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Tripodal Tetrahedral Titanium Coordination in the Silica-Grafted Titania Epoxidation Catalysts: Is Not It Only a Myth? Selective Formation of $[Cy_7Si_7O_{12}Ti]_2(\mu\text{-}OR)_2(\mu\text{-}ROH)$ Cores on Thermal "Dissociation" of Alkoxytitanasilsesquioxanes

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The molecular structures of the species crystallizing from solutions of alkoxytitanasilsesquioxanes in hydrocarbons upon reflux confirm the partial release of solvating alcohol. They feature, however, distinctly the formation of a dinuclear core with preserved hexacoordination for the metal atoms. The active titanium centers in the silica−titania epoxidation catalysts, lacking the sterically demanding ligands, are thus quite probably also hexacoordinated.

The metallasilsesquioxanes, derivatives of polyhedral oligosilsesquioxanes (POSS) with one or several metal centers included in the silsesquioxane core, are considered as attractive precursors of hybrid organic−inorganic materials[1] and, in the case of titanium, are even recognized as potent homogeneous epoxidations catalysts.[2] They are even considered as structural analogues and valuable models of the heterogeneous silica-grafted titanium oxide catalysts.[3]

The existing concepts describing the structure and reactivity of titanasilsesquioxanes are due to the works of Muerig Thomas and Johnson,[4] Crocker et al.,[5] and Edelmann et al.[6] dating to the late 1990s. It was then demonstrated that the interaction of titanium alkoxides, $Ti(OR)_4$, where R = Me, Et, and ^iPr, with an incomplete polyhedral silsesquioxane, $R'_7Si_7O_9(OH)_3$, where R′ = c-C_5H_9 and c-C_6H_{11}, results in both ether and hydrocarbon solvents in the formation of dimeric solvated molecules $\{[R'_7Si_7O_{12}Ti](ROH)(\mu\text{-}OR)\}_2$, containing hexacoordinated titanium centers. Upon heating in hydrocarbon solvents, these species were shown to eliminate the solvating alcohol,[4,5] and it was generally assumed that they are then transformed into mononuclear complexes with tetrahedral coordination for titanium atoms (see Scheme 1). The idea about tetrahedrally coordinated titanium atoms tripod-coordinated to the silica surface has been broadly used for the theoretical description of the mechanisms of catalysis in the course of epoxidation reactions.[3a,c,d] Even structural examples involving this type of coordination for the titanium centers have definitely been reported. They have all, however, involved a bulky terminal ligand such as *tert*-butoxide or trialkylsiloxide[5] or a half-sandwich fragment, incorporating an η-C_5H_5 or an η-C_5Me_5 ligand.[6,7] It is interesting to note that a comparison of experimentally determined activities for the different titanasilsesquioxane catalysts demonstrates a rather strongly nuanced view of the influence of titanium coordination on both the reaction constant and selectivity of the process.

It could clearly be seen that the tetrahedral coordination in itself was definitely not the major factor. A complex derived from two bidentate (with one protected function each) silsesquioxane ligands $R'_7Si_7O_9(OH)_2(OSiMe_3)$ attached to the same titanium atom had about 20 times lower activity than that with a tripodal titanium coordination and one bulky ligand, such as $R'_7Si_7O_{12}Ti(OSiMe_3)$, but the complexes with much smaller ligands such as OCH_2Ph or O^iPr (assumed to possess the same but less sterically hindered coordination) displayed an activity several times higher than

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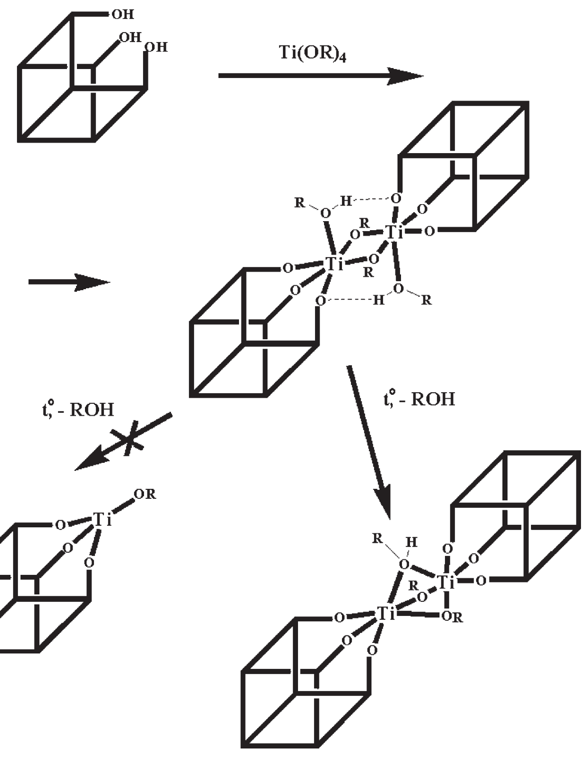
Scheme 1. Formation and Thermal Behavior of Alkoxytitanasilsesquioxanes



that of the structurally characterized species with proven tripodal coordination.[5] It appeared then extremely interesting to identify the true molecular geometry for these most active species. In the view of the trend of titanium alkoxide complexes to aggregation,[8] and of the generally easily observed clustering of titanium oxide on the silica surface,[9] it seemed, at least, peculiar that the tripodal tetrahedral coordination could be adopted by the species in question. The structural characterization of the metallasilsesquioxane complexes by means of single-crystal X-ray techniques is usually very difficult because of the lack of long distance order and the structural imperfections caused by the possible defectual packing of the molecules and the rotation of the substituents at the silsesquioxane core,[10] which explains probably why such a study has not been successful so far.

In the present work, we aimed to study the coordination equilibria in solutions of $\{[Cy_7Si_7O_{12}Ti](ROH)(\mu\text{-}OR)\}_2$, where Cy = c-$C_6H_{11}$ and R = ^{i}Pr and ^{t}Bu. The solubility of the complexes prepared in situ by the reaction of $Ti(OR)_4$ with 1 equiv of $Cy_7Si_7O_9(OH)_3$ was very high. After evaporation to dryness in a vacuum and subsequent redissolution in *n*-hexane, the complexes displayed a clear negative temperature dependence for solubility: while at room temperature it was about 0.15 g/mL, it decreased clearly upon heating, resulting in mass crystallization upon reflux. Upon cooling to room temperature, the precipitate redissolved again, leaving a clear solution. The solution was removed from refluxing reaction mixtures by syringe, and the crystalline residues were investigated by a single-crystal X-ray method.[11]

The noncentrosymmetric structures of the isolated complexes $[Cy_7Si_7O_{12}Ti]_2(\mu\text{-}ROH)(\mu\text{-}OR)_2$, where Cy = c-$C_6H_{11}$ and R = ^{i}Pr (**1**) and ^{t}Bu (**2**), are completely analogous to each other and feature a so far unprecedented metallasiloxane "fusion" of the two titanium atom coordination polyhedra (see Figures 1 and 2). The titanium apexes of the siloxane cubes turn out to be connected via three bridging ligands, two alkoxide groups, and one solvating alcohol molecule. The coordination polyhedra of the titanium atoms are then reasonably well-shaped octahedra sharing a common face (Figure 2).

The positions of the solvating alcohol and one of the bridging alkoxide functions are statistically disordered, which is represented by symmetrically duplicated atoms O14 and O14A with relatively longer and asymmetric distances to the titanium atoms. The bonds to the silsesquioxane core are shorter, corresponding in their function as terminal alkoxide moieties in the structures of titanium alkoxides.[8] An important feature of complexes **1** and **2** is a considerably shorter Ti−Ti distance compared with that for the alcohol-solvated low-temperature forms: 3.189(8) and 3.183(5) Å, respectively, compared to 3.252(4) Å in $\{[Cy_7Si_7O_{12}Ti](MeOH)(\mu\text{-}OMe)\}_2$.[4] This indicates a relatively denser packing of the cations and ligands in the cores of **1** and **2**, compared to the more solvated species. The desolvation of silsesquioxane complexes with smaller alcohol ligands has not been studied in detail,[4] most probably because of the difficulties in the characterization of the products. An apparent alternative to solvation can be coordination of a different ligand, for example, a peroxide. The structures resulting from this will definitely adopt again a more open geometry. The readsorption of the solvating alcohol is a dynamic and quick process, which correlates with the general observation that metal alkoxides are kinetically unhindered species, instantaneously achieving coordination equilibria.[12] This explains why complex **1** and its analogues display the

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(11) The data were collected at room temperature [295(2) K] on a SMART CCD 1K diffractometer, using Mo Kα radiation (λ = 0.71073 Å). Both structures were solved by direct methods, extracting the titanium and silicon atom coordinates from the initial solutions and completing the non-hydrogen atom list by subsequent difference Fourier syntheses. All non-hydrogen atoms except for the carbon atoms of the disordered interstitial hexane molecules were refined using a full matrix model first in isotropic and then in anisotropic approximations. The solvent molecules were refined only isotropically and without addition of the hydrogen atoms. The positions of the hydrogen atoms attached to other carbon atoms were calculated geometrically and included in the final refinement in an isotropic approximation. All calculations were performed using the *SHELXTL-NT* program package. Crystal data for **1**: $C_{99}H_{176}O_{27}Si_{14}Ti_2$, M_r = 2287.46, orthorhombic, *Pnn*2, a = 17.087(3) Å, b = 25.441(5) Å, c = 14.559(3) Å, V = 6329(2) Å^3, d_c = 1.200 g/cm^3, $F(000)$ = 2452, S = 1.156, R1 = 0.1327, wR2 = 0.2764 for 3334 reflections $I > 2\sigma(I)$. IR (cm^{-1}): 3368 m br, 1707 w, 1641 w, 1564 w, 1267 m, 1196 m, 1104 s br, 1078 sh, 1012 s, 891 s, 847 m, 821 w, 592 w, 544 w, 506 s, 465 m, 400 sh. ^{1}H NMR (interp.): δ 4.08 sept (3H, C*H*, ^{i}Pr, J = 6.0 Hz), 1.72 unres, 1.22 unres overlap (tot. 172H, CH_2,C*H*-Cy and CH_3- ^{i}Pr), 0.88 tripl (6H, CH_3-hex, J = 6.0 Hz), 0.76 unres (8H, CH_2-hex). Crystal data for **2**: $C_{102}H_{182}O_{27}Si_{14}Ti_2$, M_r = 2329.54, orthorhombic, *Pnn*2, a = 17.133(3) Å, b = 25.514(5) Å, c = 14.785(3) Å, V = 6463(2) Å^3, d_c = 1.197 g/cm^3, $F(000)$ = 2500, S = 1.064, R1 = 0.0975, wR2 = 0.2433 for 4560 reflections $I > 2\sigma(I)$. IR (cm^{-1}): 3381 s br, 1710 w, 1628 sh, 1565 w, 1290 sh, 1268 m, 1196 m, 1091 s br, 1078 sh, 1005 s, 889 s, 847 m, 824 w, 744 w, 627 w, 600 sh, 591 w, 532 w, 505 s, 465 s, 400 sh.

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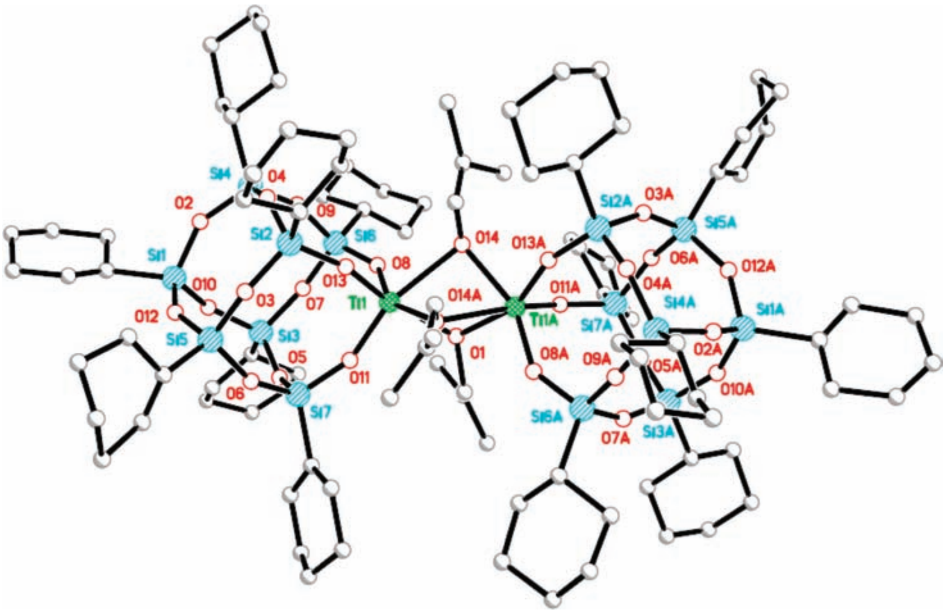

Figure 1. Ball-and-stick representation of the molecular structure of $[Cy_7Si_7O_{12}Ti]_2(\mu\text{-}^iBuOH)(\mu\text{-}O^iBu)_2$, where Cy = c-$C_6H_{11}$ (**2**): Ti1−O11 1.796(9), Ti1−O13 1.794(9), Ti1−O8 1.824(9), Ti1−O1 2.008(8), Ti1−O14 2.096(14), Ti1−O14A 2.334(12), Ti1−Ti1 3.183(5) Å.

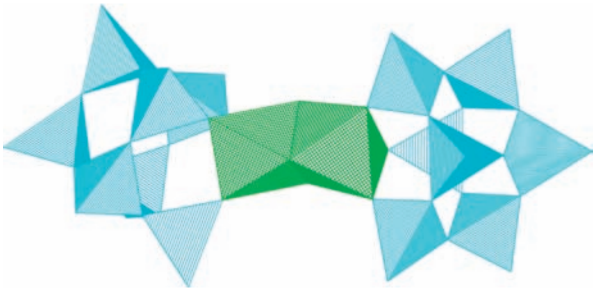

Figure 2. Polyhedral presentation of the metallasilsesquioxane core in molecules **1** and **2**.

highest known catalytic activity in epoxidation reactions according to ref 5. It has been demonstrated by numerous successful attempts for encapsulation of the titanasilsesquioxane complexes in micro- and mesoporous matrixes that this approach provides more efficient catalysts than simply deposition of titanium oxide onto silica matrixes from solutions or the sol−gel synthesis of mixed silica−titania materials.[13] Recent studies of Carniato et al.[14] have demonstrated that the grafting of Ti-POSS in silica matrixes can be achieved through anchoring via a silicon-attached aminopropyl ligand, an otherwise quite traditional approach to the functionalization of silica surfaces.[15] The secret of the efficiency of the hybrid-grafted catalysts lies rather probably in the isolation of a reactive oligotitanium core of the same type as that discovered in **1** and **2** and hindering of the formation of bigger particles of titania, where the metal atoms are no longer so easily accessible for the coordination and release of peroxide ligands. The structural analogy between the homo- and heterogeneous epoxidation catalysts earlier demonstrated in the literature[3c,d] speaks strongly in favor of this supposition.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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