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<th>Organometallics</th>
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<td>Manuscript ID</td>
<td>om-2015-009106</td>
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<tr>
<td>Manuscript Type</td>
<td>Article</td>
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<td>Date Submitted by the Author:</td>
<td>30-Oct-2015</td>
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<tr>
<td>Complete List of Authors:</td>
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Manuscripts for Organometallics

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Summary

A new set of efficient epoxidation catalysts with aqueous hydrogen peroxide based on titanium cyclopentadienyl-silsesquioxane derivatives has been prepared. The modification of the Cp ring electronic and steric properties entails important differences in the chemical and catalytic behavior of such compounds.
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\[
\text{R'} = \text{H, SiMe}_3
\]
Abstract

The reaction of titanium chlorosilylsubstituted cyclopentadienyl complexes, Ti(η⁵-C₅H₃R’SiMe₂Cl)Cl₃ (R’ = H, 1b; SiMe₃, 1c), with 1 equiv of different silsesquioxane trisilanols, R₇Si₇O₉(OH)₃ (R = ‘Bu, 2a; Ph, 2b), affords either corned-capped cyclopentadienyl derivatives, Ti(η⁵-C₅H₃R’SiMe₂Cl)(R₇Si₇O₁₂-κ³O₃) (R’ = H, R = ‘Bu, 5a, Ph, 5b; R’ = SiMe₃, R = ‘Bu, 7a, Ph, 7b), or cyclopentadienyl-silsesquioxane complexes, Ti(η⁵-C₅H₃SiMe₂OR₇Si₇O₁₁-κ²O₂)Cl (R’ = H, R = ‘Bu, 6a, Ph, 6b; R’ = SiMe₃, R = ‘Bu, 8a, Ph, 8b), depending on the reaction conditions. In any case, upon heating, the former (5 and 7; kinetic control products) are transformed into the corresponding thermodynamic product (6 and 8, respectively). Electron-donating ability of the cyclopentadienyl ring is a relevant controlling parameter for the isomerization process; a stronger π-donors character facilitates the isomerization process. In addition, nature of the silsesquioxane framework silicon substituents, type of solvent, and reaction temperature are also factors that significantly affect this process. The cyclopentadienyl-silsesquioxane complexes 6b and 8b are highly efficient and selective catalysts for the epoxidation of the cis-cyclooctene using aqueous hydrogen peroxide under mild conditions. Such a catalytic efficiency is attributed to the hydrophobic environment provided about the titanium atom by the Cp ring incorporated to the cyclopentadienyl-silsesquioxane ligand.

Keywords: Titanium; Titanasilsesquioxane; Cyclopentadienyl-silsesquioxane; Epoxidation; Hydrogen peroxide
**Introduction**

Olefin epoxidation is a crucial reaction in organic synthesis, in industry and academic world,\(^1\) since epoxides constitute a family of versatile and appealing chemicals for the production of a wide range of valuables products, both commodity\(^2\) and fine chemicals.\(^3\) Despite the enormous research effort spent on the search of efficient oxidation systems, more atom-efficient approaches carried out under mild conditions are strongly desired from the viewpoint of protecting the environment and sustainability.\(^4\) Thus, the search for environmentally friendly and economically efficient systems for oxidation reactions is currently a central synthetic goal,\(^5\) for which the choice of oxidant is a critical factor. Among the available oxidants, aqueous hydrogen peroxide is particularly desirable because it is environmentally benign (water being the only by-product)\(^6,7\) and highly atom-efficient (47% of active oxygen content).\(^7\)

Additionally, it is inexpensive, commercially available, and acceptable safe in storage and operation.

It is widely accepted that olefin epoxidation by Ti-centered catalysts proceeds via an electrophilic oxygen atom transfer from an active peroxy-intermediate (Ti-O-OR) to the olefin, through a concerted mechanism.\(^8\) According to the literature, several strategies have been developed to obtain more efficient oxidation catalysts. For instance, an increase of Lewis acidity of the metal center to generate more electrophilic oxygen atoms has a beneficial effect on the catalytic performance.\(^9\) Another method available for improving the catalytic activity relies on enhancing the accessibility of the active site to the reactants (the alkene and the oxidant).\(^10\)

Metal-containing silsesquioxanes are the focus of intensive research efforts because they offer an unique opportunity to reach an understanding of metallasilicate catalysts at a molecular level,\(^11,12\) as well as being valuables precursors of silica-supported metal oxide catalysts.\(^13\) In addition, some of these complexes exhibit an interesting catalytic behavior by themselves.\(^14,15\) Among them, a series of titanium silsesquioxane complexes have been reported to catalyze alkene epoxidation with organic peroxides showing high activities, even superiors to those of analogues heterogeneous systems.\(^14\)
However, such complexes feature an important drawback for their development as homogeneous oxidation catalysts, since none are active with hydrogen peroxide.\textsuperscript{16}

We have recently reported the first homogeneous oxidation catalysts based on Ti-silsesquioxane species capable to efficiently oxidize alkenes and sulfides using aqueous hydrogen peroxide as oxidant.\textsuperscript{17,18} The exceptional catalytic behavior displayed by these complexes relies on the robustness and stability provided by the unprecedented cyclopentadienyl-silsesquioxanate ligand (CpPOSS).\textsuperscript{17} The formation of the CpPOSS ligand occurs, at the coordination sphere of the titanium atom, through the condensation of both functionalities the silesquioxane fragment and the cyclopentadienyl ring.\textsuperscript{19} Such a reaction proceeds via a corned-capped cyclopentadienyl intermediate, detected in the case of $\text{Ti(}\eta^5\text{-}C_5\text{Me}_4\text{SiMe}_2\text{Cl})(\text{iBu})_7\text{Si}_7\text{O}_{12}\kappa^3\text{O}_3$ (complex 3a, Scheme 1), which rapidly isomerizes to render the corresponding tetramethylcyclopentadienyl-silsesquioxane complex $\text{Ti(}\eta^5\text{-}C_5\text{Me}_4\text{SiMe}_2\text{OR})(\text{iBu})_7\text{Si}_7\text{O}_{11}\kappa^2\text{O}_2\text{Cl}$ (complexes 4a (iBu) and 4b (Ph), Scheme 1).

\begin{center}
\begin{tabular}{c}
\textbf{Scheme 1.} Formation of tetramethylcyclopentadienyl-silsesquioxane complexes.
\end{tabular}
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Encouraged by the significant catalytic potential of this type of cyclopentadienyl-silsesquioxane compounds (Ti-CpPOSS) and the modular nature of the CpPOSS ligand, we envisioned the possibility to fine-tuning the electronic properties and the steric bulk of the CpPOSS ligand, by modifying the cyclopentadienyl substituents, to explore the influence of such parameters in the chemical and the catalytic behavior of this kind of complexes.
We report herein the preparation and characterization of a new set of titanasilsesquioxane complexes, including the isolation of several of the corned-capped compounds initially formed. The analysis of the obtained outcomes allows establishing the influence of the Cp ring properties on the course of the reactions and on the catalytic behavior of the metal complexes. Studies of the catalytic performance of the Ti-CpPOSS complexes in the cis-cyclooctene epoxidation with aqueous hydrogen peroxide are reported.

**Results and Discussion**

In order to increase the Lewis acidity and the accessibility of the titanium center in the cyclopentadienyl-silsesquioxane complexes, target of this research, we choose as starting material titanium chlorosilylsubstituted cyclopentadienyl derivatives such as Ti(η⁵-C₅H₅R’SiMe₂Cl)Cl₃ (R’ = H, 1b;²⁰ SiMe₃, 1c), which feature a Cp ring less electron releasing and sterically demanding than the tetramethylated ligand shown by 1a. Complex 1c is prepared by reaction of TiCl₄ with one equiv of the trisilylsubstituted cyclopentadiene C₅H₅(SiMe₃)₂(SiMe₂Cl), via specific elimination of SiMe₃Cl (Scheme 2). Complex 1c is a chiral compound as a consequence of the planar chirality imposed by the un asymmetrically disubstituted cyclopentadienyl ring.

![Scheme 2. Formation of complex 1c](image)

The influence of the electronic and steric properties of the Cp ring on the reactivity of these monocyclopentadienyl complexes is clearly showed by analyzing the results of their reactions with the incompletely condensed silsesquioxane trisilanols R₃Si₅O₉(OH)₃ (R = t-Bu, 2a; Ph, 2b), in the presence of 3 equiv of NEt₃. Thus, the reaction of 1b with an equimolar amount of 2, in aromatic solvents and at room
temperature, specifically affords the formation of the corresponding corned-capped tianasilsesquioxane derivative Ti(η^5-C₅H₄SiMe₂Cl)(R₇Si₃O₁₂-κ₉O₃) (R = tBu, 5a; Ph, 5b), contrasting with the observed outcome in the analogous reaction with the tetramethylated derivative 1a, which directly renders the corresponding cyclopentadienyl-silsesquioxane complex (Scheme 1). However, upon heating at 70 °C a solution of 5, these complexes are quantitatively transformed into the respective cyclopentadienyl-silsesquioxane complex Ti(η^5-C₅H₄SiMe₂OR;Si₇O₁₁-κ₀₂O₂)Cl (R = tBu, 6a; Ph, 6b). The rate of these transformations increases as the electron-donating properties of the silsesquioxane scaffold silicon substituents decreases (6 days, iso-butyl; 3 days, phenyl). Similar results were obtained with complexes 3.¹⁷

Alternatively, complexes 6 are directly formed when the reaction of 1b with 2 is performed at high temperature, or simply at room temperature using chlorinated solvents, (see Scheme 3).

![Scheme 3](image)

Scheme 3. Synthetic routes to tianasilsesquioxane complexes 5 and 6.

Complexes 5 and 6 are isolated in high yields and fully characterized by spectroscopic and analytical methods. The possibility of isolating the complexes 5 in a pure form allows monitoring its transformation into the corresponding complex 6 by NMR spectroscopy. Thus, when a benzene-d₈ solution of 5a is heated at 70 °C for 6 days, the corresponding complex 6a is quantitative formed, corroborating that such a transformation implies an isomerization process.
To assess the relative stability of the both isomers, density functional theory (DFT) calculations at B3LYP\textsuperscript{21,22} level have been carried out using Ti(η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{4}SiMe\textsubscript{2}Cl)(Me\textsubscript{7}Si\textsubscript{7}O\textsubscript{12}-κ\textsuperscript{3}O\textsubscript{3}) and Ti(η\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{4}SiMe\textsubscript{2}OMe\textsubscript{7}Si\textsubscript{7}O\textsubscript{11}-κ\textsuperscript{2}O\textsubscript{2})Cl as models. These calculations show values of $\Delta H^\circ$ and $\Delta G^\circ$ of 8.4 and 7.8 kcal/mol, respectively, higher for the initial corned-capped isomer (Figure 1, structure A) relative to the final cyclopentadienyl-silsesquioxane isomer (Figure 1, structure B), confirming that the former is the kinetic control product while the latter is the thermodynamic product.

![Figure 1](attachment:image.png)

**Figure 1.** Optimized structures for both isomers. Hydrogen atoms are omitted for clarity. Atom color code: light blue, silicon; light grey, carbon; red, oxygen; white, titanium.

The isomerization process slows down on going from 3 to 5, enabling the isolation of the initially formed corned-capped derivative 5. Such a different behavior is expected on the basis of electronic considerations. Replacement of the tetramethylated ring by the poorer $\pi$-donating unsubstituted one entails an increase of the Lewis acidity of the titanium atom. Therefore, in order to compensate its greater electron deficiency, the titanium atom in 5 is forced to interact stronger with the silanolic oxygen atoms. Taking into account that the isomerization process involves the cleavage of at least one of the Ti-O bonds, a strengthening of such bonds must hinder the isomerization reaction. Moreover, steric influence must be ruled out because otherwise, the reduction of the ring bulk, from 3 to 5, would have to facilitate the closeness of both moieties, silsesquioxane and cyclopentadienyl ring, and thereby the fusion process.
In order to verify this hypothesis, we explored similar reactions with complex 1c that features a Cp ligand with steric and electronic properties laying in an intermediate position respect to those shown by 1a and 1b. In agreement to that, the reactions with 1c are less selective and always afford mixtures of the corresponding two structural isomers Ti(η⁵-C₅H₃SiMe₃SiMe₂Cl)(R₇Si₇O₁₂-κ³O₃) (R = iBu, 7a; Ph, 7b) and Ti(η⁵-C₅H₃SiMe₃SiMe₂OR₇Si₇O₁₁-κ²O₂)Cl (R = iBu, 8a; Ph, 8b), reflecting that the isomerization process in this case is less and more favorable, respectively, than for 3 and 5. However, the molar ratio of the mixture varies following the aforementioned trends respect the nature of the silsesquioxane framework silicon substituents (Scheme 4).

![Scheme 4](attachment:image.png)

**Scheme 4.** Reactions of 1c with 2. i) 3 equiv of NEt₃, aromatic solvent and at room temperature; ii) extraction into hexane; iii) aromatic solvents at 70 °C or chlorinated solvents at room temperature.

The reaction of 1c with 2a, in aromatic solvents and at room temperature, gives a mixture of 7a and 8a mainly enriched in the first component, > 95%. Owing to that, complex 7a can be isolated from the reaction mixture, by extracting with hexane and
subsequent working up, in yields up to 74%. On the other hand, complex 8a is obtained as a sole product when the reaction is carried out at 70 °C or using chlorinated solvents, even working at ambient temperature.

As expected, the reactions with silsesquioxane trisilanols bearing phenyl groups are less selective and always give rise to mixtures in which 8b is the main component (> 60%). Such a behavior prevents the isolation of the initially formed corned-capped derivative 7b. Hence, the latter is only characterized by spectroscopic analysis of a sample containing both isomers. On the contrary, complex 8b is quantitatively obtained when the reaction is performed in the adequate experimental conditions (Scheme 4).

Bringing all the experimental evidences together, several conclusions can be drawn regarding the reaction parameters that determine the isomerization process rate: i) stronger π-donating ability of the Cp moiety facilities the isomerization process, probably due to the weakness of the Ti-O bonding interactions; ii) higher electron releasing ability of silsesquioxane framework silicon substituents hinders the isomerization process. It could be rationalized in terms of the higher basicity of the silenic oxygen atoms that contributes to strengthen of the Ti-O bonds; iii) higher solvent polarity favors the isomerization process, indicating that the isomerization reaction proceeds through significantly polar transient species; iv) an increase of the temperature boosts the formation of the cyclopentadienyl-silsesquioxane complexes. This trend is in accordance with the assumption that complexes 6 and 8 are the thermodynamic products, while the initially formed corned-capped titanasilsesquioxane, 5 and 7, are the kinetic control species.

All new compounds are thermally and hydrolytically rather stable. In fact, solutions of 6 and 8 can be exposed to air for a long period of time without noticeable decomposition. Both type of complexes are soluble in common organic solvents although the corned-capped derivatives are perceptibly more soluble than the corresponding cyclopentadienyl-silsesquioxane compounds.

These complexes are characterized by multinuclear NMR spectroscopy and elemental analysis, and the obtaining structural data support the proposed structures.
The planar chirality of the complexes bearing the disilylsubstituted \( \eta^5 \)-
\( \text{C}_3\text{H}_3(\text{SiMe}_3)\text{SiMe}_2\text{X} \) (X = Cl or O) ring is illustrated by the larger complexity of their
NMR spectra, e.g., the \(^1\text{H}\) NMR spectrum of \( \text{1c} \) shows two singlets at high field for the
diastereotopic methyl groups \( \text{SiMe}_2\text{Cl} \) and an ABC spin system at low field for the three
nonequivalent \( \text{Cp} \) ring protons. In the same manner, the spectra of the compounds \( \text{7} \) and
\( \text{8} \) are noticeably more intricate than those of their corresponding partners \( \text{5} \) and \( \text{6} \),
respectively.

We previously noticed that the chemical shifts for the methylic protons, in the \(^1\text{H}-\)
MNR spectra, and the silicon atom, in the \(^{29}\text{Si}-\)MNR spectra, of the \( \text{SiMe}_2\text{X} \) moiety
provide a very powerful tool to establish the silsesquioxane fragment connectivity
manner within type of complexes. When chlorine atom is substituted by a richer \( \pi\)-
donor atom as O or N, both proton and silicon resonances are significantly upfield
shifted.\(^{17,21}\) Consistently, \( \text{“SiMe}_2\text{Cl”} \) resonances for the corne-capped compounds \( \text{5} \) and
\( \text{7} \) show similar chemical shifts \((\text{H}, \delta_{\text{range}} \approx 0.50 \text{ to } 0.75; \text{Si, } \delta_{\text{range}} \approx 14 \text{ to } 20)\) than the
parents compounds \( \text{1b} \) and \( \text{1c} \), whereas the \( \text{“SiMe}_2\text{O”} \) resonances for the \( \text{Ti-CpPOSS} \)
complexes \( \text{6} \) and \( \text{8} \) appear distinctly high-field shifted \((\text{H}, \delta_{\text{range}} \approx 0.20 \text{ to } 0.40; \text{Si, } \delta_{\text{range}} \approx –3.0 \text{ to } –7.0)\).

The most striking NMR data for the silsesquioxane moiety are those derived from the
\(^{29}\text{Si} \) NMR spectra since; the number of framework silicon resonances allows
establishing the symmetry and therefore the molecular structure of these complexes.
Consistently, \(^{29}\text{Si} \) NMR spectra of these complexes show sets of 3 (\( \text{5} \)), 5 (\( \text{6} \)) and 7 (\( \text{7} \) and
\( \text{8} \)) resonances, indicating a \( \text{C}_3\nu, \text{C}_v, \) and \( \text{C}_1 \) symmetry disposition, respectively. In
addition, the absence of resonances above \( –60 \text{ ppm} \), confirms the coordination of all
three silenic oxygen atoms, after deprotonation.\(^{24-26}\) In contrast with the NMR silicon
data, the \(^1\text{H} \) NMR and \(^{13}\text{C} \) NMR data are much less informative due to the large number
of similar organic groups present that causes the overlap of many of their resonances,
preventing to obtain relevant structural information about these species. Nevertheless,
the complete disappearance of the signals ascribed to the silanol protons, in the \( \delta_{\text{range}} \approx 5.50–6.50;\)\(^{26,27}\) corroborates the deprotonation of all of them. A further evidence for that
is the absence of broad bands about 3200 cm\(^{-1}\), in the IR spectra, characteristic for the stretching band of the silanol groups in the incompletely condensed silsesquioxanes.\(^{28}\)

We have recently reported that the tetramethylcyclopentadienyl-silsesquioxane complexes 4 are capable to efficiently oxidize alkenes using aqueous hydrogen peroxide as oxidant.\(^{17}\) To gain insight into the catalytic behavior of this type of complexes, we are interested in exploring the catalytic activity of the new Ti-CpPOSS complexes in the epoxidation of alkenes using aqueous hydrogen peroxide as oxidant (Chart 1), and in assessing the influence of the electronic and the steric Cp ring characteristics on their catalytic behaviors. Thus, catalytic studies of the activity of 6b and 8b were performed and their catalytic activities were compared with that shown by the analogue complex 4b, which was recently reported by us.\(^{17}\) Therefore, we studied the epoxidation of the model substrate, cis-cyclooctene, under similar reaction conditions used for complex 4b (55 °C, 2 equiv. of aqueous H\(_2\)O\(_2\), in the presence of 0.5 mol% of catalyst).

**Chart 1.** Figures of complexes 4b, 6b, and 8b.

Complexes 6b and 8b exhibited good catalytic activity in the epoxidation of cis-cyclooctene affording quantitative yields of the corresponding epoxide in 9-11 h, under mild conditions. For both catalysts, the catalytic reactions were entirely selective for epoxidation, being 1,2-epoxycyclooctane the only product obtained.

The high catalytic efficiency displayed by the titanium cyclopentadienyl-silsesquixane complexes on olefin epoxidation using hydrogen peroxide is remarkable given that Ti-silsesquioxane complexes reported so far are not active for epoxidation with H\(_2\)O\(_2\) under homogeneous conditions. The lack of activity of the latter has been
attributed to poisoning of the active site by water coordination and deactivation of the active hydroperoxy intermediate (generated in the process). Thus, we propose that the incorporation of the Cp fragment to the tridentate cyclopentadienyl-silsesquioxane ligand creates the critical hydrophobic environment around of the titanium atom to reduce the local water concentration and to facilitate the accumulation of alkene about the metal center; enabling the catalytic performance.

The kinetic profiles of complexes 4b, 6b, and 8b show that the conversion of cis-cyclooctene is initially relatively fast. No induction period was observed, which indicates that the active oxidizing species are formed rapidly upon addition of the oxidant to the reaction medium, after which the reaction slows down over the course of time (Figure 2).

![Figure 2](image-url)

**Figure 2.** Kinetic profiles of cyclooctene epoxidation with H₂O₂ in the presence of catalysts 4b, 6b, and 8b.

As shown in Figure 2, complexes 8b and 6b resulted to be more active catalysts than complex 4b, affording quantitative conversion of epoxide after 9, 11, and 16 h of reaction, respectively. As expected, the reduction of the electron-donating ability and
the steric volume of the Cp ring have a beneficial effect in the catalytic activity of the
titanium complexes, due to the increase of the Lewis acidity and the accessibility of the
titanium atom.

Concluding remarks

The modular nature of the cyclopentadienyl-silsesquioxane ligands as well as their
versatile synthetic approach subtlety allows preparing a new set of titanasilsesquioxane
complexes, including some of the corned-capped cyclopentadienyl compounds initially
formed. The isolation and fully characterization of the latter has allow to verify their
isomerization toward the corresponding titanium cyclopentadienyl-silsesquioxane
compound and to establish the influence of the different experimental factors on the
course of this process. The novel Ti-CpPOSS complexes display good catalytic
activities in the epoxidation of cis-cyclooctane using aqueous hydrogen peroxide as
oxidant. Such a prominent catalytic behavior is ascribed to the hydrophobic
environment provided around titanium by the cyclopentadienyl fragment of the
CpPOSS ligand. The reduction of the π-donating ability and the steric volume of the Cp
ring produces a beneficial effect in the catalytic performance of the Ti-CpPOSS
complexes.

Experimental Section

General Considerations. All manipulations are performed under an argon atmosphere,
using Schlenk and high-vacuum line techniques. The solvents are dried and purified
with an MBRAUN solvent purification system. Deuterated solvents are stored over
activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. NEt₃
(Aldrich) is distilled before use and stored over 4 Å molecular sieves. Silsesquioxane
trisilanols R₇SiO(OH)₃, are purchased from commercial sources (Hybrid Plastics) and
used without further purification. Ti(η⁵-C₅H₄SiMe₂Cl)Cl₃,²⁰ C₃H₃(SiMe₃)₂(SiMe₂Cl)₃¹
and Ti(η⁵-C₅H₄SiMe₂OPh₂Si₂O₁₁-κ²O₂)Cl¹⁷ are prepared via known procedures. C, H
and N microanalyses are performed on a Perkin-Elmer 240B and/or Heraeus CHN-O-
Rapid microanalyzer. Nuclear magnetic resonance (NMR) spectra are recorded, at 25 °C, on a Bruker Model AV400 (1H NMR at 400 MHz, 13C NMR at 100.6 MHz, and 29Si NMR at 79.5 MHz).

**Synthesis of Ti(η^5-C_5H_5SiMe_3SiMe_2Cl)Cl_3 (1c).** A solution of C_5H_3(SiMe_3)_2(SiMe_2Cl) (6.2 mL, 18 mmol) in dichloromethane (20 mL) is added to a solution of TiCl_4 (2 mL, 18 mmol) in CH_2Cl_2 (20 mL), giving a brown solution. The reaction mixture is transferred into a Teflon-tight ampoule, heated at 60 °C, and maintained at this temperature for 3 d. After cooling down, the volatiles are removed under vacuum and the resultant oily solid is washed with hexane (2 x 15 mL) and dried under vacuum to give 1c as a yellow solid (4.64 g, 12.1 mmol, 67%). Anal. Calcd for C_{10}H_{18}Cl_4Si_2Ti: C 31.26, H 4.73; found: C 31.71, H 4.53.

1H NMR (CDCl_3, 400 MHz): δ 0.10 (s, 9H; SiMe_3), 0.49, 0.56 (s, 2 x 3H; SiMe_2Cl), 7.02, 7.04 (m, 1H, 2H; C_5H_3).

29Si NMR (CDCl_3): δ –1.3 (SiMe_3), 15.0 (SiMe_2Cl).

**Synthesis of Ti(η^5-C_5H_4SiMe_2Cl)(iBu_7Si_7O_12-κ^3O_3) (5a).** A solution of NEt_3 (0.40 mL, 2.88 mmol) in toluene (35 mL) is added to a mixture of Ti(η^5-C_5Me_4SiMe_2Cl)Cl_3 (0.3 g, 0.96 mmol) and iBu_7Si_7O_9(OH)_3 (0.76 g, 0.96 mmol), finely mashed and placed within a Teflon-tight ampoule. After the reaction mixture is stirred at room temperature for 6 h, the solution darkens and a white solid is formed. The ammonium salt is collected by filtration and the volatiles are removed under vacuum. The brown oily residue is extracted into hexane (3 x 15 mL) and the resultant solution is concentrated (20 mL) and cooled at –20 °C to give 5a as a pale brown microcrystalline solid (0.71 g, 0.72 mmol, 75%). Anal. Calcd for C_{35}H_{73}ClO_{12}Si_8Ti: C 42.25, H 7.34; found: C 42.41, H 7.68. 1H NMR (CDCl_3, 400 MHz): δ 0.71 (s, 6H; SiMe_2Cl), 0.54, 0.96, 1.82 (brm, 14H, 42H, 7H; iBu), 6.60, 6.77 (m, 2 x 2H; C_5H_4). 29Si NMR (CDCl_3): δ 18.9 (SiMe_2Cl), –70.8, –67.3, –66.5 (iBu_7Si_7O_12).

**Synthesis of Ti(η^5-C_5H_4SiMe_2Cl)(Ph_7Si_7O_12-κ^3O_3) (5b).** To a mixture of Ti(η^5-C_5Me_4SiMe_2Cl)Cl_3 (0.3 g, 0.96 mmol) and Ph_7Si_7O_9(OH)_3 (0.89 g, 0.96 mmol), finely
mashed and placed within a Teflon-tight ampoule, is added a solution of NEt₃ (0.40 mL, 2.88 mmol) in toluene (30 mL). The reaction mixture is stirred at room temperature for 6 h. As the reaction draws on, the mixture color darkens while a solid is formed. The white solid is collected by filtration and the volatiles are removed under vacuum to give a brownish solid. This solid is washed with hexane (2 x 15 mL) to afford 5b as a brown solid (1.02 g, 0.90 mmol, 94%). Anal. Calcd for C₄₉H₄₅ClO₁₂Si₄Ti: C 51.86, H 3.97; found: C 51.83, H 4.01. ¹H NMR (CDCl₃, 400 MHz): δ 0.74 (s, 6H; SiMe₂Cl), 6.77, 6.85 (m, 2 x 2H; C₅H₄), 7.18, 7.34, 7.72 (brm, 14H, 7H, 14H; Ph). ¹³C NMR (CDCl₃): δ 1.2 (SiMe₂Cl), 124.1, 124.4 (C₅H₄), 128.08, 128.1, 128.2, 129.3, 130.6, 130.7, 131.2, 131.9, 132.4, 134.1, 134.6, 134.7 (Ph). ²⁹Si NMR (CDCl₃): δ −19.6 (SiMe₂Cl), −83.3, −77.1, −76.2 (Ph₇Si₇O₁₂).

**Synthesis of Ti(η⁵-C₅H₄SiMe₂O′Bu₇Si₇O₁₁-κ²O₂)Cl (6a).** A solution of NEt₃ (0.40 mL, 2.88 mmol) in toluene (25 mL) is added to a mixture of Ti(η⁵-C₅H₄SiMe₂Cl)Cl₃ (0.3 g, 0.96 mmol) and ‘Bu₇Si₇O₉(OH)₃ (0.76 g, 0.96 mmol), finely mashed. The reaction mixture is heated at 70 ºC and stirred for 6 d. The resultant suspension is cooled down to room temperature and the ammonium salt is collected by filtration. The filtrate is concentrated under vacuum and the brown oily residue is extracted into hexane (3 x 15 mL). The resultant solution is concentrated (20 mL) and cooled at −20 ºC to give 6a as a pale brown microcrystalline solid (0.76 g, 0.77 mmol, 80%). Anal. Calcd for C₃₅H₇₃ClO₁₂Si₈Ti: C 42.25, H 7.34; found: C 42.30, H 7.36. ¹H NMR (CDCl₃, 400 MHz): δ 0.39 (s, 6H; SiMe₂O), 0.60, 0.96, 1.82 (brm, 14H, 7H, 42H, 7H; ‘Bu), 6.63, 6.88 (m, 2 x 2H; C₅H₄). ²⁹Si NMR (CDCl₃): δ −6.7 (SiMe₂O), −71.3, −71.0, −68.4, −67.6, −66.9 (‘Bu₇Si₇O₁₂).

**Synthesis of Ti(η⁵-C₅H₃SiMe₃SiMe₂Cl)(‘Bu₇Si₇O₁₂-κ³O₃) (7a).** A solution of NEt₃ (0.33 mL, 2.34 mmol) in toluene (25 mL) is added to a mixture of Ti(η⁵-C₅H₃SiMe₃SiMe₂Cl)Cl₃ (0.3 g, 0.78 mmol) and ‘Bu₇Si₇O₉(OH)₃ (0.62 g, 0.78 mmol), finely mashed. The reaction mixture is stirred at room temperature for 6 h. The ammonium salt is collected by filtration and the volatiles are removed under vacuum.
The dark yellow residue is a mixture of 7a and 8a in a ratio ≈ 95%/5%, from which 7a is extracted into hexane (3 x 15 mL). This solution is concentrated (20 mL) and cooled at −20 °C to give 7a as a yellow solid (0.62 g, 0.58 mmol, 74%). Anal. Calcd for C_{38}H_{81}ClO_{12}Si_9Ti: C 42.83, H 7.60; found: C 42.65, H 7.52. \(^1\)H NMR (CDCl, 400 MHz): δ 0.28 (s, 9H; SiMe), 0.67, 0.70 (s, 2 x 3H; SiMeCl), 0.52, 0.91, 1.80 (brm, 14H, 7H; \(^7\)Bu), 6.72, 6.78, 6.89 (m, 3 x 1H; C, H3). \(^2\)Si NMR (CDCl): δ −7.8 (SiMe), 15.6 (SiMeCl), −70.4, −69.2, −68.1, −66.3, −65.5, −65.3, −64.7 (\(^7\)Bu\(_5\)SiO\(_{12}\)).

**Spectroscopic Data for Ti(\(\eta^5\)-C\(_5\)H\(_3\)SiMe\(_3\)SiMe\(_2\)Cl)(Ph\(_7\)SiO\(_{12}\)-\(\kappa^2\)O\(_2\)) (7b).** \(^1\)H NMR (CDCl, 400 MHz): δ 0.07 (s, 9H; SiMe), 0.32, 0.56 (s, 2 x 3H; SiMeCl), 6.84, 6.87, 6.94 (m, 3 x 1H; C, H3), 7.17, 7.38, 7.73 (brm, 14H, 7H, 14H; Ph). \(^13\)C NMR (CDCl): δ −0.7 (SiMe), 0.02, 2.3 (SiMeCl), 6.76, 6.85, 6.97 (m, 3 x 1H; C, H3). \(^29\)Si NMR (CDCl): δ −9.0 (SiMe), 14.1 (SiMeCl), −80.4, −78.6, −76.5, −76.0, −66.3, −64.3, −62.7 (Ph\(_7\)SiO\(_{12}\)).

**Synthesis of Ti(\(\eta^5\)-C\(_5\)H\(_3\)SiMe\(_3\)SiMe\(_2\)O\(_5\)\(^7\)Bu\(_7\)SiO\(_{12}\)-\(\kappa^2\)O\(_2\))Cl (8a).** A solution of NEt\(_3\) (0.40 mL, 2.88 mmol) in toluene (25 mL) is added to a mixture of Ti(\(\eta^5\)-C\(_5\)H\(_3\)SiMe\(_3\)SiMe\(_2\)Cl)Cl\(_3\) (0.3 g, 0.78 mmol) and \(^7\)Bu\(_7\)SiO\(_3\)(OH)\(_3\) (0.76 g, 0.96 mmol), finely mashed. The resultant reaction mixture is heated at 70 °C and stirred for 3 d. The resultant suspension is cooled down and the solid is collected by filtration. The volatiles are removed under vacuum and the brown oily residue is extracted into hexane (3 x 15 mL). The hexane solution is concentrated (20 mL) and cooled at −20 °C to give 8a as a pale brown microcrystalline solid (0.56 g, 0.53 mmol, 80%). Anal. Calcd for C\(_{38}\)H\(_{81}\)ClO\(_{12}\)Si_9Ti: C 42.83, H 7.60; found: C 42.70, H 7.72. \(^1\)H NMR (CDCl, 400 MHz): δ 0.26 (s, 9H; SiMe), 0.36, 0.39 (s, 2 x 3H; SiMeCl), 0.48, 0.99, 1.82 (brm, 14H, 42H, 7H; \(^7\)Bu), 6.76, 6.85, 6.97 (m, 3 x 1H; C, H3). \(^13\)C NMR (CDCl): δ −0.7 (SiMe), 0.02, 2.3 (SiMeCl), 20.7, 20.9, 21.7, 22.2, 22.6, 22.7, 23.5, 23.9, 24.1, 24.5, 25.6, 25.7, 26.6, 26.8, 26.9, 27.2, 27.5, 27.7, 27.9, 28.0, 28.3 (\(^7\)Bu), 124.2, 133.5, 135.9.
(C₅H₃). ²⁹Si NMR (CDCl₃): δ –6.9 (SiMe₃), –4.8 (SiMe₂O), –75.4, –70.4, –69.1, –68.0, –66.5, –65.5, –64.7 (‘Bu₇SiO₁₂).

Synthesis of Ti(η⁵-C₅H₃SiMe₂SiMe₂OPh₇SiO₁₁-K₂O₂)Cl (8b). A solution of NEt₃ (0.40 mL, 2.88 mmol) in toluene (25 mL) is added to a mixture of Ti(η⁵-C₅H₃SiMe₂SiMe₂Cl)Cl₃ (0.3 g, 0.78 mmol) and Ph₇SiO₉(OH)₃ (0.73 g, 0.78 mmol) finely mashed. The resultant reaction mixture is heated at 70 ºC and stirred for 24 h. The resultant suspention is cooled down to room temperature and the ammonium salt is removed by filtration. The filtrate is concentrated under vacuum and the brown residue is extracted into hexane (3 x 15 mL). The hexane solution is concentrated (20 mL) and cooled at –20 ºC to give 8b as a brown solid (1.03 g, 0.91 mmol, 95%). Anal. Calcld for C₅₂H₅₃ClO₁₂Si₉Ti: C 51.77, H 4.40; found: C 51.83, H 4.61. ¹H NMR (CDCl₃, 400 MHz): δ 0.07 (s, 9H; SiMe₃), 0.24, 0.61 (s, 2 x 3H; SiMe₂O), 6.76, 6.82, 7.12 (m, 3 x 1H; C₅H₃), 7.23, 7.35, 7.66 (brm, 14H, 7H, 14H; Ph). ¹³C NMR (CDCl₃): δ –0.7 (SiMe₃), 0.02, 2.3 (SiMe₂O), 120.2, 124.2, 127.8, 127.9, 128.0, 128.1, 130.6, 130.7, 130.8, 131.1, 131.2, 131.4, 131.6, 132.5, 133.5, 134.1, 134.3, 134.4, 134.42, 134.6, 135.9 (C₅H₃, Ph). ²⁹Si NMR (CDCl₃): δ –7.1 (SiMe₃), –3.2 (SiMe₂O), –82.7, –82.3, –78.8, –78.6, –78.4, –76.5, –76.1 (Ph₇SiO₁₂).

Alkene epoxidation. The catalytic tests are carried out in a reaction vessel equipped with a magnetic stirrer and immersed in an oil bath at the appropriate temperature. A catalyst:alkene:H₂O₂ ratio 0.5:100:200 is used, with 2 mL of MeCN. Olefin, acetonitrile, mesitylene (as internal standard), and the catalyst are transferred into the reaction vessel, and H₂O₂ (30% aqueous solution) is added to the mixture. The course of the reaction is monitored by quantitative GC analysis.

Acknowledgements. We gratefully acknowledge Spanish MCYT (project CTQ2011-23497), FCT-Fundação para a Ciência e Tecnologia, UID/Multi/04551/2013, and RECI/BBB-BQB/0230/2012, and CRUP and Ministerio de Economia y Competitividad for Bilateral Action Program (project PRI-AIBPT-2011-1157). We thank M.T. for the
DFT calculations. M.V. thanks University of Alcalá for a fellowship. B.R thanks FCT for IF/00346/2013.

Supporting Information Available

$^1$H and $^1$H-$^{29}$Si HMBC spectra of representative examples of these complexes and partial $^1$H NMR spectra of the transformation of 5a into 6a, and chromatograms.

References


