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Cyclopentadienyl−Silsesquioxane Titanium Complexes: Highly Active Catalysts for Epoxidation of Alkenes with Aqueous Hydrogen Peroxide

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Supporting Information

ABSTRACT: Titanium complexes bearing an unprecedented tridentate cyclopentadienyl−silsesquioxanate ligand provide a new class of efficient and selective catalysts for epoxidation of olefins with aqueous hydrogen peroxide under homogeneous conditions.

Epoxidation of olefinic compounds is a fundamental reaction in industrial organic synthesis,[1] because epoxides are key intermediates for the manufacture of a wide variety of valuables products, both bulk[2] and fine chemicals.[3] Despite the enormous research effort dedicated to the development of efficient catalysts for the oxidation of olefins, some problems remain, in particular, those concerning the nature of the oxidant and the product selectivity. Thus, the search for efficient, selective, and environmentally benign catalysts for these oxidation reactions is currently an important synthetic goal.[4] In this context, the development of environmentally benign processes based on nontoxic metals, such as titanium,[5] and clean oxidants deserves special emphasis.[6] Among the latter, hydrogen peroxide is particularly attractive, because it is inexpensive and environmentally friendly, since it produces water as the only side product.[7]

Metal−silsesquioxane complexes have been the focus of intensive attention, as well-defined molecular models for siliceous heterogeneous catalysts.[8] Metallasilsesquioxanes not only offer an unique opportunity to reach an understanding of metallasilicate catalysts at a molecular level but they also show an interesting catalytic behavior by themselves.[9] In this regard, a series of titanium silsesquioxane complexes have been reported to catalyze alkene epoxidation with organic peroxides, exhibiting activities that are comparable, or even superior, to those shown by the heterogeneous analogues.[10] However, the titanasilsesquioxanes reported so far feature an important drawback for its development as homogeneous oxidation catalysts, since none are capable of performing alkene epoxidation with aqueous hydrogen peroxide as the oxidant.[11]

In view of this, our target was synthesizing a novel family of Ti catalyst based on silsesquioxanes, robust enough to be used as catalysts with aqueous hydrogen peroxide. We envisioned that assembling a silsesquioxane fragment with a cyclopentadienyl ring would form unprecedented tridentate cyclopentadienyl−silsesquioxanate ligand (see Figure 1) capable to form highly stable titanium complexes.

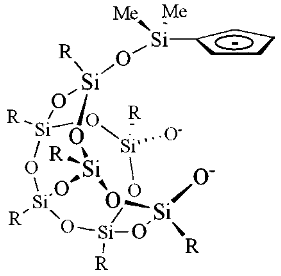

Figure 1. Tridentate cyclopentadienyl−silsesquioxanate ligand.

Following the synthetic strategy developed in our research group,[12] reaction of the titanium monocyclopentadienyl derivative Ti(η^5-$C_5Me_4SiMe_2Cl$)Cl_3 (**1**) with an equimolar amount of incompletely condensed silsesquioxane trisilanol, $R_7Si_7O_9(OH)_3$ (R = ^{i}Bu, **2a**; Ph, **2b**), in chlorinated solvents affords the desired derivative Ti(η^5-$C_5Me_4SiMe_2OR_7Si_7O_{11}$-$\kappa^2O_2$)Cl (R = ^{i}Bu, **3a**; Ph, **3b**) as the sole product (see Scheme 1). The formation of side products is not observed. These complexes comprise an unprecedented tridentate ligand cyclopentadienyl−silsesquioxane disilanolate coordinated to titanium, which involves the condensation of both functionalities with the consequent elimination of three equivalents (3 equiv) of HCl.

Although the formation of complexes **3** globally entails rupturing the Si−Cl bond, as well as two Ti−Cl bonds, such a transformation does not occur via the direct protonolysis of the Si−Cl bond, as inferred from the result attained when the reaction with **2a** is carried out in aromatic solvents. In this reaction, the formation of complex **3a**, along with a new corned-capped cyclopentadienyl derivative Ti(η^5-$C_5Me_4SiMe_2Cl$)(^{i}$Bu_7Si_7O_{12}$-κ^3O_3) (**4a**), which is the result of the rupture of the three Ti−Cl bonds, is detected. Nevertheless, upon heating the reaction mixture, **4a** is quantitatively converted into **3a** (see Scheme 2, as seen by NMR spectroscopy). Therefore, it is reasonable to assume that complex **4a** is the initially formed compound (kinetic control product) while complex **3a** is the thermodynamic product.[13]

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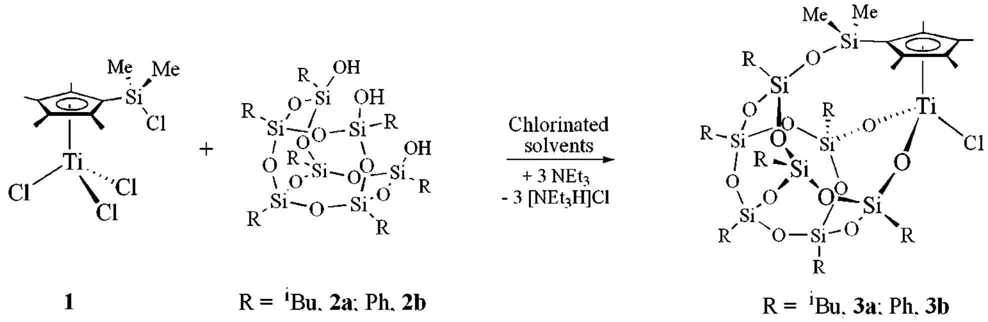
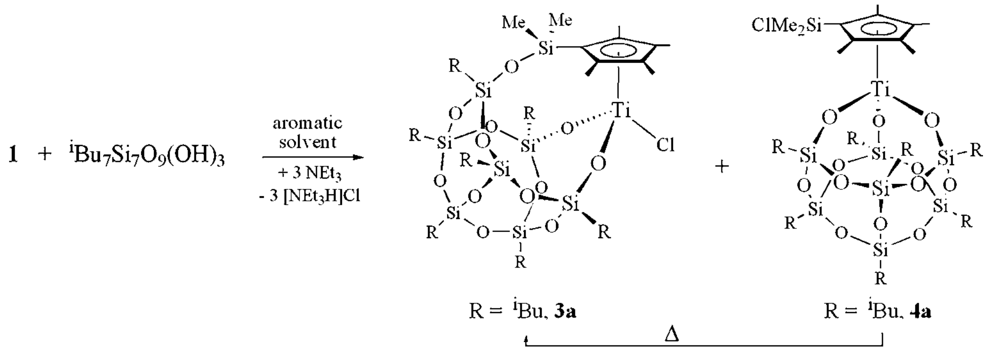
Scheme 1. Synthetic Route to Titanium Complexes 3



Scheme 2. Formation of the Mixture of 3a and 4a



All attempts to isolate **4a** were unfortunately unfruitful; nonetheless, its structural disposition has been unambiguously formulated by spectroscopic analysis of a sample containing **3a** and **4a**.

The spectroscopic behavior of compounds **3** and **4a** supports the proposed structures. ^{29}Si NMR spectra are particularly informative, indicating a C_s- and a C_{3v}-symmetry disposition, respectively. The absence of resonances for the silsesquioxane framework Si atoms above −60 ppm[14,15] reveals the deprotonation and coordination of the three silanol functions. The most striking spectroscopic features are the chemical shifts of the SiMe$_2$X moiety in the ^{1}H and ^{29}Si NMR spectra. Following the tendency observed in our previous works,[11] upfield shifted resonances for compounds **3** and downfield shifted for **4a**, compared with those found for **1**, confirm the proposed silsesquioxane cage connectivity within such complexes.

The crystal structure of **3a** has been verified by X-ray diffraction (XRD) study (Figure 2), showing a monomeric disposition with a pseudo-tetrahedral coordination geometry around the Ti atom. The silsesquioxane framework is clearly linked to the cyclopentadienyl ring by one silanolate group, giving rise to the cyclopentadienyl−silsesquioxane moiety, which acts as a tridentate ligand coordinating to the Ti atom through the Cp- and two silsesquioxane silanolate groups. The condensation of both functionalities does not bring about relevant distortions within the cyclopentadienyl coordination manner to titanium, which may be attributed to the flexibility of the silsesquioxane cage that makes it possible to accommodate the steric demands of the "Ti(C$_5$Me$_4$SiMe$_2$)Cl" fragment.

The cyclopentadienyl−silsesquioxane complexes **3** efficiently catalyze the epoxidation of both cyclic and linear alkenes with aqueous hydrogen peroxide (see Table 1), under mild conditions.

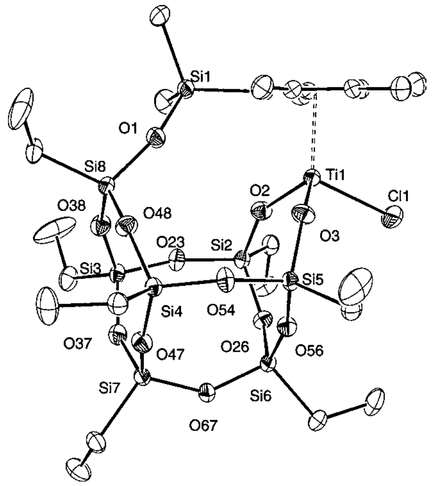


Figure 2. Perspective ORTEP plot of **3a** showing 30% thermal ellipsoids. Hydrogen atoms and *iso*-butyl methyl groups are omitted for clarity. Selected bond distances and angles: Ti(1)−O(2), 1.809(3) Å; Ti(1)−O(3), 1.810(3) Å; Si(1)−O(1), 1.634(3) Å; O(2)−Ti(1)−O(3), 105.49(13)°; O(2)−Ti(1)−Cl(1), 101.30(10)°; and O(3)−Ti(1)−Cl(1), 101.92(11)°.

The efficiency of **3a** and **3b** as catalysts for the epoxidation of cyclooctene with H$_2$O$_2$ (30% in water) has been investigated at 55 °C in MeCN (in a substrate:oxidant molar ratio of 1:2). Complex **3b** (0.5 mol %) affords quantitative conversion (>99%) to the corresponding epoxide in 16 h (Table 1, entry 3). Under similar conditions, complex **3a** results to be less active, affording an epoxide yield of 71% in 20 h of reaction (Table 1, entry 1). Increasing the temperature accelerates the catalytic reactions. At 70 °C, quantitative conversions are obtained within only 8 h, achieving turnover frequencies (TOF) of 124 (for **3a**) and 160 (for **3b**) h^{-1} (calculated at 30 min). The catalytic

Table 1. Olefin Epoxidation with H_2O_2 Catalyzed by 3[a]

entry	catalyst	substrate	temperature, T (°C)	% cat.	time, t (h)	yield[b] (%)	turnover number, TON
1	**3a**	cyclooctene	55	0.5	20	71	142
2	**3a**	cyclooctene	70	0.5	8	88	176
3	**3b**	cyclooctene	55	0.5	16	>99	198
4	**3b**	cyclooctene[c]	55	0.5	24	78	156
5	**3b**	cyclooctene	70	0.5	8	>99	198
6	**3b**	cyclooctene	70	0.2	24	58	290
7	**3b**	cyclooctene	70	0.1	24	30	300
8	**3a**	1-octene	70	0.5	8	68	136
9	**3b**	1-octene	70	0.5	6	91	190

[a] Unless noted otherwise, all reactions were performed in MeCN with a substrate:oxidant molar ratio of 1:2. [b] Yield determined by gas chromatography (GC), using mesitylene as an internal standard. [c] Reaction was carried out in methanol.

amount of catalyst can be reduced to 0.1 mol %, achieving turnover number (TON) values of 300 for catalyst **3b**. Interestingly, the somewhat-difficult epoxidation of 1-octene is effectively catalyzed by complexes **3a** and **3b**, at 70 °C, affording epoxide yields of 68% and 91% in 8 and 6 h, respectively (see Table 1, entries 8 and 9). All catalytic reactions are entirely selective for epoxidation, with the corresponding epoxides (1,2-epoxycyclooctane and 1-octene oxide) being the only products obtained. The use of methanol as a solvent, instead of acetonitrile, does not improve the catalytic performance of complexes **3**, as shown in Table 1 (entry 4).

The lower activity of **3a**, relative to **3b**, can be rationalized in terms of the bigger steric bulk of the silsesquioxane silicon substituents in **3a** (*iso*-butyl) than in **3b** (phenyl), which hinders the accessibility of the titanium center to the reactants (alkene and oxidant) in the former complex.

The kinetic profiles of **3a** and **3b** show that the conversion of cyclooctene is initially relatively fast, and no induction periods are observed, after which the reaction slows down over the course of time (Figure 3).

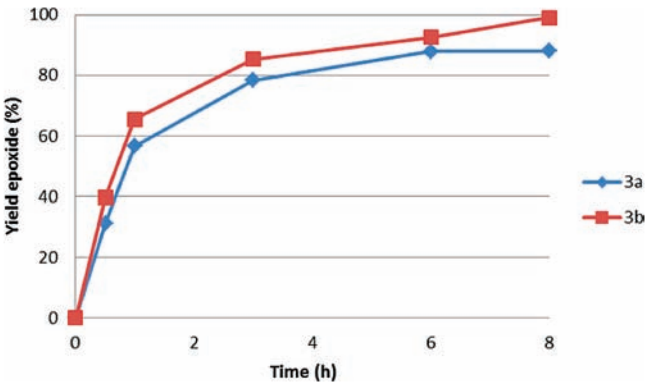


Figure 3. Kinetic profiles of cyclooctene epoxidation with H_2O_2 in the presence of complexes **3a** and **3b**.

The catalyst **3b** can be used for at least three batches of olefin epoxidation. Second and third runs have been performed by recharging the reaction mixture with the same amount of oxidant and substrate used initially in the first run. The kinetic curves for the first and second runs are practically coincident, giving quantitative conversions at similar reaction times. However, longer reaction time is needed in the third run to achieve 100% yield of epoxide (Figure 4). Thus, it seems that the systems formed by **3b**/H_2O_2/MeCN are fairly stable under catalytic conditions.

The high efficiency of catalysts **3a** and **3b** is remarkable, since Ti silsesquioxane complexes have been reported to be inactive for epoxidation olefins with H_2O_2 under homogeneous conditions. To the best of our knowledge, these are the first homogeneous systems based on Ti silsesquioxane species that catalyze the epoxidation of olefins with aqueous hydrogen peroxide.

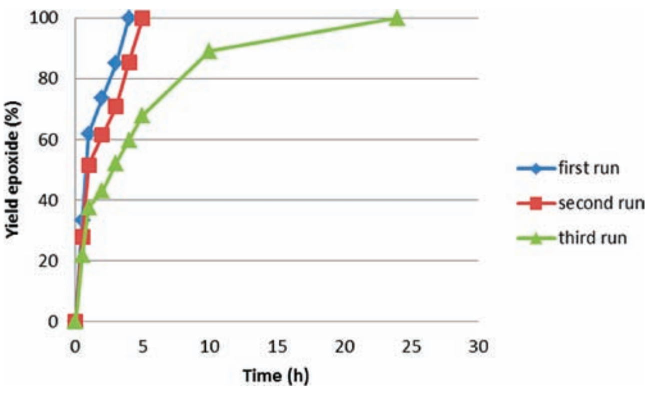


Figure 4. Kinetic profiles of cyclooctene epoxidation with H_2O_2 using catalyst **3b**. Reactions were carried out in MeCN at 70 °C, with a substrate:oxidant molar ratio of 1:2, and a catalyst content of 5 mol %.

In summary, a new class of robust titanium cyclopentadienyl–silsesquioxane compounds have been prepared and used in catalytic epoxidation using H_2O_2. The novel titanium complexes show excellent reactivity and selectivity toward both cyclic and lineal alkenes. The remarkable stability of these catalysts has been proved by their good performance in successive epoxidations carried out by recharging the reaction mixture with new charges of oxidant and substrate.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an argon atmosphere, using Schlenk and high-vacuum line techniques. The solvents were dried and purified with an MBRAUN solvent purification system. Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze–thaw cycles. NEt_3 (Aldrich) was distilled before use and stored over 4 Å molecular sieves. Silsesquioxane trisilanol $R_7Si_7O_9(OH)_3$ was purchased from commercial sources (Hybrid Plastics) and used without further purification. $Ti(\eta^5\text{-}C_5Me_4SiMe_2Cl)Cl_3$[16] was prepared via a known procedure. C, H, and N microanalyses were performed on a Perkin–Elmer Model 240B and/or Heraeus CHN-O-Rapid microanalyzer. Nuclear magnetic resonance (NMR) spectra, at 25 °C, were recorded on a Bruker Model AV400 (^1H NMR system at 400 MHz, a ^{13}C NMR system at 100.6 MHz, and a ^{29}Si NMR system at 79.5 MHz).

Synthesis of $Ti(\eta^5\text{-}C_5Me_4SiMe_2O^iBu_7Si_7O_{11}\text{-}\kappa^2O_2)Cl$ *(**3a**).* A solution of NEt_3 (0.34 mL, 2.45 mmol) in CH_2Cl_2 (30 mL) was added to a mixture of $Ti(\eta^5\text{-}C_5Me_4SiMe_2Cl)Cl_3$ (0.3 g, 0.8 mmol) and $^iBu_7Si_7O_9(OH)_3$ (0.65 g, 0.8 mmol), finely mashed. After the reaction mixture was stirred for 12 h, the white solid formed was collected by filtration, and the volatiles were removed under vacuum. The residue was extracted into hexane (3 × 15 mL) and the resultant solution was concentrated (20 mL) and cooled at −20 °C to give **3a** (0.56 g, 0.53 mmol, 75% yield) as a microcrystalline solid. Anal. Calcd for $C_{39}H_{81}ClO_{12}Si_8Ti$: C 44.63, H 7.72; found: C 44.56, H 7.57. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.39 (s, 6H; $SiMe_2$), 0.53, 0.95, 1.82 (m, 14H, 42H, 7H; ^{i}Bu), 2.11, 2.24 (s, 2 × 6H; C_5Me_4). ^{13}C NMR ($CDCl_3$): δ 3.08 ($SiMe_2$), 12.66, 14.48 ($C_5\mathit{Me}_4$), 22.69, 22.96, 23.30, 24.00, 24.08, 24.13, 24.40, 24.54, 25.80, 25.86, 25.94, 25.96, 25.99, 26.18 (^{i}Bu), 127.87, 134.49, 135.08 (C_5Me_4). ^{29}Si NMR ($CDCl_3$): δ −3.0 ($SiMe_2$), −66.7, −67.7, −67.8, −68.6, −69.8 ($^iBu_7Si_7O_{12}$).

Synthesis of $Ti(\eta^5\text{-}C_5Me_4SiMe_2OPh_7Si_7O_{11}\text{-}\kappa^2O_2)Cl$ *(**3b**).* A method similar to that described for **3a** was adopted, using $Ph_7Si_7O_9(OH)_3$ (1.27 g, 1.36 mmol) to give **3b** (1.31 g, 1.10 mmol, 81% yield) as a yellow solid. Anal. Calcd for $C_{53}H_{53}ClO_{12}Si_8Ti$: C 53.55, H 3.99; found: C 53.48, H 4.45. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.43 (s, 6H; $SiMe_2$), 2.05, 2.28 (s, 2 × 6H; C_5Me_4), 7.27, 7.39, 7.66 (m, 14H, 7H, 14H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 3.13 ($SiMe_2$), 12.87, 14.87 ($C_5\mathit{Me}_4$), 128.01, 128.14, 128.22, 128.58, 129.39, 130.55, 130.68, 130.80, 130.82, 131.47, 132.03, 134.14, 134.44, 134.49, 134.53, 134.56, 134.63, 135.90, 136.70 (C_6H_5, C_5Me_4). ^{29}Si NMR ($CDCl_3$): δ −2.3 ($SiMe_2$), −77.2, −78.0, −79.0, −79.7, −79.9 ($Ph_7Si_7O_{12}$).

Spectroscopic Data for $Ti(\eta^5\text{-}C_5Me_4SiMe_2Cl)(^iBu_7Si_7O_{12}\text{-}\kappa^3O_3)$ *(**4a**).* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.73 (s, 6H; $SiMe_2$), 0.50, 0.94, 1.80 (m, 14H, 42H, 7H; ^{i}Bu), 2.03, 2.25 (s, 2 × 3H; C_5Me_4). ^{29}Si NMR ($CDCl_3$): δ 15.2 ($SiMe_2$), −66.2, −66.3, −68.7 ($^iBu_7Si_7O_{12}$).

Single-Crystal X-ray Structure Determination of Compound 3a. Crystal data and details of the structure determination are presented in the Supporting Information. Suitable single crystals of **3a** for the X-ray diffraction (XRD) study were selected, covered with perfluorinates polyether oil, and mounted on a Bruker−Nonius Kappa CCD single-crystal diffractometer. Data collection was performed at 200(2) K. The structure was solved, using the WINGX package,[17] by direct methods (SHELXS-97) and refined using full-matrix least-squares against F^2 (SHELXL-97).[18] Al non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms, except for the hydrogen atoms H1 an H2 that were found in the Fourier map and refined. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err <0.001.

*Crystal Data for **3a**.* $C_{39}H_{81}ClO_{12}Si_8Ti$, M = 1050.11, triclinic, space group $P\bar{1}$, a = 11.0572(10) Å, b = 13.5568(8) Å, c = 19.3775(14) Å, α = 92.099(5)°, β = 104.946(6)°, γ = 92.199(6)°, V = 2801.1(4) Å^3. Z = 2, D_{calcd} = 1.245 g cm^{-3}, $F(000)$ = 1124, λ(Mo K$_\alpha$) = 0.71073 Å. At the conclusion of the refinement, $wR_2(F^2 > 2\sigma(F^2)$ = 0.1391, conventional R [on F values for 12306 reflections] ($F^2 > 2\sigma(F^2)$) = 0.0599 for 558 parameters.

Alkene Epoxidation. The catalytic tests were carried out in a reaction vessel equipped with a magnetic stirrer and immersed in an oil bath at the appropriate temperature. A catalyst:alkene:H_2O_2 ratio of 0.5(0.2, 0.1):100:200 was used, with 2 mL of MeCN. Olefin, acetonitrile, mesitylene (as internal standard), and the catalyst were transferred into the reaction vessel, and H_2O_2 (30% aqueous solution) was added to the mixture. The course of the reaction was monitored by quantitative gas chromatography (GC) analysis.

■ ASSOCIATED CONTENT

Supporting Information

Tables of crystallographic data, including fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates in CIF format of complex **3a.** ^{1}H and ^{1}H−^{29}Si HMBC spectra for **3a**, **3b**, and the mixture of **3a** and **4a** and chromatograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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