 52.6$, (*E*)-**7** $\delta = 52.4$, (*Z*)-**8** $\delta = 48.9$, (*E*)-**8** $\delta = 49.5$] in comparison to that of the 1.2-dihydroxyhexasilanes (*meso*)-**4** ($\delta = 18.4$), (*rac*)-**4** ($\delta = 20.1$), (*meso*)-**6** ($\delta = 15.3$) and (*rac*)-**6** ($\delta = 16.9$).



Scheme 2. Synthesis of the titanacycles **7/8**.

The solid state structures of (*Z*)-**7** and (*E*)-**8** were investigated by single crystal X-ray diffraction. Single crystals suitable for an X-ray structure analysis were grown from pentane at 0 °C. A perspective view of the molecular structures of (*Z*)-**7** and (*E*)-**8** is shown in Figs. 2 and 3.

In complex (*E*)-**8**, the tetrahedrally surrounded titanium atom is bonded in a chelate fashion to both siloxide groups of the ligand, giving a nearly planar five-membered ring. The roughly eclipsed conformation of the substituents at the two ring silicon atoms is comparable to that found in the dihydroxyhexasilane (*rac*)-**6**. The geometry around the titanium atom is described best as distorted tetrahedral, with a Cp–Ti–Cp (centroid) angle of 129.5° and a O1–Ti1–O2 chelate angle of 91.05(9)°. The Ti1–O1 [1.886(2) Å] and Ti1–O2 [1.881(2) Å] bond lengths are considerably longer than those found in other related Si–O–Ti complexes. Of course, as a consequence of the five-membered ring formation the Si3–O1–Ti1 [127.83(12)°] and Si1–O2–Ti1 [128.40(12)°] bond angles are remarkably smaller than values observed for linear complexes containing Si–O–Ti units. The geometry around the two ring-silicon atoms is also strongly distorted tetrahedral with small Si–Si–O bond angles being 94.25(9)° and 95.06(9)° and remarkably widened central Si–Si–Si angles being 121.99(5)° and 125.82(5)°. The Si1–O2 [1.637(2) Å] and Si3–O1 [1.644(2) Å] bond lengths of (*E*)-**8** are somewhat shorter than those found in the dihydroxyhexasilane (*rac*)-**6**. Due to the space demand of the $(Me_3Si)_2PhSi$ substituents and the ring strain in the titanacycle the central Si1–Si3 bond [2.3908(14)Å] is elongated.

As the most interesting result the structural analysis of (*Z*)-**7** revealed that the two $(Me_3Si)_3Si$ substituents adopt a *Z* position. Nevertheless, the structural feature of the titanacycle in (*Z*)-**7** is quite similar to that in (*E*)-**8**. Only the Si1–O1–Ti1 [129.18(13)°] and Si2–O2–Ti1 [130.78(13)°] angles of (*Z*)-**7** are somewhat larger than those found in (*E*)-**8**. Interestingly, the spatial demand of the two extended hemispherical $(Me_3Si)_3Si$ groups leads to a significant elongation of the Si–Si bonds [Si2–Si4 2.3933(16) Å; Si1–Si3 2.3898(16) Å] and an extreme widening of the Si–Si–Si angles to values of 136.84(6)° and 136.29(6)°. Moreover, the Si1–Si2 distance [2.4404(15) Å] is remarkably longer than the value observed for (*E*)-**8** [Si1–Si3, 2.3908(14) Å], presumably due to the high steric congestion of the $(Me_3Si)_3Si$ substituents, which adopt a (*Z*)-position.

In summary, it should be stated that in both complexes relatively long Ti–O and short Si–O distances as well as small Ti–O–Si bond angles allow only weak oxygen p_π–d_π donation of both siloxide groups to the titanium centre. Interestingly, the values of the O–

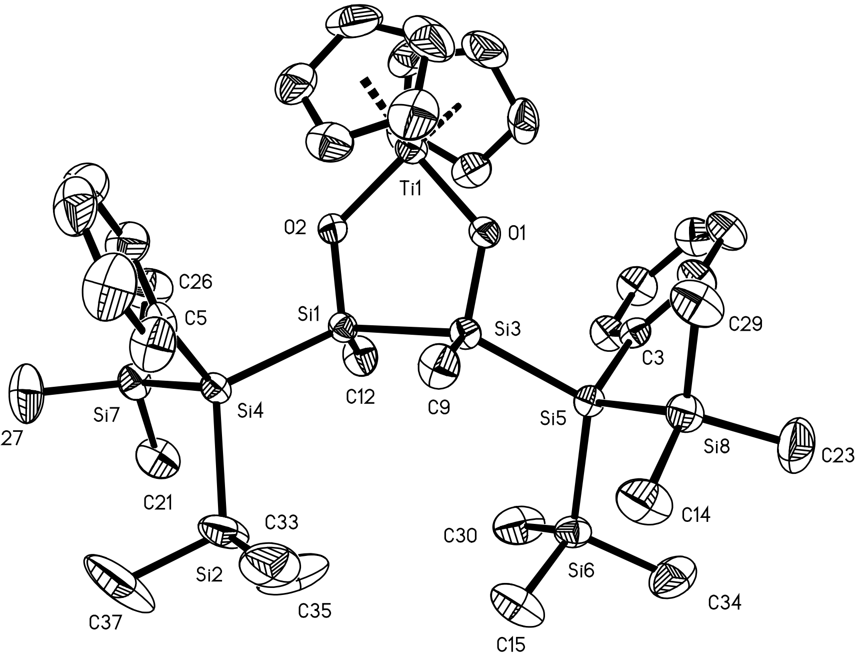


Fig. 2. Molecular structure of (*E*)-**8** in the crystal (ORTEP, 30% probability level, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ti1–O1 1.886(2), Ti1–O2 1.893(2), Si1–O2 1.637(2), Si3–O1 1.644(2), Si1–Si3 2.3908(14), Si1–Si4 2.3773(14), Si3–Si5 2.3794(14), O1–Ti1–O2 91.05(9), O2–Si1–Si3 94.25(9), O1–Si3–Si1 95.06(9), Si3–O1–Ti1 127.83(12), Si1–O2–Ti1 128.40(12), Si5–Si3–Si1 125.82(5), Si4–Si1–Si3 121.99(5), O2–Si1–Si3–O1 16.13(11), Si1–Si3–O1–Ti1 15.43(15), O2–Ti1–O1–Si3 8.06(16), Si3–Si1–O2–Ti1 16.81(15), O1–Ti1–O2–Si1 10.08(17).

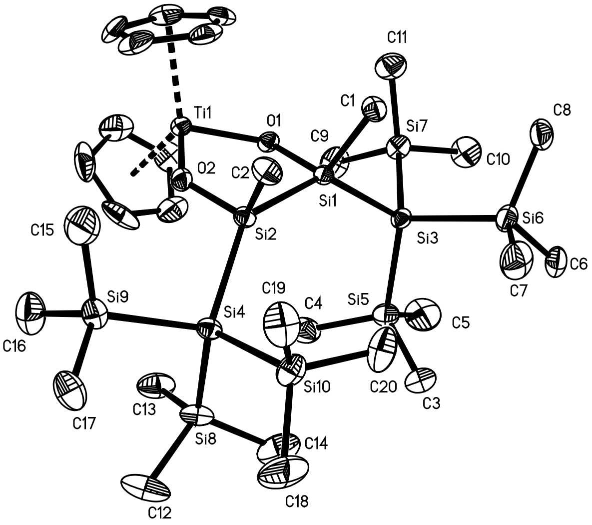


Fig. 3. Molecular structure of (*Z*)-**7** in the crystal (ORTEP, 30% probability level, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ti1–O1 1.886(2), Ti1–O2 1.881(2), Si1–O1 1.652(2), Si2–O2 1.644(3), Si1–Si2 2.4404(15), Si2–Si4 2.3933(16), Si1–Si3 2.3898(16), O2–Ti1–O1 90.66(10), O1–Si1–Si2 94.40(9), O2–Si2–Si1 93.76(9), Si1–O1–Ti1 129.18(13), Si2–O2–Ti1 130.78(13), Si3–Si1–Si2 136.84(6), Si4–Si2–Si1 136.29(6), O1–Si1–Si2–O2 5.20(13), Si2–Si1–O1–Ti1 11.95(17), O2–Ti1–O1–Si1 12.49(18), O1–Ti1–O2–Si2 6.52(19), Si1–Si2–O2–Ti1 1.40(18).

Ti–O, Ti–O–Si and O–Si–Si bond angles are similar to those found in the five-membered and isoelectronic dithia [9] and diaza [10] titanium complexes. The dithia cycle adopts a half-chair conformation with bond angles S–Ti–S = 93.9(2)°, Ti–S–Si = 113.2(2)°, 109.7(2)° and S–Si–Si = 99.0(2)°, 100.9(2)°, whereas the diaza one has an envelope conformation: N–Ti–N = 100.2(3)°, Ti–N–Si = 119.0(4)°, 118.0(4)° and N–Si–Si = 99.5(3)°, 98.2(3)°. However, these are the only other structurally characterized compounds with comparable ring structures [11].

2.3. Conclusions

We have prepared diastereomerically pure hexasilanes **4** and **6** containing two vicinal hydroxy groups which are surrounded by sterically demanding substituents. These chelate ligands react cleanly with Cp_2TiCl_2 to give the (*Z*) and (*E*) configurated dioxadisilatitanacyclopentanes **7** and **8** in high yields. The X-ray structural analysis of the complexes (*Z*)-**7** and (*E*)-**8** revealed nearly planar but strained geometries of the five-membered ring structures. Despite the extensive shielding of the two Si–OH functions, the ligands **4** and **6** are proven to be reactive, and their complex behaviour towards early transition metals is the subject of current studies.

3. Experimental

3.1. General procedures and materials

All reactions involving organometallic reagents were carried out under an atmosphere of Ar using standard

Schlenk techniques. 1,2-Dimethyl-1,1,2,2-tetrachlorodisilane [12], tris(trimethylsilyl)silylpotassium × 3THF (**1**) and phenylbis(trimethylsilyl)silyl-potassium × 3THF (**2**) were prepared as previously described [13]. NMR: Bruker AC 250, Bruker ARX 300, Bruker ARX 400 (250, 62.9, 79.5 and 235.3 MHz, for ^{1}H, ^{13}C and ^{29}Si respectively). For ^{1}H-, ^{13}C- and ^{29}Si-NMR, benzene-d_6 as solvent, Me_4Si as internal standard. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402, chemical ionization with isobutane as the reactant gas.

3.2. *Synthesis of the dichlorohexasilanes **3** and **5***

3.2.1. *General procedure*

To a solution of 40 mmol tris(trimethylsilyl)silylpotassium × 3THF (**1**) and phenyl-bis(trimethylsilyl)silylpotassium × 3THF (**2**) in 200 ml of pentane, respectively, were added 20 mmol of 1,2-dimethyl-1,1,2,2-tetrachlorodisilane at -78 °C. Stirring was continued for 1 h and the mixture was allowed to warm up to room temperature (r.t.) within 2 h. After filtration of the reaction mixture, the solvent was removed under reduced pressure. Drying in the vacuum (10^{-2} mbar, 70 °C) yielded white powders, respectively, consistent with a 1.3:1 diastereomeric mixture of **3** and a 10:1 diastereomeric mixture of **5**, as determined by ^{1}H-NMR analysis.

3.2.2. *3,4-Dichloro-1,1,1,3,4,6,6,6-octamethyl-2,2,5,5-tetrakis(trimethylsilyl)hexasilane (**3**)*

Raw **3** was suspended in cold acetonitrile and filtered off, yield 11.2 g (86%). m.p. 245–250 °C. ^{1}H-NMR: $\delta =$ 1.06, 0.85 (2s, SiMeCl, 6H), 0.39, 0.38 (2s, $SiMe_3$, 54H). ^{13}C-NMR: $\delta = 6.9$, 6.6 (SiMeCl), 3.4, 3.3 ($SiMe_3$). ^{29}Si-NMR: $\delta = -119.6$, -120.1 ($\underline{Si}SiMe_3$), 22.3, 19.9 (SiMeCl), -9.3, -9.4 ($SiMe_3$). MS: (CI) *m/z* (%) = 652 (12) [M^+], 637 (55) [$M^+ - Me$], 615 (95) [$M^+ - Cl$], 290 (100) [$SiMeSi(SiMe_3)_3$]; exact mass calc. for $C_{19}H_{57}Si^{35}_{10}Cl_2$ 635.1530; found 635.1540. Anal. Calc. for $C_{20}H_{60}Si_{10}Cl_2$, (652.46): C, 36.82; H, 9.27. Found: C, 34.79; H, 8.98%.

3.2.3. *3,4-Dichloro-2,5-diphenyl-1,1,1,3,4,6,6,6-octamethyl-2,5-bis(trimethylsilyl)hexasilane (**5**)*

Raw **5** was suspended in cold acetonitrile and filtered off, yield 10.55 g (80%). m.p. 124 °C. ^{1}H-NMR: $\delta =$ 7.80–7.63, 7.19–7.10 (2m, phenyl, 10H), 1.05, 0.63 (2s, SiMeCl, 6H), 0.43, 0.31, 0.38, 0.34 (4s, $SiMe_3$, 2 × 18H). ^{13}C-NMR: $\delta = 137.4$, 133.2, 128.7, 128.3 (C-aromat.), 3.7 (SiMeCl), 1.8, 1.5 ($SiMe_3$). ^{29}Si-NMR: $\delta = -68.8$ (SiPh), 16.3 (SiMeCl), -10.9, -12.9 ($SiMe_3$). MS: (CI) *m/z* (%) = 660 (12) [M^+], 645 (30) [$M^+ - Me$], 623 (100) [$M^+ - SiMe_3$]. Anal. Calc. for $C_{26}H_{52}Cl_2Si_8$, (660.29): C, 47.30; H, 7.94. Found: C, 47.05; H, 7.79%.

3.3. *Hydrolysis of the dichlorohexasilanes **3** and **5***

3.3.1. *General procedure*

Without isolation, the crude products **3** and **5**, prepared as described above, were dissolved in 200 ml of ether and added to 40 ml (1 M) of an aqueous solution of $NH_4(NH_2COO)$ and 100 ml of water. The mixture was vigorously stirred at r.t. After 3 days the organic phases were separated, dried with $MgSO_4$, and evaporated. Drying in the vacuum (10^{-2} mbar, 70 °C) yielded white powders consistent with a 1:1 diastereomeric mixture of **3** and a 2:1 diastereomeric mixture of **5**, respectively, as determined by ^{1}H-NMR analysis. The mixtures were purified and separated as described below.

4: The residue was separated by column chromatography on silica gel (heptane–EtOAc = 100/1) to give over all 5.05 g of (*meso*)-**4** (41%) and 4.75 g of (*rac*)-**4** (39%).

3.3.2. *(meso)-3,4-Dihydroxy-1,1,1,3,4,6,6,6-octamethyl-2,2,5,5-tetrakis(trimethylsilyl)hexasilane (**4**)*

M.p. 213–214 °C. IR (nujol) $\tilde{\nu} = 3670.7$ cm^{-1} (OH). ^{1}H-NMR: $\delta = 0.70$ (s, OH, 2H), 0.83 (s, SiMeOH, 6H), 0.35 (s, $SiMe_3$, 54H). ^{13}C-NMR: $\delta = 7.2$ (SiMeOH), 3.5 ($SiMe_3$). ^{29}Si-NMR: $\delta = -128.9$ ($\underline{Si}SiMe_3$), 18.3 (SiMeOH), -9.9 ($SiMe_3$). MS: (CI) *m/z* (%) = 614 (35) [M^+], 597 (70) [$M^+ - OH$], 541 (50) [$M^+ - SiMe_3$], 351 (100) [$M^+ - OSi(SiMe)_3$]; exact mass calc. for $C_{20}H_{62}Si_{10}O_2$ 614.2443; found 614.2467. Anal. Calc. for $C_{20}H_{62}O_2Si_{10}$, (615.57): C, 39.02; H, 10.15. Found: C, 38.47; H, 9.89%.

3.3.3. *(rac)-3,4-Dihydroxy-1,1,1,3,4,6,6,6-octamethyl-2,2,5,5-tetrakis(trimethylsilyl)hexasilane (**4**)*

M.p. 217–218 °C. IR (nujol) $\tilde{\nu} = 3668.2$ cm^{-1} (OH). ^{1}H-NMR: $\delta = 1.02$ (s, OH, 2H), 0.67(s, SiMeOH, 6H), 0.36 (s, $SiMe_3$, 54H). ^{13}C-NMR: $\delta = 5.8$ (SiMeOH), 3.3 ($SiMe_3$). ^{29}Si-NMR: $\delta = -129.1$ ($\underline{Si}SiMe_3$), 20.1 (SiMeOH), -9.9 ($SiMe_3$). MS: (CI) *m/z* (%) = 614 (40) [M^+], 597 (33) [$M^+ - OH$], 541 (99) [$M^+ - SiMe_3$], 351 (100) [$M^+ - OSi(SiMe)_3$]; exact mass calc. for $C_{20}H_{62}Si_{10}O_2$ 614.2443; found 614.2391. Anal. Calc. for $C_{20}H_{62}O_2Si_{10}$, (615.57): C, 39.02; H, 10.15. Found: C, 38.00; H, 9.88%.

6: The residue was separated by column chromatography on silica gel (heptane–EtOAc = 50/1) to give over all 3.32 g of (*meso*)-**6** (27%) and 6.63 g of (*rac*)-**6** (53%).

3.3.4. *(meso)-3,4-Dihydroxy-2,5-diphenyl-1,1,1,3,4,6,6,6-octamethyl-2,5-bis(trimethylsilyl)hexasilane (**6**)*

M.p. 76 °C. IR (nujol) $\tilde{\nu} = 3666.1$ and 3596.2 cm^{-1} (OH). ^{1}H-NMR: $\delta = 0.63$ (s, OH, 2 H), 7.74–7.70, 7.21–7.07 (2m, phenyl, 10H), 0.50 (s, SiMeOH, 6H), 0.35, 0.30 (2s, $SiMe_3$, 2 × 18H). ^{13}C-NMR: $\delta = 137.1$, 135.6, 128.4, 128.3 (C-aromat.), 4.6 (SiMeOH), 1.7, 1.4 ($SiMe_3$). ^{29}Si-NMR: $\delta = -73.8$ (SiPh), 15.3 (SiMeOH), -13.7, -12.0 ($SiMe_3$). MS: (CI) *m/z* (%) = 622 (3) [M^+], 604 (9) [$M^+ - H_2O$], 451 (100) [$M^+ - Me$-$2C_6H_6$]. Anal. Calc. for $C_{26}H_{54}O_2Si_8$, (623.40): C, 50.09; H, 8.73. Found: C, 49.74; H, 8.88%.

3.3.5. (*rac*)-3,4-Dihydroxy-2,5-diphenyl-1,1,1,3,4,6,6,6-octamethyl-2,5-bis(trimethylsilyl)hexasilane (6)

M.p. 90–91 °C. IR (nujol) $\tilde{\nu} = 3604.1$ cm^{-1} (OH). ^{1}H-NMR: $\delta = 0.83$ (s, OH, 2H), 7.74–7.71, 7.20–7.05 (2m, phenyl, 10H), 0.56 (s, SiMeOH, 6H), 0.34, 0.33 (2s, $SiMe_3$, 2 × 18H). ^{13}C-NMR: $\delta = 137.0$, 135.6, 128.6, 128.4 (C-aromat.), 4.1 (SiMeOH), 1.6, 1.4 ($SiMe_3$). ^{29}Si-NMR: $\delta = -73.7$ (SiPh), 16.9 (SiMeOH), -13.7, -11.9 ($SiMe_3$). MS: (CI) *m/z* (%) = 622 (11) [M^+], 604 (23) [$M^+ - H_2O$], 451 (100) [$M^+ - Me - 2C_6H_6$]. Anal. Calc. for $C_{26}H_{54}O_2Si_8$, (623.40): C, 50.09; H, 8.73. Found: C, 49.91; H, 8.79%.

3.4. Synthesis of the dioxadisilatitanacyclopentanes 7 and 8

3.4.1. General procedure

To a solution of 1 mmol of **4** or **6** in 10 ml of toluene, 3.2 ml (2 mmol) of 1.6 M *n*-BuLi were added at −78 °C. After the mixture was stirred for 1 h, a solution of 0.25 g (1 mmol) of titanocendichloride in 10 ml of toluene was added at −78 °C. After stirring for 1 h the mixture was allowed to warm up, stirred overnight and then filtered to remove LiCl. The solvent was evaporated under reduced pressure, yielding the dioxadisilatitanacyclopentanes **7** and **8**, which were purified as described below.

3.4.2. (*Z*)-1,1-Dicyclopentadienyl-3,4-dimethyl-3,4-bis[tris(trimethylsilyl)silyl]-2,5-dioxa-3,4-disilatitanacyclopentane (7)

Crystallization from pentane at −40 °C afforded (*Z*)-**7** as orange needles, yield 0.56 g (71%). M.p. 183–185 °C (dec.). ^{1}H-NMR: $\delta = 6.14$, 5.99 (2s, C_5H_5, 2 × 5H), 0.95 (s, SiMeOTi, 6H), 0.45 (s, $SiMe_3$, 54H), 0.88 (t, $\underline{CH_3}$–$(CH_2)_3$–$\underline{CH_3}$, 3H), 1.19–1.31 (m, CH_3–$(\underline{CH_2})_3$–CH_3, 3H).^{13}C-NMR: $\delta = 117.0$, 116.2 (C_5H_5), 11.2 (SiMeOTi), 4.0 ($SiMe_3$), 14.3 ($\underline{CH_3}$–$(CH_2)_3$–$\underline{CH_3}$), 22.7 (CH_3–$(\underline{CH_2})_3$–CH_3). ^{29}Si-NMR: $\delta = -120.5$ ($\underline{Si}$ $SiMe_3$), 52.6 (SiMeOTi), -10.2 ($SiMe_3$). MS: (70 eV) *m/z* (%) = 790 (4) [M^+], 725 (7) [$M^+ - Cp$], 178 (100) [Cp_2Ti^+]. Anal. Calc. for $C_{30}H_{70}O_2Si_{10}Ti$, (791.629): C, 45.52; H, 8.91. Found: C, 45.39; H, 8.58%.

3.4.3. (*E*)-1,1-Dicyclopentadienyl-3,4-dimethyl-3,4-bis[tris(trimethylsilyl)silyl]-2,5-dioxa-3,4-disilatitanacyclopentane × pentane (7)

Crystallization from pentane at −78 °C afforded (*E*)-**7** as orange microcrystalline material, yield 0.74 g (86%). M.p. 240 °C (dec.). ^{1}H-NMR: $\delta = 6.07$ (s, C_5H_5, 10H), 1.12 (s, SiMeOTi, 6H), 0.44 (s, $SiMe_3$, 54H). ^{13}C-NMR: $\delta = 116.6$ (C_5H_5), 10.7 (SiMeOTi), 3.8 ($SiMe_3$). ^{29}Si-NMR: $\delta = -125.2$ ($\underline{Si}SiMe_3$), 52.4 (SiMeOTi), -9.9 ($SiMe_3$). MS: (70 eV) *m/z* (%) = 790 (11) [M^+], 725 (8) [$M^+ - Cp$], 178 (100) [Cp_2Ti^+]. Anal. Calc. for $C_{35}H_{82}O_2Si_{10}Ti$, (863.777): C, 48.67; H, 9.57. Found: C, 48.23; H, 9.27%.

3.4.4. (*Z*)-1,1-Dicyclopentadienyl-3,4-dimethyl-3,4-bis[phenyl-bis(trimethylsilyl)silyl]-2,5-dioxa-3,4-disilatitanacyclopentane (8)

The residue was dried in vacuum (10^{-2} mbar, 100 °C), leaving (*Z*)-**8** as an orange foam, yield 0.67 g (84%). Due to its extreme solubility of in common organic solvents, purification by means of recrystallization proved to be impossible. M.p. 65 °C (dec.). ^{1}H-NMR: $\delta = 7.83$–7.80, 7.16–7.01 (2m, phenyl, 10H), 6.01, 5.91 (2s, C_5H_5, 2 × 5H), 0.94 (s, SiMeOTi, 6H), 0.38, 0.31 (2s, $SiMe_3$, 2 × 18H). ^{13}C-NMR: $\delta = 137.6$, 136.0, 128.4, 128.1 (C-aromat.), 117.4, 116.5 (C_5H_5), 7.2 (SiMeOTi), 2.1, 1.8 ($SiMe_3$). ^{29}Si-NMR: $\delta = -68.7$ (SiPh), 48.9 (SiMeOTi), -14.8, -11.3 ($SiMe_3$). MS: (CI) *m/z* (%) = 798 (21) [M^+], 733 (33) [$M^+ - Cp$], 178 (100) [(Cp_2Ti^+]. Anal. Calc. for $C_{36}H_{62}O_2Si_8Ti$, (799.452): C, 54.09; H, 7.82. Found: C, 53.87; H, 7.69%.

3.4.5. (*E*)-1,1-Dicyclopentadienyl-3,4-dimethyl-3,4-bis[phenyl-bis(trimethylsilyl)silyl]-2,5-dioxa-3,4-disilatitanacyclopentane (8)

Crystallization from pentane at −40 °C afforded (*E*)-**8** as red crystals, yield 0.63 g (79%). M.p. 135 °C (dec.). ^{1}H-NMR: $\delta = 7.89$–7.85, 7.30–7.10 (2m, phenyl, 10H), 5.78 (s, C_5H_5, 10H), 0.84 (s, SiMeOTi, 6H), 0.44, 0.39 (2s, $SiMe_3$, 2 × 18H). ^{13}C-NMR: $\delta = 137.6$, 136.5, 128.2, 128.2 (C-aromat.), 116.9 (C_5H_5), 7.9 (SiMeOTi), 2.1 ($SiMe_3$). ^{29}Si-NMR: $\delta = -71.0$ (SiPh), 49.5 (SiMeOTi), -14.1, -12.0 ($SiMe_3$). MS: (CI) *m/z* (%) = 798 (60) [M^+], 733 (50) [$M^+ - Cp$], 178 (100) [(Cp_2Ti^+]. Anal. Calc. for $C_{36}H_{62}O_2Si_8Ti$, (799.452): C, 54.09; H, 7.82. Found: C, 53.85; H, 7.68%.

3.5. Crystal structure determination of (*rac*)-**6**, (*E*)-**8** and (*Z*)-**7**

The crystal structure determinations of (*E*)-**8** and (*Z*)-**7** were performed on a STOE-IPDS diffractometer with graphite monochromated Mo–K_α radiation at 293 K. Crystals of (*rac*)-**6** were investigated by using a Bruker P4 diffractometer after taking rotational photographs at 293 K. The structures were solved by direct methods (SHELXS-86) [14] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93) [15]. XP (Siemens Analytical X-ray Instruments) was used for structure representations (for full crystallographic data see Table 1).

Table 1
Summary of crystal and structure solution data of (*rac*)-**6**, (*Z*)-**7** and (*E*)-**8**

Compound	(*rac*)-**6**	(*Z*)-**7**	(*E*)-**8**
Empirical formula	$C_{26}H_{54}O_2Si_8$	$C_{35}H_{82}O_2Si_{10}Ti$	$C_{36}H_{62}O_2Si_8Ti$
Formula weight	623.41	863.78	799.48
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions			
a (Å)	8.842(2)	9.840(2)	18.152(4)
b (Å)	38.166(10)	14.740(3)	9.5950(19)
c (Å)	12.306(3)	18.710(4)	27.152(5)
α (°)	90	84.12(3)	90
β (°)	106.690(10)	85.10(3)	99.43(3)
γ (°)	90	72.15(3)	90
β (°)			99
V (Å^3)	3977.9(17)	2565.3(9)	4665.1(16)
Z	4	2	4
D_{calc} (Mg m^{-3})	1.041	1.025	1.138
Absorption coefficient (mm^{-1})	0.289	0.422	0.417
F(000)	1352	856	1712
Crystal size (mm^3)	0.57 × 0.44 × 0.30	0.4 × 0.3 × 0.2	0.4 × 0.3 × 0.2
Theta range for data collection (°)	2.03–22.00	1.89–24.18	1.52–21.06
Index ranges	$-9 \le h \le 1$, $-40 \le k \le 1$, $-12 \le l \le 12$	$-10 \le h \le 10$, $-16 \le k \le 16$, $-21 \le l \le 21$	$-18 \le h \le 18$, $-9 \le k \le 9$, $0 \le l \le 27$
Reflections collected	6224	16137	9043
Independent reflections	4867	7553	4943
[R_{int}]	0.0692	0.0532	0.0314
Completeness to Θ	22°/99.9%	24.18°/91.9%	21.06°/97.8%
Data/restraints/parameters	4867/0/327	7553/0/388	4943/0/424
Goodness-of-fit on F^2	1.001	0.709	0.868
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0646$, $wR_2 = 0.1507$	$R_1 = 0.0400$, $wR_2 = 0.0641$	$R_1 = 0.0342$, $wR_2 = 0.0693$
R indices (all data)	$R_1 = 0.1176$, $wR_2 = 0.1805$	$R_1 = 0.1063$, $wR_2 = 0.0728$	$R_1 = 0.0575$, $wR_2 = 0.0744$
Largest difference peak and hole (e Å^{-3})	0.276 and −0.206	0.290 and −0.183	0.262 and −0.205

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 148053 [(*rac*)-**6**], 148054 [(*Z*)-**7**] and 148055 [(*E*)-**8**], respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) G. Perego, G. Ballussi, C. Corno, M. Tamarasso, F. Buonomo, A. Esposito, in: Y. Murakami, A. Iijima, J.W. Word (Eds.), Studies in Surface Science and Catalysis: New Developments in Zeolite Science and Technology, Elsevier, Amsterdam, 1986;
(b) A. Bhaumik, R.J. Kumar, J. Chem. Soc. Chem. Commun. (1995) 869;
(c) B. Notari, Stud. Surf. Sci. Catal. 37 (1988) 413.

[2] (a) H.C.L. Abbenhuis, S. Krijnen, R.A. van Santen, J. Chem. Soc. Chem. Commun. (1997) 331;
(b) I.E. Buys, T.W. Hambley, D.J. Houlten, T. Maschmeyer, F.A. Masters, A.K. Smith, J. Mol. Catal. 86 (1994) 309;
(c) M. Crocker, R.H.M. Herold, A.G. Orpen, Chem. Commun. (1997) 2411;
(d) T. Maschmeyer, M.C. Klunduk, C.M. Martin, D.S. Shepard, J.M. Thomas, B.F.G. Johnson, Chem. Commun. (1997) 1847.

[3] (a) P.D. Lickiss, Adv. Inorg. Chem. 42 (1995) 147;
(b) N. Auner, J. Weis, in: R. Murugavel, A. Voigt, M.G. Walawalkar, H.W. Roesky (Eds.), Organosilicon Chemistry III, VCH, Weinheim, 1998, p. 376.

[4] (a) R. Muragavel, A. Voigt, M.G. Walawalkar, H.W. Roesky, Chem. Rev. 96 (1996) 2205;
(b) A. Voigt, R. Murugavel, V. Chandrasekhar, N. Winkhofer, H.W. Roesky, I. Uson, Organometallics 15 (1996) 1610.

[5] (a) F.J. Feher, D.A. Newman, F.J. Walzer, J. Am. Chem. Soc. 111 (1989) 1741;
(b) F.J. Feher, T.A. Budzichowski, R.L. Blanski, K.J. Weller, J.W. Ziller, Organometallics 10 (1991) 2526.

[6] (a) H. Bürgy, G. Calzaferri, D. Herren, A. Zhdanov, Chimia 45 (1991) 3;
(b) F.J. Feher, T.A. Budzichowski, Polyhedron 14 (1995) 3239;
(c) R. Murugavel, V. Chandrasekhar, H.W. Roesky, Acc. Chem. Res. 29 (1996) 183;
(d) A. Provatas, J.G. Matisons, Trends Polym. Sci. 5 (1997) 327.

[7] (a) R. West, E.K. Pham, J. Organomet. Chem. 403 (1991) 43;
(b) M. Prasse, H. Reinke, C. Wendler, H. Kelling, J. Organomet. Chem. 577 (1999) 342;
(c) J. Beckmann, K. Jurkschat, Coord. Chem. Rev. 215 (2001) 267;
(d) L. Parkanyi, H. Stüger, E. Hengge, J. Organomet. Chem. 333 (1987) 187;
(e) Y.E. Ovchinikov, V.E. Shklover, Y.T. Struchkov, V.V. Dement′ev, T.M. Frunze, B.A. Antipova, J. Organomet. Chem. 335 (1987) 157.

[8] V.V. Semenov, E. Ladilina, A. Kurskii, S. Korshev, N.P. Makarenko, G.A. Domrachev, L.N. Zakharov, G.K. Fukin, T. Struchkov, Izv. Akad. Nauk. Ser. Khim. 10 (1996) 2550.

[9] N. Choi, S. Morino, S. Sugi, W. Ando, Bull. Chem. Soc. Jpn. 69 (1996) 1613.

[10] P. Böttcher, K. Wraage, H.W. Roesky, M. Lanfranchi, A. Tiripicchio, Chem. Ber./Recueil 130 (1997) 1787.

[11] The corresponding diaza titanium ring compounds possessing alkyl substituent on the nitrogen have been structurally characterized by: (a) H. Burger, K. Wiegel, U. Thewalt, D. Schomburg, J. Organomet. Chem. 87 (1975) 301;
(b) F. Jäger, H.W. Roesky, H. Dorn, S. Shah, M. Noltemeyer, H.-G. Schmidt, Chem. Ber./Recueil 130 (1997) 399.

[12] R. Lehnert, M. Höppner, H. Kelling, Z. Anorg. Allg. Chem. 591 (1990) 209.

[13] C. Marschner, Eur. J. Inorg. Chem. (1998) 221.

[14] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.

[15] G.M. Sheldrick, University of Göttingen, Göttingen, Germany, 1993.