Synthesis and structural characterisation of tripodal titanium silsesquioxane complexes: a new class of highly active catalysts for liquid phase alkene epoxidation

Mark Crocker,*[a] Ruud H. M. Herold[a] and A. Guy Orpen[b]

[a] *Shell Research and Technology Centre Amsterdam, Postbus 38000, 1030 BN Amsterdam, The Netherlands*
[b] *School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS*

Titanium silsesquioxane complexes [Ti(L)($R_7Si_7O_{12}$)], possessing tripodal geometry, represent models for heterogeneous titanosilicate catalysts; the new complexes are exceptionally active and selective catalysts for liquid phase alkene epoxidation reactions.

The remarkable catalytic properties of titanosilicates such as titanium silicalite-1 (TS-1) have generated considerable scientific interest, particularly with regard to the nature of the active titanium species present. It is now generally accepted that a four-coordinate lattice titanium site is the catalytically active species in these materials.[1] Furthermore, recent studies point toward the involvement of titanium sites possessing tripodal geometry, representing so-called open lattice sites,[2,3] although the presence of closed lattice sites ('tetrapodal' sites) and bipodal sites has also been inferred (see Fig. 1).[1,2] With this in mind we have prepared soluble analogues of these different titanium species based on incompletely condensed silsesquioxane precursors and have studied the catalytic properties of the resulting complexes.[4] Recently we became aware of related studies aimed at modelling heterogeneous titanium-based epoxidation catalysts, which also employ silsesquioxane derivatives;[5,6] prompted by these reports we now describe our own findings.

Incompletely condensed silsesquioxanes have recently attracted interest as models for the silica surface.[7,8] Elegant work by Feher and coworkers has revealed that the molecular structure of **1** (see Scheme 1) shares many structural similarities with β-cristobalite (111) and β-tridymite (0001). Although the exact nature of the silica surface is a matter of great controversy, the occurrence of cristobalite- and tridymite-like surface structures has been frequently postulated on the basis of both experimental and theoretical studies. On this basis, we have prepared titanium complexes of **1** in which the silsesquioxane ligand functions as a model for the siliceous surface in a tripodal titanium site. Similarly, the monosilylated form of **1**, disilanol species **2** (Scheme 2) has been used to model the siliceous surface in bipodal and tetrapodal titanium sites.

Reaction of **1** with homoleptic titanium(IV) complexes TiL_4 (L = CH_2Ph, NMe_2, $OSiMe_3$, OPr^i) occurs with protonolysis, affording in each case a product with the empirical formula [TiL{(c-C_6H_{11})$_7$$Si_7O_{12}$}] (Scheme 1) on the basis of elemental analysis and solution ^{1}H NMR data. ^{29}Si NMR spectra of the products are particularly informative, the observation in each case of three resonances for the silsesquioxane Si atoms in a 3 : 1 : 3 ratio being consistent with the C_{3v} symmetry expected for a tripodal TiL(silsesquioxane) species. In the case of **6**, ^{29}Si NMR data indicate the presence of a second species containing five distinct silicon environments (with relative ratios 2 : 2 : 1 : 1 : 1), corresponding to the dimer [Ti{(c-C_8H_{11})$_7$$Si_7O_{12}$}(μ-$OPr^i$)]$_2$ recently reported by Maschmeyer *et al.*[7] Freshly prepared solutions of **6** were found to contain exclusively the monomer, while at longer equilibration times a monomer : dimer ratio of *ca.* 5 : 2 was observed in C_6D_6.

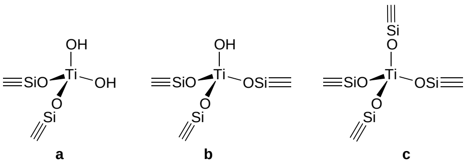
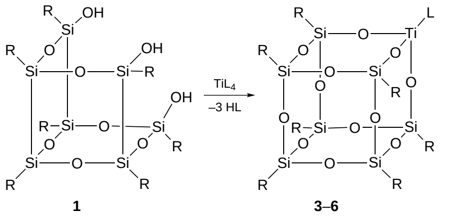
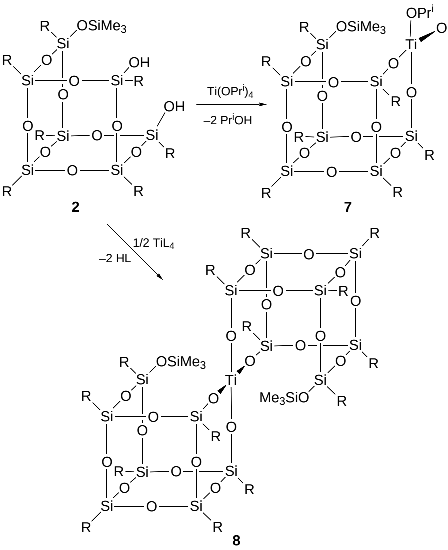


Fig. 1 Possible framework titanium sites in titanosilicates: (*a*) bipodal site, (*b*) tripodal (open lattice) site, (*c*) tetrapodal (closed lattice) site



Scheme 1 Synthesis of compounds **3–6**: L = CH_2Ph **3**, NMe_2 **4**, $OSiMe_3$ **5**, OPr^i **6**; R = cyclohexyl

The monomeric nature of **5** was confirmed by the results of a single crystal X-ray diffraction study (see Fig. 2). The crystal structure of **5** consists of isolated molecules separated by normal van der Waals contacts. Molecules of **5** lie in crystallographic special positions of $\bar{3}$ site symmetry and are consequently disordered; only one of the two centrosymmetrically related images of the disordered molecule is shown. The molecular structure of **5** consists of a pseudo-tetrahedral titanium(IV) centre coordinated by the tridentate silsesquioxane ligand and siloxy ($OSiMe_3$) ligand such that the complex has exact C_3 symmetry [disregarding the cyclohexyl substituent at Si(1′), the silicon opposite titanium]. As a consequence of the disorder the details of the apparent molecular geometry must be treated with scepticism. However, the gross geometry of **5** in the



Scheme 2 Synthesis of **7** and **8** (L = CH_2Ph, R = cyclohexyl)

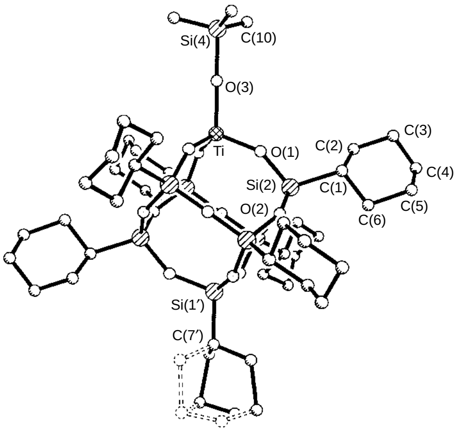


Fig. 2 Molecular structure of **5** showing atom labelling scheme. All hydrogen atoms have been omitted for clarity. Only one of the two centrosymmetrically related images of the disordered molecule is shown. Selected distances (Å) and angles (°): Ti–O(1) 1.658(6), Ti–O(3) 1.84(2), Si(2)–O(1) 1.625(6), Si(2)–O(2) 1.641(6), O(3)–Si(4) 1.79(2); O(1′)–Ti–O(1) 107.4(2), O(1)–Ti–O(3) 111.4(2), O(1)–Si(2)–O(2) 108.0(3), Si(2)–O(1)–Ti 151.0(4), Si(4)–O(3)–Ti 180.0.

solid state is clearly established, and by inference so is the structure of the monomer form of the isopropoxy analogue **6**, which also crystallises in space group $R\bar{3}$ with similar cell dimensions to **5**, and has molecules lying at the same special positions as **5**. For **6** the disorder is less well resolved and refinement less satisfactory.

The reaction of disilanol **2** with [Ti(OPr^i)$_4$] was examined as a possible route to a model bipodal titanium site. Addition of a diethyl ether solution of **2** to the titanium complex resulted in a smooth reaction and the subsequent isolation of [Ti(OPr^i)$_2${(c-C$_6$H$_{11}$)$_7$Si$_7$O$_{11}$(OSiMe$_3$)}] **7** as the sole product (Scheme 2). ^{1}H NMR data are consistent with the presence of two inequivalent isopropoxy groups in **7**, while the observation of the five signals in the ^{29}Si NMR spectrum corresponding to the silsesquioxane Si$_7$O$_{11}$ core indicates that, as for the free ligand, a plane of symmetry runs through the silsesquioxane ligand, with the alkoxide ligands lying in the plane.

The reaction of 2 equiv. of silsesquioxane **2** with [Ti(CH$_2$Ph)$_4$] was chosen as a convenient means of preparing a model for the closed lattice site. In aprotic solvents a rapid reaction occurs with the formation of a colourless solution, from which bis(silsesquioxane) complex **8** can be isolated in quantitative yield (Scheme 2).

^{1}H and ^{29}Si NMR spectroscopy reveal the presence of only one type of –OSiMe$_3$ group in **8**, suggesting equivalence of the {(c-C$_6$H$_{11}$)$_7$Si$_7$O$_{11}$(OSiMe$_3$)} ligands. The presence of molecular C_2 symmetry in **8** is confirmed by the results of X-ray crystallography.[9] Consistent with tetrahedral coordination of the Ti^{IV} centre, seven resonances are observed in the ^{29}Si NMR spectrum for the framework silsesquioxane Si atoms, indicating that the local mirror symmetry of the silsesquioxane ligands is not retained at titanium.

The epoxidation of oct-1-ene with Bu^{t}OOH (TBHP) was chosen as a convenient test of the epoxidation activity of complexes **3**–**8**. At the alkene/TBHP molar ratio of *ca.* 20 employed, pseudo-first order kinetics are observed corresponding to the rate equation:

$$\mathrm{d[epoxide]/d}t = k_1[\mathrm{TBHP}]$$

(where $k_1 = k_2[\mathrm{Ti}] = k_3[\mathrm{Ti}][\mathrm{alkene}]$)

At high TBHP conversions (generally > 80%), some deviation from first order kinetics is observed, corresponding to a decrease in the reaction rate. This can be attributed to the fact that the reaction is autoretarded by the *tert*-butanol co-product, a phenomenon observed previously for epoxidation catalysts.[10]

The calculated second order rate constants for TBHP conversion ($k_2 = k_1$/[Ti]) for complexes **3**–**8** are shown in Table 1. Most striking is the finding that the measured values of k_2 for the tripodal complexes **3**–**6** are *ca.* one order of magnitude greater than for **7** and **8**, while the former complexes also show superior selectivity. Complexes **3**–**6** are also considerably more active under these test conditions than titanosilicate catalysts such as Ti-MCM-41,[11] when compared on the basis of k_2 values. Our conclusion is that the (most) active site in these materials, as far as epoxidation catalysis is concerned, corresponds to the tripodal, open-lattice type of titanium site. The comparatively low epoxidation activity of Ti-MCM-41 can be ascribed to the fact that only a small fraction of the titanium sites in the material are exposed at the surface and possess the correct coordination environment.

Table 1 Epoxidation of oct-1-ene with TBHP catalysed by titanium silsesquioxane complexes[a]

Catalyst	$10^2\,k_2$/ dm^3 mol^{-1} s^{-1}	Selectivity to epoxide[b] (%)
3	123	95
4	63	99
5	97	97
6	149	93
7	9.3	75
8	4.7	83
Ti-MCM-41[c]	2.6	94

[a] Conditions: T = 80 °C, Ti = 0.2 mmol, TBHP = 30 mmol, oct-1-ene (75 g) as solvent. [b] Selectivity = (mol 1,2-epoxyoctane formed/mol TBHP consumed) × 100; selectivities were determined at 90% TBHP consumption. Data quoted are derived from at least two runs. [c] Ti content = 1.43 mass%.

Footnotes and References

* E-mail: m.crocker@siop.shell.nl

† NMR data for selected compounds: **5**: ^{1}H NMR (C$_6$D$_6$, 250.1 MHz): δ 2.13–0.97 (m, 77 H, c-C$_6$H$_{11}$), 0.21 (s, 9 H, SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ 2.76 (s, OSiMe$_3$), −65.80, −67.90, −68.85 (s, 3 : 1 : 3). **7**: ^{1}H NMR (C$_6$D$_6$, 500.1 MHz); δ 4.62 [spt, 1 H, C*H*(CH$_3$)$_2$, *J* 6.1 Hz], 4.57 [spt, 1 H, C*H*(CH$_3$)$_2$, *J* 6.1 Hz], 2.17–1.05 (m, 77 H, *c*-C$_6$H$_{11}$), 1.32 (d, 6 H, CH$_3$, *J* 6.1 Hz), 1.30 (d, 6 H, CH$_3$, *J* 6.1 Hz), 0.47 [s, 9 H, Si(CH$_3$)$_3$]. ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ 10.94 (s, OSiMe$_3$), −65.64, −66.37, −66.58, −67.49, −68.86 (s, 1 : 1 : 1 : 2 : 2). **8**: ^{1}H NMR (C$_6$D$_6$, 250.1 MHz): δ 2.14–1.00 (m, 154 H, *c*-C$_6$H$_{11}$), 0.52 (s, 18 H, SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ 10.42 (s, SiMe$_3$), −66.35, −66.79, −66.92, −68.22, −69.26, −69.50, −69.72 (s, all × 1). All compounds analysed satisfactorily.

‡ *Crystal data* for **5**: C$_{45}$H$_{86}$O$_{13}$Si$_8$Ti, M_r = 1107.8, rhombohedral, space group $R\bar{3}$ (no. 148), a = 16.955(4), c = 17.853(6) Å, $\alpha = \beta = 90$, γ = 120°, U = 4445(2) Å^3, Z = 3, D_c = 1.24 g cm^{-3}, λ = 0.710 73 Å, μ(Mo-Kα) = 0.36 mm^{-1}, $F(000)$ = 1782, T = 200 K. The structure was solved by direct and Fourier methods: 1296 unique reflections collected; 113 parameters (11 restraints); wR_2 = 0.287, R_1 = 0.107 for the 775 data with $I > 2\sigma(I)$. CCDC 182/626.

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