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Synthesis and characterisation of titanium silasesquioxane complexes: soluble models for the active site in titanium silicate epoxidation catalysts†

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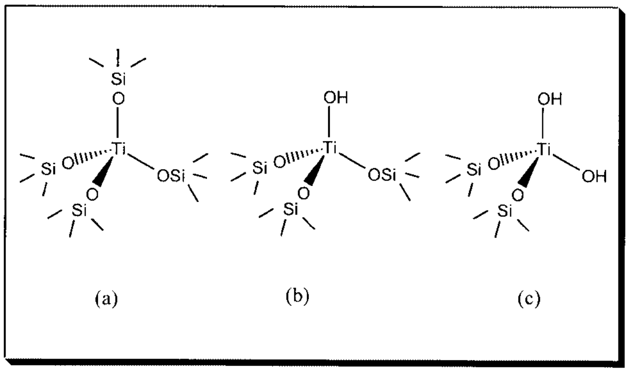
Titanium silasesquioxane complexes have been prepared as models for the catalytically active centres in titanium silicate oxidation catalysts. Complexes $[\mathrm{TiL(R_7Si_7O_{12})}]$ [R = c-C_6H_{11}, L = CH_2Ph **5**, NMe_2 **6**, $OSiMe_3$ **7**, OPr^i **8** or OBu^t **9**; R = c-C_5H_9, L = CH_2Ph **13** or OPr^i **14**] were prepared from the reactions of incompletely condensed silasesquioxanes $R_7Si_7O_9(OH)_3$ **1**, **2** with homoleptic complexes TiL_4. Aryloxy derivatives $[\mathrm{TiL(R_7Si_7O_{12})}]$ [R = c-C_6H_{11}, L = OPh **10**, O-C_6H_4F-p **11** or O-$C_6H_4NO_2$-p **12**] were prepared from the reaction of **8** with the corresponding aryl alcohols. The ^{29}Si and ^{13}C NMR spectroscopic data obtained on **5**–**14** indicate that the local C_{3v} symmetry of the silasesquioxane ligand is retained at titanium, consistent with the formation of monomeric complexes possessing tripodal geometry. The monomeric nature of **7** was confirmed by X-ray crystallography. For complexes **8**–**12** solution NMR spectroscopy reveals the presence of a dimer, containing μ-alkoxy ligands, in equilibrium with the monomer. The zirconium analogue of **9**, $[\mathrm{Zr(OBu^t)}\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}]$ **15**, was similarly isolated as a monomer–dimer mixture from the reaction of the incompletely condensed silasesquioxane $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ with $[\mathrm{Zr(OBu^t)_4}]$. Reaction of the disilanol $(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)(OH)_2$ **4** with an excess of $[\mathrm{Ti(OPr^i)_4}]$ afforded $[\mathrm{Ti(OPr^i)_2}\{(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}]$ **16**, containing a bidentate silasesquioxane ligand, while reactions with TiL_4 (L = CH_2Ph, NMe_2 or $OSiMe_3$) afforded $[\mathrm{Ti}\{(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}_2]$ **17**, independent of the stoichiometry of the reactants. Complexes **5**–**14** serve as soluble models for putative tripodal (open lattice) sites in titanium silicates, while **16** and **17** represent models for bipodal and tetrapodal (closed lattice) sites, respectively. From a study of the catalytic properties of complexes **5**–**17** in the epoxidation of oct-1-ene with *tert*-BuOOH (TBHP), revealing high activity for **5**–**14** and low activity for **16** and **17**, it is concluded that the most active site in titanium silicate epoxidation catalysts corresponds to a four-co-ordinate site possessing tripodal geometry. Studies using IR and NMR spectroscopy show that, in the absence of olefins, putative alkylperoxo complexes formed by the addition of TBHP to tripodal complexes decompose rapidly at ambient temperature. Based on the high TBHP-to-epoxide selectivities observed under epoxidising conditions, it is apparent that the rate of epoxidation is significantly greater than that of alkylperoxo intermediate decomposition.

The catalytic properties of the synthetic titanium-containing zeolite, titanium silicalite-1 (TS-1),[1] are of considerable scientific and commercial interest:[2,3] using hydrogen peroxide as oxidant, TS-1 is active for a range of oxidation reactions including the epoxidation of alkenes to epoxides, the oxidation of primary alcohols to aldehydes and secondary alcohols to ketones, the hydroxylation of aromatics, the ammoxidation of ketones and the oxidation of alkanes to alcohol–ketone mixtures. The remarkable properties of TS-1, coupled with a desire to overcome the pore size limitations imposed by the MFI structure, have in turn generated significant interest in the catalytic properties of amorphous titania–silica mixed oxides[4–8] and amorphous forms of titania supported on silica,[9–12] as well as research directed at the synthesis of large[13–15] and ultralarge[16–18] pore zeolites in which titanium is incorporated in the framework.

In recent years particular attention has been focused on elucidating the nature of the active titanium species present in titanium zeolites in order to achieve a better understanding of their unique catalytic properties. It is now generally accepted that the catalytically active species in these materials correspond to isolated titanium sites occupying tetrahedral positions in the silicate lattice.[2] Furthermore, recent studies point toward the involvement of titanium sites possessing tripodal geometry, representing so-called open lattice sites (structure (b) in Scheme 1). Titanium species possessing this geometry were first postulated by Shell workers to be the active site in amorphous titania on silica epoxidation catalysts.[19] More recently, Maschmeyer



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

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3791/

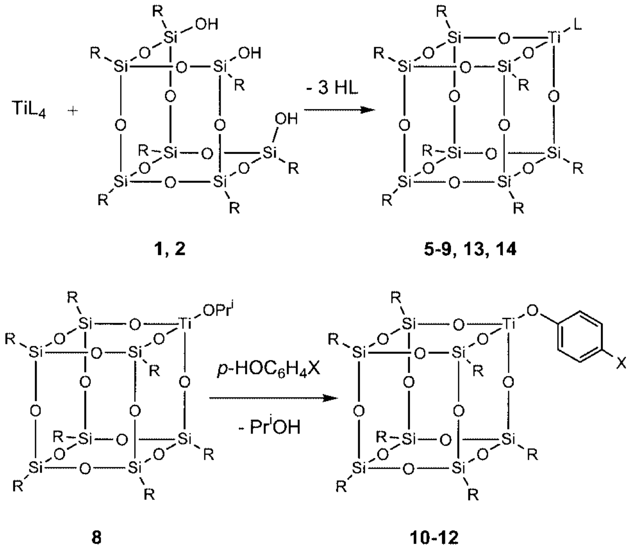
et al.[20] have shown that tripodal titanium species, prepared by the grafting of a suitable titanium precursor onto the inner surface of MCM-41 (a mesoporous silica), show high activity in alkene epoxidation using alkyl hydroperoxides. Enichem researchers[21] have proposed that an analogous tripodal species is readily formed by hydrolysis of lattice TiO_4 species in TS-1, the driving force for its formation being the release of lattice strain around the titanium site, and have presented EXAFS and photoluminescence data which support the presence of both closed lattice sites ("tetrapodal" sites, structure (a) in Scheme 1) and open lattice sites in dehydrated TS-1 samples.[22] Le Noc *et al.*[23] have reached similar conclusions on the basis of EXAFS, UV-vis and ^1H MAS NMR spectroscopic data and have suggested that the open lattice site may even predominate in dehydrated TS-1 samples.

In addition to the closed and open lattice sites, the presence of bipodal sites (structure (c) in Scheme 1) can also be inferred. For crystalline titanosilicates the closed lattice site might be expected to be predominant in dehydrated samples, with tripodal and bipodal titanium species occurring at defect sites in the silicate lattice. In the presence of water, formation of additional tripodal and bipodal sites is anticipated to occur *via* successive hydrolysis of the Ti–O(Si) bonds of the closed lattice titanium sites,[24] a process which appears to be energetically favourable according to a recent computational study.[25] Despite the many studies on heterogeneous titanium silicate catalysts, the relative importance of these different titanium sites in selective oxidation catalysis has yet to be ascertained.

With this in mind we have prepared soluble analogues of these different titanium species based on silasesquioxanes and have studied the catalytic properties of the resulting titanium complexes in an effort to elucidate structure–activity effects.[26,27] Related work, also employing silasesquioxane precursors, has recently been reported by Abbenhuis *et al.*[28] and by Maschmeyer *et al.*,[29] while Roesky and co-workers[30–32] have described the use of silanetriol precursors for the preparation of a number of titanium compounds which model titanium silicates.

Incompletely condensed silasesquioxanes, $R_7Si_7O_9(OH)_3$ {R = *c*-C_5H_9 **1**, *c*-C_6H_{11} **2** or *c*-C_7H_{13} **3**} prepared by hydrolysis of the corresponding trichlorosilanes, $RSiCl_3$, have recently attracted considerable interest as models for the silica surface.[33,34] Feher *et al.*[35] have established that the molecular structure of **2** (see Scheme 2) 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 frequently been postulated on the basis of both experimental and theoretical studies.[36] On this basis, silasesquioxanes appear to represent the best molecular models for the silica surface prepared to date. Indeed the vanadium silasesquioxane complex $[\{(c\text{-}C_6H_{11})_7Si_7O_{12}VO\}_2]$ has been shown to be a useful model for vanadia supported on silica, comparison of ^{51}V NMR and Raman spectroscopic data revealing structural similarities to the extent that the vanadia species found at the silica surface could be unambiguously assigned as a tripodal $(SiO)_3V{=}O$ unit.[37]

Following this rationale, we have prepared titanium complexes of compounds **1** and **2** in which the silasesquioxane ligand functions as a model for the siliceous surface in a tripodal titanium site. Similarly, the monosilylated form of **2**, disilanol $(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)(OH)_2$ **4** has been used to model the siliceous surface in bipodal and tetrapodal titanium sites. In this paper we report on the preparation and characterisation of these complexes, together with the results of a study into their catalytic properties in alkene epoxidation. The implications these results hold for titanosilicate epoxidation catalysts are discussed.



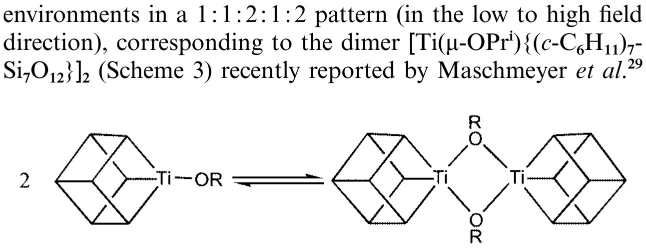
Scheme 2 Synthesis of compounds **5**–**14**: R = *c*-C_6H_{11}; L = CH_2Ph **5**, NMe_2 **6**, $OSiMe_3$ **7**, OPr^i **8** or OBu^t **9**; X = H **10**, F **11** or NO_2 **12**; R = *c*-C_5H_9; L = CH_2Ph **13** or OPr^i **14**.

Results and discussion

Preparation and characterisation of tripodal titanium silasesquioxane complexes

Reaction of silasesquioxane **2** with homoleptic titanium(IV) complexes TiL_4 (L = CH_2Ph, NMe_2, $OSiMe_3$, OPr^i or OBu^t) occurs with protonolysis in diethyl ether or toluene solution, affording in each case a product with the empirical formula $[TiL\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}]$ (L = CH_2Ph **5**, NMe_2 **6**, $OSiMe_3$ **7**, OPr^i **8** or OBu^t **9**; see Scheme 2) on the basis of elemental analysis and solution ^1H NMR data. The ^{29}Si NMR spectra of the products (measured over the range +30 to −70 °C) are particularly informative, the observation in each case of three resonances for the silasesquioxane Si atoms in a 3 : 1 : 3 ratio being consistent with the C_{3v} symmetry expected for a tripodal TiL(silasesquioxane) species. As observed previously for titanium silasesquioxane complexes,[38,39] the resonance for the Si atoms bearing OH groups (δ −60.2 for **2**) shifts upfield by *ca.* 5 ppm upon co-ordination of the oxygen with titanium. Further evidence for the tripodal geometry of complexes **5**–**9** is provided by ^{13}C NMR spectra, which likewise exhibit three resonances for the *ipso*-carbons of the cyclohexyl groups with integrated intensities of 3 : 1 : 3.

In the case of compound **8** ^{29}Si NMR data indicate the presence of a second species containing five distinct silicon environments in a 1 : 1 : 2 : 1 : 2 pattern (in the low to high field direction), corresponding to the dimer $[Ti(\mu\text{-}OPr^i)\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}]_2$ (Scheme 3) recently reported by Maschmeyer *et al.*[29]



Scheme 3 Monomer–dimer interconversion for titanosilasesquioxane alkoxide complexes.

Freshly prepared solutions of **8** were found to contain exclusively the monomer, while at equilibration times of several days a monomer : dimer ratio of *ca.* 5 : 2 was observed in C_6D_6 by ^{29}Si NMR spectroscopy. In the case of **9**, syntheses in toluene or diethyl ether similarly afforded the product exclusively as a monomer, ^{13}C and ^{29}Si NMR spectra of the monomer measured after 2 weeks in benzene solution showing the absence of any dimer. However, syntheses performed in THF consistently afforded a mixture of monomer and dimer, in ratios (monomer : dimer) of *ca.* 4 : 1. In this context it is pertinent

Table 1 Bond lengths [Å] and angles [°] for compound **7**[a]

Ti(1)–O(1)	1.658(6)	Ti(1)–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(1)–O(1)	107.4(2)	O(1)–Ti(1)–O(3)	111.4(2)
O(1)–Si(2)–O(2)	108.0(3)	Si(2)–O(1)–Ti(1)	151.0(4)
Si(4)–O(3)–Ti(1)	180.0		

[a] Primed atoms related to unprimed equivalents by $-y, x-y, z$.

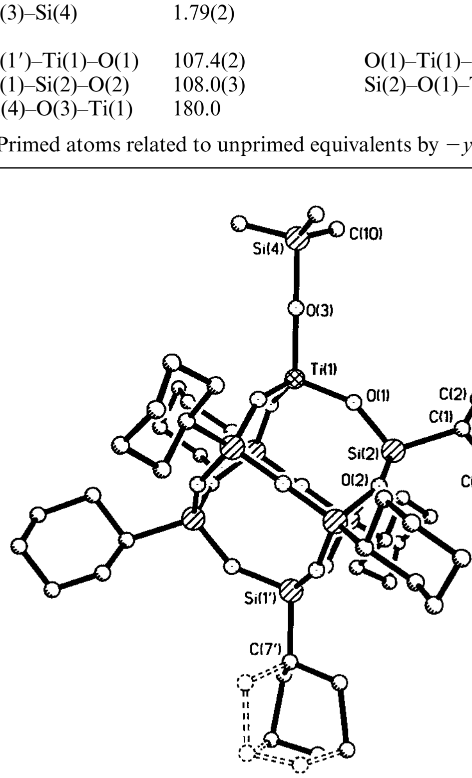


Fig. 1 Molecular structure of compound **7** showing the atom labelling scheme. All hydrogen atoms have been omitted for clarity. Only one of the two centrosymmetrically related images of the disordered molecule is shown.

that while the reaction of [Ti(η-C_5H_5)Cl_3] with **2** cleanly affords the monomer [Ti(η-C_5H_5){$R_7Si_7O_{12}$}] (R = *c*-C_6H_{11}),[38,39] the reaction of **2** with [Ti(η-C_5H_5)$_2$$Cl_2$] has been shown to afford [Ti(η-C_5H_5){$R_7Si_7O_{12}$}] as the thermodynamic product, the dimer [Ti(η-C_5H_5){$R_7Si_7O_{12}$}]$_2$ being the initially formed (kinetic) product.[39] Similarly, the monomer of **9** appears to represent a thermodynamic product: heating the monomer in the presence of 10 equivalents of THF at 55 °C for 10 d failed to afford any trace of the dimer, there being no discernible interaction between the complex and the added THF. On this basis it appears that the relative thermodynamic stability of the monomer and dimer in these systems is determined principally by the steric properties of the ancillary ligand, bulky ligands favouring formation of the monomer.

The monomeric nature of compound **7** was confirmed by the results of a single crystal X-ray diffraction study (Fig. 1; Table 1). The crystal structure consists of isolated molecules separated by normal van der Waals contacts. Molecules lie in crystallographic special positions of -3 site symmetry and are consequently disordered; only one of the two centrosymmetrically related images of the disordered molecule is shown in Fig. 1. The molecular structure consists of a pseudo-tetrahedral titanium(IV) centre co-ordinated by the tridentate silasesquioxane 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 **7** in the solid state is clearly established, and by inference so is the structure of the monomer form of the isopropoxy analogue **8**, which also crystallises in space group $R\bar{3}$ with similar cell dimensions to those of **7**, and has molecules lying at the same special positions as **7**. For **8** the disorder is less well resolved and refinement less satisfactory.

In order to extend the range of titanium silasesquioxane complexes available, the reactions of **5** and **8** with phenol were studied. In both cases addition of 1.0 equivalent of phenol to a diethyl ether solution of the titanium complex resulted in protonation of the capping ligand, as evidenced by ^1H NMR spectroscopy, and formation of the phenoxy complex **10**. Similarly, the reactions of 4-fluorophenol and 4-nitrophenol with **8** afforded the corresponding phenoxy derivatives **11** and **12** (Scheme 2). As for **8**, solution ^{29}Si NMR data obtained on **10**–**12** in each case reveal the presence of a dimer, in addition to the main monomeric product. For the dimers of **10**–**12** there are, as for **8**, five distinct environments for the silicon atoms, giving rise to the same 1 : 1 : 2 : 1 : 2 pattern. The observed monomer : dimer ratio for **10**, measured in C_6D_6 (0.06 M solution) after equilibration for *ca.* 24 h at room temperature, was typically around 5 : 1, the corresponding ratios for **11** and **12** being respectively 10 : 1 and 28 : 1. For syntheses of **10**–**12** performed in THF, approximately equimolar mixtures of the monomer and dimer were obtained in each case. The ^1H and ^{13}C spectra revealed the presence of co-ordinated THF in the mixtures; based on the integrated intensities of signals in ^1H NMR spectra and the number of ^{29}Si NMR signals observed for the silasesquioxane silicons, the THF appears to be associated with the dimer. In this context we note that Maschmeyer *et al.*[29] have reported the synthesis and structural characterisation of the methanol-solvated dimer of **8**, *i.e.* [Ti(μ-OPr^i){(*c*-C_6H_{11})$_7$$Si_7O_{12}$}(MeOH)]$_2$. By analogy, we suggest that the dimers of **10**–**12**, when prepared in THF, exist as THF solvates of the type [Ti(μ-OR){(*c*-C_6H_{11})$_7$$Si_7O_{12}$}(THF)]$_2$.

Compounds **10**–**12** were also characterised using mass spectrometry, field desorption (FD) mass spectra containing a strong signal corresponding to the parent ion. In the case of **7** the parent ion is not observed in FD or electron impact mass spectra, while for **8** it is a very weak signal only. For both these complexes an intense signal is observed at *m*/*z* 1970, corresponding to the species {(*c*-C_6H_{11})$_7$$Si_7O_{12}$Ti}$_2$(μ-O) formed in the mass spectrometer *via* bimolecular ether elimination from the parent complex.

Reaction of silasesquioxane **1** with homoleptic complexes TiL_4 in diethyl ether solution likewise affords complexes [TiL{(*c*-C_5H_9)$_7$$Si_7O_{12}$}] (L = CH_2Ph **13** or OPr^i **14**), which were found to be monomeric in solution. The preparation of **13** from **1** and [Ti(CH_2Ph)$_4$] has recently been reported by Duchateau *et al.*[40] As for complexes **5**–**9**, ^{29}Si and ^{13}C NMR data for **13** and **14** show that the complexes possess C_{3v} symmetry. The successful synthesis of tripodal complexes of **1** is significant, owing to the ready availability of silasesquioxane **1**, in comparison with **2**. Thus 30–40% yields of **1** can be obtained from the hydrolysis of (*c*-C_5H_9)$SiCl_3$ after 3 d at reflux,[41] whereas reaction times of around 2–3 years are required for comparable yields of **2** to be attained from the hydrolysis of (*c*-C_6H_{11})$SiCl_3$.[35] Unfortunately, complexes **13** and **14** are only sparingly soluble in organic solvents, as is the case for the parent silasesquioxane **1**,[41] rendering them rather unsuitable for liquid phase studies.

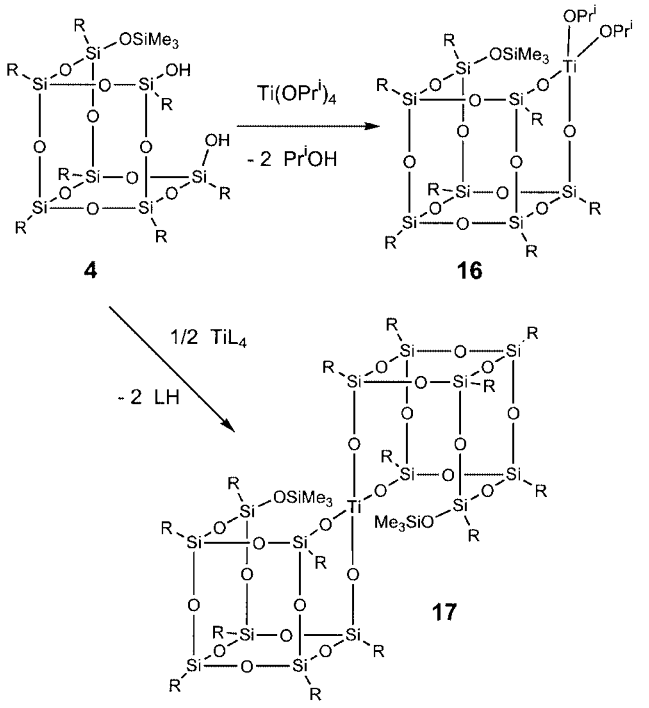
Preparation and characterisation of zirconium silasesquioxane complexes

Zirconium-containing silicates have recently been shown to possess catalytic properties in several selective oxidation reactions,[42–44] making the preparation of zirconium silasesquioxane complexes of interest. Whilst the synthesis and structural characterisation of a monomeric species [Zr(η-C_5Me_5){(*c*-C_6H_{11})$_7$$Si_7O_{12}$}] has been reported by Feher,[45] the reaction of **2** with [Zr(CH_2Ph)$_4$] has been shown to afford a dimeric species containing bridging siloxy groups.[40] Similarly, attempts in this work to prepare a simple tripodal species from the reaction of **2** with [Zr(NEt_2)$_4$] in THF were unsuccessful, an intractable mixture of products being obtained. However, the use of

$[Zr(OBu^t)_4]$ did afford a product with the empirical formula $[Zr(OBu^t)\{(c\text{-}C_6H_{11})_7Si_7O_{12}\}]$ **15**, solution NMR spectroscopy indicating that it exists as a mixture of monomer and dimer in a ratio (monomer:dimer) of *ca.* 4:1. As for the titanium analogue, **9**, bridging *tert*-butoxy groups are present in the dimer.

Preparation and characterisation of titanium complexes derived from disilanol 4

The reaction of $(c\text{-}C_6H_{11})_7Si_7O_9(OSiMe_3)(OH)_2$ **4** with $[Ti(OPr^i)_4]$ was examined as a possible route to a model bipodal titanium epoxidation catalyst. Slow addition of a diethyl ether solution of **4** to the titanium complex resulted in a smooth reaction and the subsequent isolation of $[Ti(OPr^i)_2\{(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}]$ **16** as the sole product (Scheme 4). The ^1H and ^{13}C NMR data are consistent with the presence of two inequivalent isopropoxy groups in **16**, while the observation of five signals in the ^{29}Si NMR spectrum corresponding to the silasesquioxane Si_7O_{11} core indicates that, as for the "free" ligand, a plane of symmetry runs through the silasesquioxane ligand, with the alkoxide ligands lying in the plane.



Scheme 4 Synthesis of compounds **16** and **17** ($R = c\text{-}C_6H_{11}$, $L = CH_2Ph$).

Interestingly, reaction of one equivalent of compound **4** with the complexes TiL_4 ($L = CH_2Ph$, NMe_2 or $OSiMe_3$) does not afford the corresponding mixed ligand complex $[TiL_2\{(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}]$, but yields instead equimolar amounts of the bis(silasesquioxane) complex $[Ti\{(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}_2]$ **17** (Scheme 4; see below) and the unchanged TiL_4 complex.

The reaction of two equivalents of disilanol **4** with $[Ti(CH_2Ph)_4]$ was chosen as a convenient means of preparing a model for the closed lattice titanium site. In aprotic solvents a rapid reaction occurs with the formation of a colourless solution, from which the bis(silasesquioxane) complex $[Ti\{(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}_2]$ **17** can be isolated in quantitative yield (Scheme 4). Proton and ^{13}C NMR spectroscopy reveal the presence of only one type of $OSiMe_3$ group in **17**, suggesting equivalence of the $\{(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}$ ligands. Consistent with tetrahedral co-ordination of the titanium(IV) centre, seven resonances are observed in the >CH region of the ^{13}C NMR spectrum, indicating that the local mirror symmetry of the silasesquioxane ligands is not retained at Ti. This is confirmed by ^{29}Si NMR spectroscopy, seven resonances being observed for the framework silasesquioxane Si atoms in the range δ −66.35 to −69.72, together with one at δ 10.42 corresponding to the $OSiMe_3$ group.

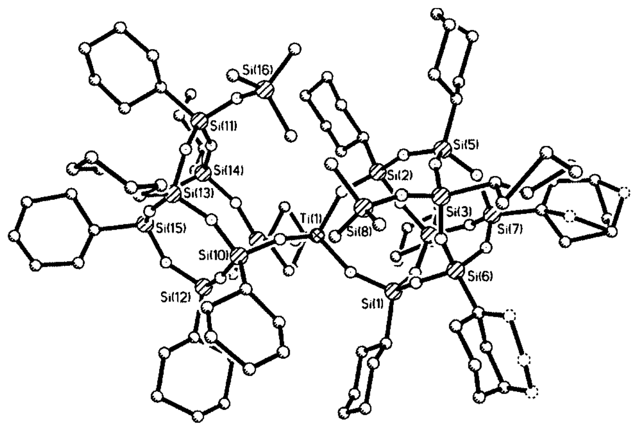


Fig. 2 Molecular structure of the first independent molecule of compound **17** showing the atom labelling scheme. All hydrogen atoms have been omitted for clarity. Both orientations of the disordered atoms are shown.

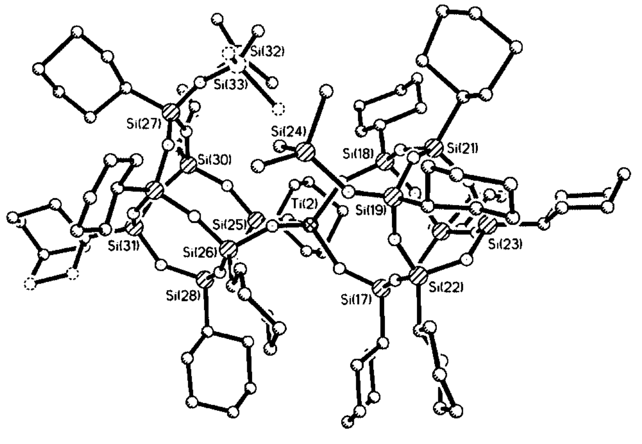


Fig. 3 Molecular structure of the second independent molecule of compound **17**. Details as in Fig. 2.

Further information concerning the molecular structure of compound **17** was provided by the results of a single crystal X-ray diffraction study on its toluene solvate (see Table 2). Perspective views of the molecular structure of the two independent molecules of $[Ti\{(c\text{-}C_6H_{11})_7Si_7O_{11}(OSiMe_3)\}_2]$ **17** in the crystal structure are given in Figs. 2 and 3. The crystal structure consists of isolated molecules of **17** and toluene separated by normal van der Waals contacts. Molecules of **17** lie in crystallographic general positions and consist of a pseudo-tetrahedral titanium(IV) centre co-ordinated by two silasesquioxane $\{R_7Si_7O_{11}(OSiMe_3)\}$ ligands such that the complex has approximate C_2 symmetry (but see below). The two independent molecules have very similar $Ti\{Si_8O_{12}\}_2$ cores with both having significant distortions away from C_2 symmetry. Displacement ellipsoid plots indicate considerable variation in the motion of the $Ti\{Si_8O_{12}\}_2$ cores, consistent with considerable framework flexibility (and possibly dynamic or static disorder).

The co-ordination geometry at titanium is close to tetrahedral (O–Ti–O angles range from 107.2(5) to 111.2(6)°), with Ti–O distances between 1.786(6) and 1.828(11) Å with mean 1.797(5) Å (Table 2). The Si–O–Ti angles range from 138.5(6) to 159.9(7)° with mean 148.4(28)°, the largest variations in angles and distances being around Ti(2). The Si–O(Ti) distances range from 1.594(13) to 1.661(7) with mean 1.628(7) Å. Other Si–O distances range from 1.540(12) to 1.654(8) with mean 1.619(2) Å

Table 2 Selected bond lengths [Å] and angles [°] for compound **17** (molecule 1)

Ti(1)–O(1)	1.786(6)	Ti(1)–O(13)	1.796(6)
Ti(1)–O(2)	1.788(7)	Ti(1)–O(14)	1.787(6)
O(1)–Ti(1)–O(2)	109.7(3)	O(2)–Ti(1)–O(13)	109.8(4)
O(1)–Ti(1)–O(13)	109.9(3)	O(14)–Ti(1)–O(2)	110.5(3)
O(1)–Ti(1)–O(14)	108.6(3)	O(14)–Ti(1)–O(13)	108.4(3)
Si(2)–O(2)–Ti(1)	140.6(5)	Si(1)–O(1)–Ti(1)	153.7(5)
Si(10)–O(14)–Ti(1)	151.0(4)	Si(9)–O(13)–Ti(1)	146.7(5)

Table 3 The IR and UV-vis spectroscopic data for titanium silasesquioxane complexes and related materials

Complex/material	$\tilde{\nu}$[Ti(OSi)$_x$]/cm^{-1}	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})[a]
5	941 (Nujol)	222 (45 000)[b]
6	946 (KBr)	215 (46 500)[c]
7	932 (KBr)	212 (47 200)
8	938 (KBr)	217 (46 100)
10	939 (KBr)	n.d.
11	942 (KBr)	n.d.
16	967 (KBr)	214 (46 700)
17	932 (Nujol)	228 (43 900)
[Ti(OSiMe$_3$)$_4$]	918 (Neat)	234 (42 700)
TS-1 (Ti = 1.5 wt%)	960 (KBr)	210 (47 600)
Amorphous TiO_2–SiO_2 (Ti = 8.2 wt%)	945 (KBr)	215, 260, (46 500, 38 500)

[a] Absorption measurements made on pentane solutions (*ca.* 1 mM), except for TS-1 and amorphous TiO_2–SiO_2 which were measured in the reflectance mode. [b] A CT band also observed at 376 nm associated with the benzyl ligand. [c] A CT band also observed at 312 nm associated with the dimethylamido ligand.

and Si–O–Si angles range from 138.3(4) to 163.4(9)° with mean 150.2(11)°.

The Ti–O distances in the seven tetrahedral titanium(IV) complexes in the Cambridge Structural Database (May 1993 version), in which titanium is co-ordinated by four oxygens only, average 1.783(6) Å (range 1.730 to 1.853 Å). The most similar of these to **17** is [Ti{(SiPh$_2$)$_4$O$_5$}$_2$].[46] Additionally, we note that the mean Ti–O distance in **17** of 1.797(5) Å is very similar to the Ti–O distance of 1.793(7) Å in TS-1 determined in a recent EXAFS study,[22] this figure representing the averaged value from the two main site types thought to be present: the closed lattice site, Ti(OSi)$_4$, and a five-co-ordinate open lattice species, SiOH $\cdots$ Ti(OH)(OSi)$_3$.

Comparison of IR and UV-vis spectra of titanium silasesquioxane complexes with titanium silicates

UV-vis and IR spectroscopic methods have been extensively used to characterise the titanium phases present in titanosilicates,[2] making a comparison of the spectroscopic properties of the titanium complexes described above with those of titanosilicate catalysts of interest (Table 3). The IR spectra of tripodal complexes **5**–**14**, as well as **16** and **17**, contain a band of medium intensity falling in the range 932–967 cm^{-1}, which is not present for the parent silasesquioxane ligands (Fig. 4). We note that the complex [Ti(OSiMe$_3$)$_4$] similarly shows an absorption at 918 cm^{-1}, not observed for Me$_3$SiOH. This band must therefore be associated with the presence of Si–O–Ti linkages, and is most readily assigned to a Si–O–Ti stretching vibration. Roesky and co-workers[31] have similarly reported the observation of an intense absorption band at 960–970 cm^{-1} for a number of cubic titanasiloxane compounds, assignment of the band to a Si–O–Ti stretching vibration being supported by the results of ^{18}O labelling.

For titanium silicates such as TS-1 and Ti-MCM-41 an absorption band is found at 960–970 cm^{-1} (Fig. 4),[2,3] while for amorphous titania–silica mixed oxides a similar band is observed in the region 940–960 cm^{-1}.[4–6] For amorphous titania supported on silica some workers report an absorption band at 960 cm^{-1},[47,48] although the presence of this band appears to depend on the preparation procedure employed.[49] Assignment of this band has led to considerable debate: some workers initially attributed it to the stretching vibration of a titanyl group, (SiO)$_2$Ti=O, by analogy with the spectra of molecular titanyl complexes,[47,50] while others have assigned it to a Si–O–Ti stretching vibration[51,52] or to an Si–O$^-$ absorption.[53] We have recently shown, on the basis of both synthetic studies and IR spectroscopy (employing SO$_2$ as a reactive probe molecule), that titanyl groups do not exist in titanium silicates in detectable concentrations.[49,54] In our opinion Roesky's observations, coupled with the above findings for titanium silasesquioxane complexes, provide convincing evidence that the 960 cm^{-1} absorption band of titanium silicates corresponds to a Si–O–Ti stretching vibration. This of course does not exclude the possibility that some contribution to this absorption may arise from Si-OH stretching, particularly for titanosilicates possessing highly hydroxylated surfaces.[6]

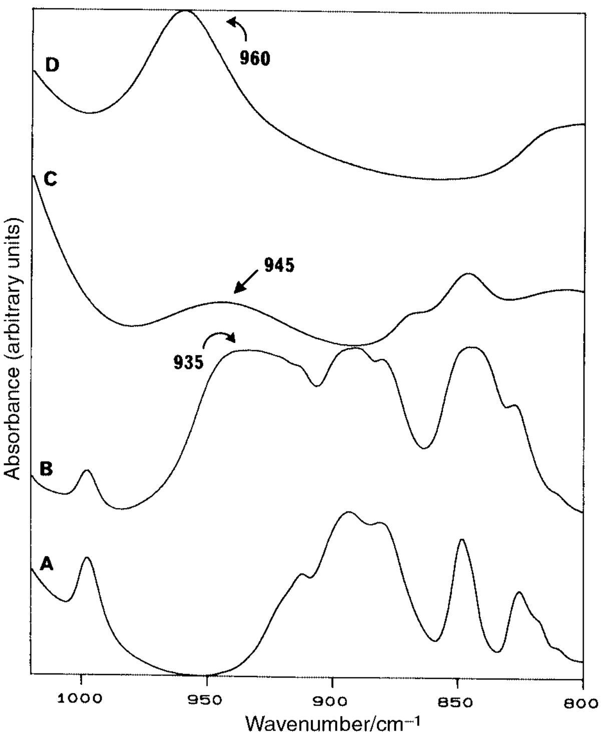


Fig. 4 The IR spectra (800–1050 cm^{-1}) of (A) compound **2**, (B) **7**, (C) amorphous titania–silica, (D) TS-1.

The UV-vis spectra of the (silasesquioxane)titanium complexes are also informative, containing an intense absorption in the range 212–228 nm, absent for the corresponding silasesquioxanes. These absorptions are assigned to a ligand to metal charge transfer transition involving four-co-ordinated titanium bearing oxygen ligands. A similar band is observed for TS-1 (Fig. 5; Table 3), being assigned to tetrahedrally co-ordinated titanium species which occupy sites in the titanosilicate lattice.[50,55] In the case of amorphous titania–silica mixed oxides two absorption maxima are typically observed: a band at *ca.* 215 nm is similarly assigned to titanium species in tetrahedral co-ordination, while a band at longer wavelength (*ca.* 260 nm) corresponds to the presence of highly dispersed titanium species which are five- or six-co-ordinate[49] (note that some contribution to this latter band may arise from the presence of titanium sites with increased co-ordination number formed by the interaction of water with the tetrahedral sites).[56]

Recently several groups have attempted to use UV-vis reflectance and/or photoluminescence spectroscopy to differentiate between closed and open lattice titanium sites in titanium

Table 4 Epoxidation of oct-1-ene with TBHP catalysed by titanium silasesquioxane complexes and related materials

Catalyst	$10^2 k_2$/dm^3 mol^{-1} s^{-1}	Selectivity to epoxide^a (%)
5	123	95
6	63	99
7	97	97
8	149	93
10	184	93
11	157	88
12	138	92
13	206	89
14	249	90
15	1.0	0
16	9.3	75
17	4.7	83
[Ti(η-C_5H_5){(*c*-C_6H_{11})$_7$$Si_7O_{12}$}]	18.2	91
Ti-MCM-41 (Ti = 1.43 wt%)	2.6	94
Amorphous TiO_2–SiO_2 (Ti = 3.91 wt%)	4.2	98
TiO_2–SiO_2 (Ti = 8.2 wt%)	2.3	83
No catalyst	—^{b}	0

Conditions: $T = 353$ K, Ti = 0.2 mmol, TBHP = 30 mmol, oct-1-ene (75 g) as solvent. ^{a} 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. ^{b} 10% TBHP conversion measured after 240 min.

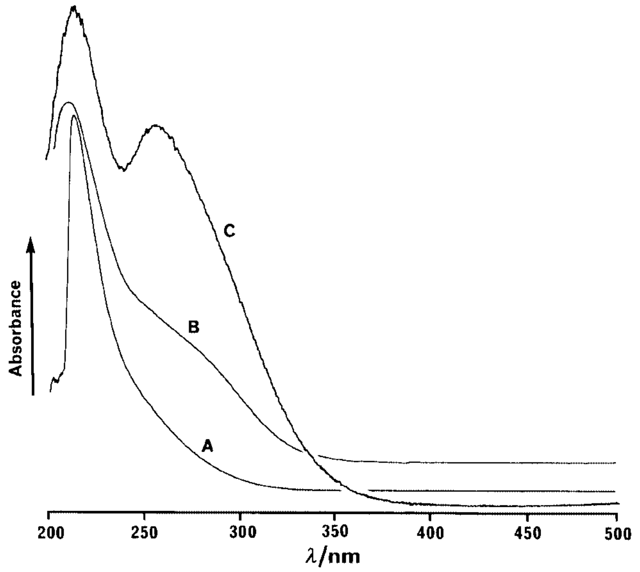


Fig. 5 The UV-vis spectra of (A) compound **7**, (B) TS-1 and (C) amorphous titania–silica.

silicalites.[22,23,57,58] Opening the Ti–O–Si bond angle shifts the hybridisation of the oxygen from sp^3 to sp^2 and eventually sp, thereby favouring π donation into the empty "e" level of titanium in T_d symmetry. According to Le Noc *et al.*,[23] increased π donation should lead to a blue shift of the ligand to metal electron transfer (LMET) band, *i.e.* the LMET absorption for the open lattice site should occur at lower wavelength than that of the closed lattice site. In this context it is interesting that the LMET absorption maxima of the tripodal silasesquioxane complexes are found in the range 212–222 nm, while that for **17** corresponds to a wavelength of 228 nm. Comparison of the crystal structures of **7** and **17** shows the Ti–O–Si (silasesquioxane) bond angles to be similar, being 151(4) and *ca.* 148°, respectively (the latter figure being the average of four Ti–O–Si angles). The most significant difference between **7** and **17**, in terms of Ti–O–Si bond angles, is the presence of the (apparently) linear Ti–O–$SiMe_3$ group in **7**. The lower wavelength of the absorption maximum observed for **7**, relative to **17**, appears, therefore, to be consistent with the explanation put forward by Le Noc and co-workers. Studies employing photoluminescence spectroscopy are currently in progress in order to verify these suggestions.

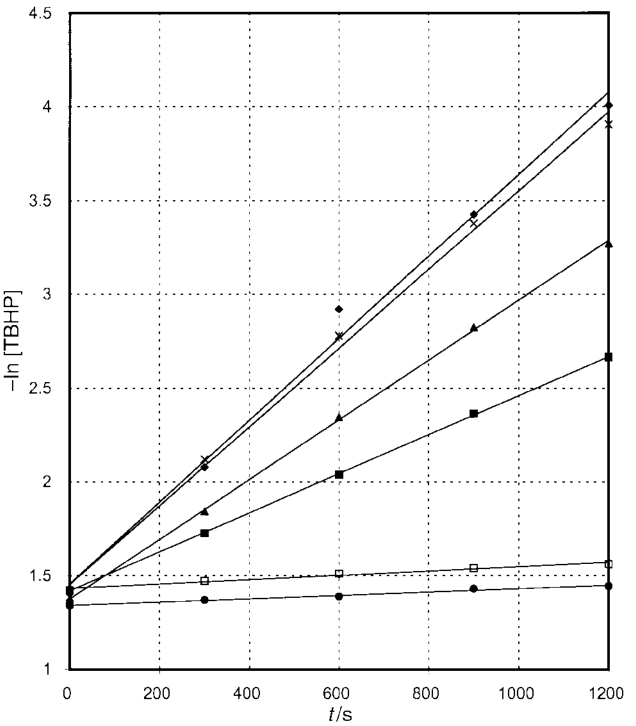


Fig. 6 Selected pseudo-first order rate plots for the epoxidation of oct-1-ene with TBHP catalysed by titanium silasesquioxane complexes: ◆ **5**, ■ **6**, ▲ **7**, × **8**, □ **16** and ● **17**.

Epoxidation of oct-1-ene using *tert*-BuOOH

The epoxidation of oct-1-ene with *tert*-BuOOH (TBHP) was chosen as a convenient test of the epoxidation activity of complexes **5**–**17**. At the olefin:TBHP molar ratio of *ca.* 20:1 employed pseudo-first order kinetics are observed corresponding to rate equation (1). At high TBHP conversions (generally >80%), however, 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 Bu^{t}OH co-product, a phenomenon observed previously for a variety of homogeneous and heterogeneous titanium and vanadium catalysts.[59] The calculated second order rate constants for TBHP conversion ($k_2 = k_1$/[Ti]) for complexes **5**–**17**, determined at a reaction temperature of 353 K, are shown in Table 4. Representative rate plots are collected in Fig. 6. For selected tripodal titanium silasesquioxane complexes additional epoxidation experiments were performed in the temperature range 293–353 K. In all cases plots of ln *k* against 1/*T* afforded straight lines, the resulting kinetic parameters being collected in Table 5.

$$\mathrm{d[epoxide]}/\mathrm{d}t = k_1[\mathrm{TBHP}] \qquad (1)$$
$$(\text{where } k_1 = k_2[\mathrm{Ti}] = k_3[\mathrm{Ti}][\mathrm{olefin}])$$

Most striking is the finding that the measured values of k_2 for the tripodal complexes **5**–**14** are approximately an order of magnitude greater than for **16** and **17**, while the former complexes also show superior selectivity. For all the titanium complexes tested 1,2-epoxyoctane was the only product formed under the reaction conditions employed, selectivity referring to the yield of epoxide based on TBHP consumed. In contrast, the zirconium complex **15** showed only slight activity for TBHP decomposition, without formation of the epoxide, this presumably being a consequence of its lower Lewis acidity relative to titanium.

Table 5 Kinetic parameters for oct-1-ene epoxidations with TBHP catalysed by titanium silasesquioxane complexes[a]

Complex	E_a/kJ mol^{-1}	ln A
5	42.5	14.56
6	42.4	13.80
8	49.8	17.31
10	55.4	19.30
11	57.2	19.88
12	59.4	20.55
13	41.0	14.51

[a] Epoxidation conditions as for Table 4 (T = 295–353 K).

Complexes **5**–**14** are also considerably more active under these test conditions than titanosilicate catalysts such as Ti-MCM-41 and amorphous titania–silica mixed oxides, when compared on the basis of k_2 values (*i.e.* activity per titanium site). The Ti-MCM-41 sample tested showed low activity coupled with good selectivity (94%), while an amorphous titania–silica sample containing 3.91 wt% titanium showed slightly higher activity and selectivity. In line with literature reports,[6] an amorphous titania-silica sample prepared by the same procedure but containing 8.20 wt% titanium showed lower activity per titanium site and also lower selectivity than the material with the lower titanium content, a reflection of the increased proportion of octahedrally co-ordinated titanium in the sample with the higher titanium content.

Consideration of the k_2 values obtained for the tripodal complexes **5**–**14** raises two important points. First, the fact that the catalytic properties of **5**–**12** show significant differences implies that the ligand, L, occupying the fourth co-ordination site on titanium, must be reasonably stable with respect to ligand exchange with the *tert*-butyl hydroperoxide anion, at least for the limited number of turnovers (150) in the epoxidation test. The exception to this would appear to be complexes **5** and **6**, the basic benzyl and dimethylamino ligands in these complexes being readily protonated by weak acids such as alcohols, with the formation of the corresponding alkoxy complexes. Addition of TBHP to **5** or **6** would therefore be anticipated to result in formation of the peroxometal species $[\mathrm{Ti(OOBu^t)}\{(c\text{-}\mathrm{C_6H_{11}})_7\mathrm{Si_7O_{12}}\}]$, which after one epoxidation cycle is converted into *tert*-butoxy complex **9** (see below). Note that the lower epoxidation activity of **6**, relative to **5**, can be rationalised by the inhibiting effect that Lewis bases such as $\mathrm{NHMe_2}$ (formed by protonation of **6**) exert on Ti$^{\mathrm{IV}}$-catalysed epoxidation (due to co-ordination to the Ti$^{\mathrm{IV}}$).[59]

Secondly, it is apparent that steric factors significantly influence the epoxidation activity of titanium silasesquioxane complexes. For **7**, **8** and **10** the measured k_2 values decrease with increasing steric bulk of the alkoxo ligand, *i.e.* $\mathrm{OPh > OPr^i > OSiMe_3}$. (Note that if the k_2 value for **5** is taken as being representative of the *tert*-butoxy complex **9**, which was itself not measured in this study, then the OBu^t ligand can be seen to conform to this ordering, *i.e.* $\mathrm{OPh > OPr^i > OBu^t > OSiMe_3}$.) A similar observation has been made by Maschmeyer *et al.*,[29] who found that the activity of the complexes $[\mathrm{TiL}\{(c\text{-}\mathrm{C_6H_{11}})_7\mathrm{Si_7O_{12}}\}]$ ($\mathrm{L = OMe, OPr^i}$ or $\mathrm{OBu^n}$) in cyclohexene epoxidation with *tert*-BuOOH followed the order $\mathrm{OMe > OBu^n \gg OPr^i}$. On this basis it was reasoned that linear alkoxy groups allow better access to the titanium centre than the non-linear isopropoxy group, indicating that accessibility to the Ti$^{\mathrm{IV}}$ is the main parameter controlling reactivity. The greater reactivity of **13** and **14** in epoxidation catalysis relative to **5** and **8** can similarly be rationalised in terms of the greater accessibility of the titanium centre in complexes based on the cyclopentyl-substituted silasesquioxane ligand, relative to complexes containing the bulkier cyclohexyl-substituted ligand.

In the case of complexes **10**–**12**, containing *para*-substituted phenoxy ligands, electronic effects would be anticipated to overrule any steric effects associated with the *para* substituent. Somewhat unexpectedly, the presence of electron-withdrawing substituents (F or $\mathrm{NO_2}$) results in a decrease of the reactivity of the complex relative to the simple phenoxy complex, this despite the fact that electron-withdrawing substituents might be expected to increase the Lewis acidity of the titanium(IV) centre and thereby the epoxidation activity of the complex. In explanation we suggest that under epoxidising conditions the higher Lewis acidity of **11** and **12** favours a higher degree of solvation in these complexes relative to **10** (*i.e.* favouring a dimer of the type $[\mathrm{Ti}(\mu\text{-}\mathrm{OC_6H_4X}\text{-}p)\{(c\text{-}\mathrm{C_6H_{11}})_7\mathrm{Si_7O_{12}}\}(\mathrm{Bu^tOH})]_2$), thereby rendering the metal less accessible to the TBHP reactant and effectively reducing the Lewis acidity of the metal centre. From this it follows that there exists an optimum in Lewis acidity with respect to the epoxidation activity of titanium silasesquioxane catalysts, an observation which may hold implications for the design of new heterogeneous titanium-based epoxidation catalysts.

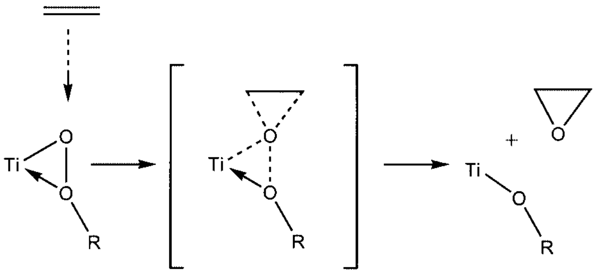
Finally, we note that complexes **5**–**12** are considerably more active as epoxidation catalysts than is $[\mathrm{Ti}(\eta\text{-}\mathrm{C_5H_5})\{(c\text{-}\mathrm{C_6H_{11}})_7\mathrm{Si_7O_{12}}\}]$ (see Table 4), previously prepared by Feher[38] and by Maschmeyer[39] and co-workers. Abbenhuis *et al.*[28] have recently reported that this complex is a catalyst for alkene epoxidation with TBHP and have shown using NMR spectroscopy that the cyclopentadienyl ligand remains bound to titanium under epoxidising conditions. Based on the present work, together with the findings of Maschmeyer *et al.*,[29] it is apparent that the low activity of the cyclopentadienyl complex can be ascribed to the steric bulk of the cyclopentadienyl ligand.

Mechanism of Ti$^{\mathrm{IV}}$-catalysed olefin epoxidation

The first detailed studies to be reported concerning the mechanism of Ti$^{\mathrm{IV}}$-catalysed epoxidation using alkyl hydroperoxides were performed on the Sharpless epoxidation catalyst.[60] A key feature of the mechanism proposed by Sharpless and co-workers is the formation of an alkylperoxo species, Ti(OOR), formed by protonolysis of the alkoxo ligand by the hydroperoxide, eqns. (2) and (3). The η^2 bonding mode of the peroxo ligand is supported by the results of quantum mechanical calculations,[61] as well as by the recent report by Boche *et al.*[62] of a structurally characterised titanium alkylperoxo complex containing the Ti(η^2-OOR) unit. Significantly, the authors demonstrated the capacity of the complex to oxidise nucleophiles, consistent with the electrophilic character of the peroxo group. Note that oxygen transfer from the peroxide to the olefin is proposed to occur *via* attack of the olefinic bond on the σ-bound oxygen of the Ti(η^2-OOR) moiety and proceeds *via* a "bi-triangular" transition state,[60] with the generation of a labile titanium (epoxo)(alkoxide) complex (Scheme 5). A recent study by Sinclair and Catlow[63] employing density functional theory (DFT) calculations supports the main features of this

$$\mathrm{M(OR) + ROOH \longrightarrow M(\eta^2\text{-}OOR) + ROH} \qquad (2)$$

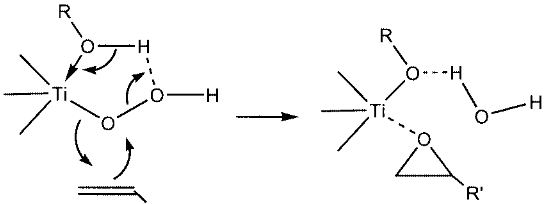
$$\mathrm{M(\eta^2\text{-}OOR) + olefin \longrightarrow M(OR) + epoxide} \qquad (3)$$



Scheme 5 Proposed transition species for oxygen transfer from peroxotitanium species.

proposition: ethene epoxidation by H_2O_2 over titanium silicate catalysts was found to proceed *via* the formation of a Ti(η^2-OOH) species, transfer of the oxygen being governed largely by the ethene HOMO (π) to catalyst LUMO (σ*) interaction.

In the case of TS-1, the most frequently invoked mechanism for olefin epoxidation with H_2O_2 (in alcoholic solvents) resembles that discussed above, in that a metal peroxide species is proposed as the key intermediate, proton abstraction from the hydroperoxide occurring at a co-ordinated hydroxide or siloxide group. The chief difference arises in the oxygen transfer step: based on the observation of strong solvent and pH effects in TS-1 and titanium β-catalysed epoxidation,[64–68] it is suggested that hydrogen bonding between co-ordinated solvent (ROH) and the terminal OH group of the bound hydroperoxide enhances the stability of the intermediate and the transition state required to form the epoxide (Scheme 6). Calculated transition states (using DFT and *ab initio* methods) reported in two recent papers broadly support this picture,[69,70] although co-ordination of a protic solvent does not appear to be a pre-requisite.[63]



Scheme 6 Proposed mechanism for oxygen transfer from peroxotitanium species in TS-1 and Ti-β.

When applying the generalised mechanism summarised in eqns. (2) and (3) to tripodal titanium silasesquioxane catalysts it is apparent that proton abstraction from the alkyl hydroperoxide can occur at either the silasesquioxane ligand or the ancillary ligand, L, thereby generating peroxometal species of the type [Ti(OOBu^t)L{$R_7Si_7O_{11}(OH)$}] or [Ti(OOBu^t)(HL)-($R_7Si_7O_{12}$)], respectively, where HL may or may not be dissociated from the metal. In an effort to assess the relative importance of these species, the reactions of complexes **5**, **7** and **8** with *tert*-BuOOH were studied.

Reaction of tripodal titanium silasesquioxane complexes with *tert*-BuOOH

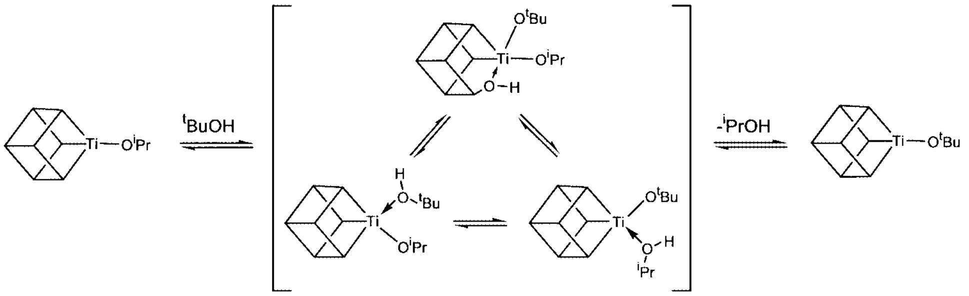
Addition of 1.2 equivalents of TBHP (5.0 M in decane) to a 0.06 M solution of compound **8** in C_6D_6 at ambient temperature resulted in a fast reaction, as evidenced by the complete disappearance within 20 min of ^{1}H and ^{13}C NMR signals corresponding to the starting materials. Concomitantly, the formation of *ter*t-butoxy complex **9**, Pr^{i}OH, Bu^{t}OH, and Bu^{t}OOBu^t (trace) was observed. Signals corresponding to a putative alkylperoxotitanium complex were not detected. In the ^{13}C NMR spectrum separate, broad resonances were observed for the quaternary carbons of **9** and Bu^{t}OH, while their methyl carbons appeared as one averaged signal, indicating that the OBu^t ligand in **9** undergoes exchange with free Bu^{t}OH. Although complex **8** was not detected in the product mixture, the signals for the Pr^{i}OH formed were broad, implying that it also exchanges with the OBu^t ligand in **9**. A similar result was obtained upon addition of 1.0 equivalent Bu^{t}OH to **8**, the observed Pr^{i}OH : Bu^{t}OH ratio at equilibrium being 0.8 : 1. In the ^{29}Si NMR spectrum of the product mixture obtained from **8** and TBHP the 3 : 1 : 3 pattern of the silasesquioxane silicons is retained, although the signal at δ −66.3, corresponding to the silicon atoms nearest to titanium (*i.e.* Ti–O–Si), is considerably broadened. A similar effect is observed when 1 equivalent of Bu^{t}OH or water is added to **8**, the peak broadening being indicative of a fluxional process whereby the protic species adds to titanium, with the proton migrating between the oxygen atoms of the Ti–O–Si linkages (see Scheme 7).

Addition of 3 or more equivalents of TBHP to compound **8** led to the formation of the same products as above, albeit that the evolution of oxygen from the reactant mixture was clearly visible. Additionally, at high TBHP : titanium mole ratios some decomposition of the titanium complex occurred, as evidenced by the presence of ^{29}Si NMR signals corresponding to the free silasesquioxane. Logically, this is formed *via* sequential protonation of the Ti–O–Si linkages by TBHP. Thus addition of 10 equivalents of TBHP to **8** resulted in 33% decomposition to the "free" ligand after 24 h. The fate of the titanium is unclear, although the final product is presumably a titanium alkoxide species.

Similar results were obtained with compound **7**, although the reaction with 1 equivalent TBHP was found to be considerably slower than for the less sterically crowded **8**, TBHP disappearance occurring with a half-life of approximately 12 h at room temperature. Principal reaction products were complex **9**, Bu^{t}OH and Bu^{t}OOBu^t, together with two trimethylsilyl-containing species (based on the observation of broad signals at δ 0.190 and 0.196 in the ^{1}H NMR spectrum). The ^{29}Si NMR spectrum contained the expected 3 : 1 : 3 pattern for the silasesquioxane silicon atoms, the signal at the low field side again being somewhat broadened. In the $OSiMe_3$ region of the spectrum a single broad resonance was observed, being slightly shifted relative to the starting material (δ 16.30 *vs.* 16.52 for **7**). By analogy with **8**, it is concluded that Me_3SiOH is formed which undergoes rapid exchange with the *tert*-butoxy ligand in **9**.

The formation of Me_3SiOH was confirmed by IR spectroscopy (Fig. 7). The disappearance of the TBHP absorption band, ν(OH), at 3556 cm^{-1} was accompanied by the simultaneous appearance of new absorptions at 3617 and 3695 cm^{-1} assigned to the OH stretching vibration of Bu^{t}OH and Me_3SiOH, respectively. Additionally, weak, new absorptions were observed at 3630 and 3683 cm^{-1}; whilst definitive assignment of these bands is not possible, the position of the latter is characteristic for an organic silanol species. In fact, assuming the absence of intra- or inter-molecular hydrogen bonding, either signal may correspond to a silasesquioxane silanol group, formed *via* protolysis of a Ti–OSi bond.

Finally, the reaction of compound **5** with TBHP was examined. Upon addition of 1.2 equivalents of TBHP the orange



Scheme 7 Reaction of compound **8** with Bu^{t}OH. Only one of the three possible intermediates containing a co-ordinated silanol group is shown.

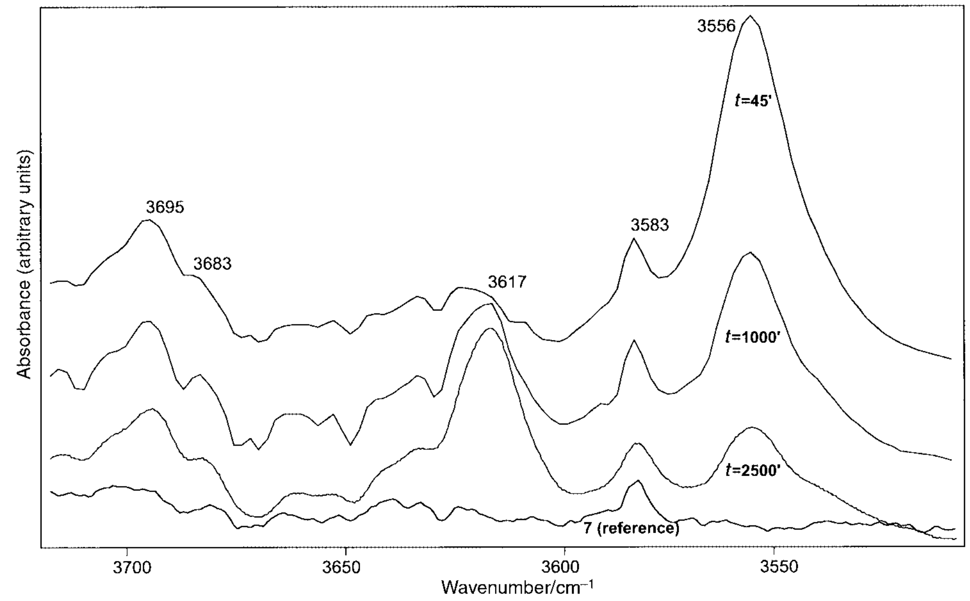
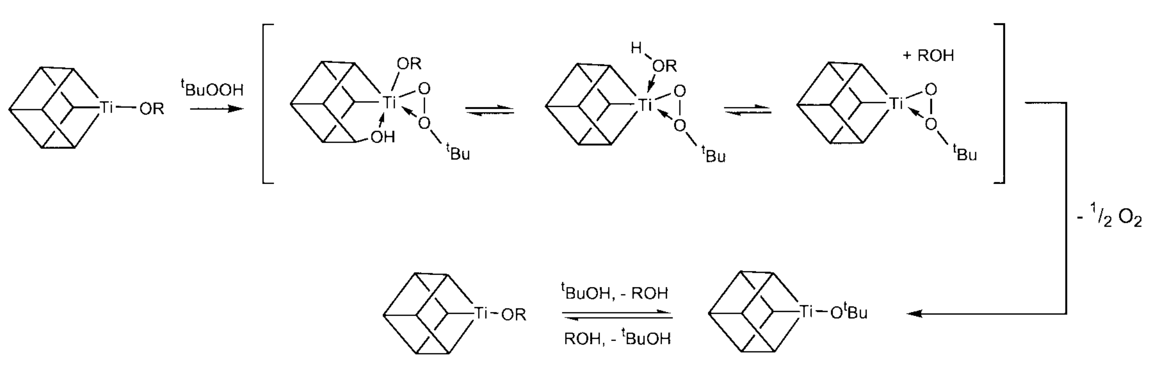


Fig. 7 Reaction of compound **7** with 1.0 equivalent TBHP in CCl_4: IR spectra measured at 45, 1000 and 2500 min reaction time.



Scheme 8 Generalised scheme for the reaction of (alkoxo)titanium silasesquioxane complexes with Bu^tOOH.

solution immediately decolourised, ^1H NMR spectroscopy indicating the formation of toluene and complex **9**. Upon standing, the excess of TBHP was slowly converted into Bu^tOH, Bu^tOOBu^t and oxygen.

Based on the above observations, the reaction of TBHP with tripodal titanium silasesquioxane complexes can be summarised as shown in Scheme 8. It is apparent that proton abstraction from the alkyl hydroperoxide can indeed occur at either the silasesquioxane ligand or anciliary ligand. The resulting alkylperoxotitanium species formed are not stable at room temperature and decompose rapidly with loss of oxygen, presumably *via* pathways involving homolytic fission of the Ti–peroxo bond, as observed previously in molybdenum chemistry,[71] eqns. (4)–(7). The titanium product, **9**, formed according to eqn. (6),

$$TiOOBu^t \longrightarrow Ti^{\bullet} + Bu^tOO^{\bullet} \qquad (4)$$

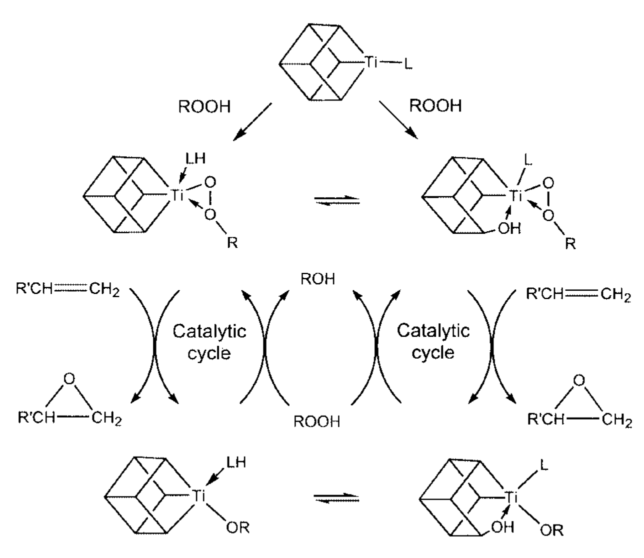
$$2\,Bu^tOO^{\bullet} \longrightarrow 2\,Bu^tO^{\bullet} + O_2 \qquad (5)$$

$$Ti^{\bullet} + Bu^tO^{\bullet} \longrightarrow TiOBu^t \qquad (6)$$

$$2\,Bu^tO^{\bullet} \longrightarrow Bu^tOOBu^t \qquad (7)$$

similarly catalyses the decomposition of excess of TBHP to Bu^tOH and oxygen (although note that radical chain decomposition of the TBHP may also play a role). The formation of Bu^tOOBu^t was also consistently observed, albeit in lower yield than that of Bu^tOH, consistent with the generation of alkylperoxo radicals. Under epoxidising conditions, decomposition of the peroxotitanium complex competes, in principal, with the epoxidation reaction. However, based on the high TBHP-to-epoxide selectivities observed, it is clear that the kinetics of olefin attack on the peroxo complex is much faster than that of decomposition to Bu^tOH or Bu^tOOBu^t.

Based on the generalised mechanism summarised in eqns. (2) and (3), combined with the above observations, the mechanism of olefin epoxidation catalysed by tripodal titanium silasesquioxane complexes can be described by the sequence of events depicted in Scheme 9. We note that the suggestion that formation of the peroxotitanium complex can occur either *via*



Scheme 9 Proposed mechanism for olefin epoxidation catalysed by titanium silasesquioxane complexes.

cleavage of an alkoxy ligand or *via* cleavage of a siloxy group is supported by the results of recent DFT calculations reported by Sinclair and Catlow: [63] for the case of ethene epoxidation with H_2O_2 over the putative site $Ti(OH)(OSiH_3)_3$, little energetic preference was found for either pathway, the calculated (absolute) activation barrier in both cases being estimated at 48–56 kJ mol^{-1}.

In a broader context, we conclude that the most active site in titanium silicates, 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 and amorphous titania–silica 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 co-ordination environment. The question then arises as to why the tripodal site is so much more active in epoxidation catalysis than are the bipodal or closed lattice sites. Based on the significant difference in the rates of reaction of compounds **7** and **8** with TBHP, steric factors can most obviously explain the low epoxidation activity of **17** and, by implication, closed lattice sites in titanosilicates: the more sterically congested co-ordination sphere of the titanium site relative to tripodal and bipodal titanium sites, can be expected to result in a lower reactivity towards alkyl hydroperoxides. In the case of the bipodal titanium site steric arguments are clearly not applicable. That bipodal sites show low activity in epoxidation catalysis is confirmed by previous studies in this laboratory.[49] Model epoxidation catalysts (prepared by grafting $Ti(CH_2Ph)_4$ onto silica, followed by hydrolysis), containing predominantly bipodal sites, $(SiO)_2$-$Ti(OH)_2$, were found to possess low epoxidation activity under the same test conditions employed in this work ($k_2 < 6 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} for oct-1-ene epoxidation with TBHP). In the absence of steric factors, electronic effects would appear to play the determining role. In this context we note that Feher and Budzichowski [33] have estimated, on the basis of the correlation between ^{13}C chemical shifts and Hammett substituent parameters, that the electron-withdrawing tendency of the Si_8O_{12} framework in a completely condensed silasesquioxane is similar to that of a CF_3 group. Based on simple electronic effects alone, therefore, the order tetrapodal > tripodal > bipodal would be anticipated regarding the epoxidation activity of four-co-ordinate titanium(IV) sites, since this follows the expected order of Lewis acidity of the titanium centre. If this line of reasoning is extrapolated to simple titanium alkoxides, $Ti(OR)_4$, one would therefore expect these compounds to show low epoxidation activity, as is indeed the case.[59] According to this logic, the tripodal site therefore represents the best compromise between high Lewis acidity and a sterically accessible titanium(IV) centre.

Concluding remarks

Identification of the active site in heterogeneous catalysts is a task which is typically complicated by the presence of a broad spectrum of chemically inequivalent sites. For this reason, knowledge of the mechanism of action of most solid catalysts remains extremely limited. One means of circumventing this problem is to prepare well defined model catalysts, such that direct correlations can be drawn between the structure of a particular site and its catalytic properties. In this respect incompletely condensed silasesquioxanes have proven to be structurally well suited to the preparation of co-ordination complexes modelling the different sites present in silicate-based metal oxide catalysts. Based on the structural and spectroscopic similarities exhibited by titanium silasesquioxane complexes and titanosilicates, we conclude that the former are valid models for this important class of heterogeneous catalysts.

A further benefit of this approach is the opportunity it affords to prepare new types of homogeneous catalyst, possessing in the most favourable case activity and selectivity superior to that of the heterogeneous analogue, due to the greater uniformity of catalytic centres. Indeed, tripodal titanium silasesquioxane complexes are the most active titanium-based epoxidation catalysts reported to date, and are among the most active and selective of all known homogeneous epoxidation catalysts. On this basis, we conclude that the most active site in titanosilicates, as far as epoxidation catalysis is concerned, corresponds to the tripodal, open-lattice type of titanium site. The tripodal site appears to represent an optimum in high Lewis acidity *versus* steric accessibility. The comparatively low epoxidation activity of heterogeneous titanosilicate catalysts such as Ti-MCM-41 and amorphous titania–silica 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 co-ordination environment.

Experimental

All manipulations of air- and/or moisture-sensitive materials were performed under an atmosphere of argon using standard Schlenk techniques, or in a nitrogen-filled Braun model MB-200 glove-box. Argon and nitrogen were purified by passage through columns filled with manganese(II) oxide supported on vermiculite. Glassware was dried in a vacuum oven (110 °C) before use.

Diethyl ether and THF were distilled from purple solutions of sodium–benzophenone under nitrogen. Pentane was distilled from purple solutions of potassium–benzophenone containing tetraglyme (2,5,8,11,14-pentaoxapentadecane). Toluene was distilled from sodium, acetonitrile from CaH_2, carbon tetrachloride from 3 Å molecular sieves and C_6D_6 was vacuum distilled (25 °C, 10^{-4} mbar) from CaH_2 and degassed by repeated freeze–pump–thaw cycles. Anhydrous *tert*-butyl hydroperoxide (TBHP, 3 M in isooctane or 5.0–6.0 M in decane) was purchased from Aldrich and stored over 4 Å molecular sieves. Oct-1-ene (>98%) was obtained from Merck and dried over 3 Å molecular sieves before use. Phenol (99+%), 4-fluorophenol (99%) and 4-nitrophenol (99+%) were obtained from Aldrich Chemical Co. and dried in a vacuum desiccator over P_2O_5. Silasesquioxanes **1**, **2** and **4** were prepared according to the literature procedures.[35,41] In the case of **2** it was found that removal of resinous material from the crude product could most efficiently be performed by washing with pentane, as opposed to the literature method (washing with acetone). The compound $[Ti(OPr^i)_4]$ (97%) was purchased from Aldrich Chemical Co. and $[Ti(OSiMe_3)_4]$ and $[Ti(NMe_2)_4]$ from ABCR GmbH; $[Ti(CH_2Ph)_4]$ was synthesized according to a literature method.[72] TS-1 and Ti-MCM-41 were prepared by direct hydrothermal synthesis.[1,16] Amorphous titania–silica samples were prepared by a homogeneous precipitation procedure using $[Ti(OPr^i)_4]$ and $[Si(OEt)_4]$; [73] characterisation of these materials has been reported elsewhere.[73,74]

The NMR spectra were recorded either on Bruker AM-500 (^1H, 500.1; ^{13}C, 125.8; ^{29}Si, 99.4 MHz), AM-400 (^{13}C, 100.6; ^{29}Si, 79.5 MHz), AM-300 (^1H, 300.2 MHz) or AM-250 (^1H, 250.1; ^{13}C, 62.9 MHz) spectrometers. All chemical shifts are reported in units of δ (downfield from tetramethylsilane) and were referenced to residual protio solvent (^1H) and solvent (^{13}C) resonances (C_6D_6; δ 7.16 for ^1H, 128.0 for ^{13}C). The ^{29}Si NMR spectra were generally recorded with inverse-gated proton decoupling in order to increase resolution and minimise nuclear Overhauser enhancement effects. To ensure accurate integrated intensities, $[Cr(acac)_3]$ (0.05 M) was added to ^{13}C and ^{29}Si NMR samples as a shiftless relaxation agent and a delay of at least 5 s was used between observation pulses for ^{13}C measurements and 10 s for ^{29}Si measurements.

Field desorption (FD) mass spectra were recorded on a JEOL JMS HX110 magnetic sector instrument. Acceleration and cathode voltages were set to 10 and −1 kV, respectively. An activated emitter was dipped into C_6D_6 solutions of the samples, mass spectra being obtained by heating the emitter linearly from 0 to 60 mA (ramp 1 mA min^{-1}). The resulting spectra were summed to afford one mass spectrum showing predominantly molecular ion masses of the desorbed species.

The FT-IR spectra of solids were collected as Nujol mulls or KBr pellets on a Bio-Rad FTS 50 instrument. Solution spectra were collected on carbon tetrachloride solutions contained in a NaCl cell on the same instrument. Stock solutions of the silasesquioxane complexes were prepared on a 1% m/m basis; TBHP was diluted in carbon tetrachloride to the same molarity as the silasesquioxane solutions. Equal volumes of the two solutions were mixed in a glove-box and immediately transferred to the IR cell. Spectra were recorded at a resolution of 2 cm^{-1}. The UV-vis spectra were collected where appropriate in the absorption mode on pentane solutions sealed under nitrogen in 1 cm cuvettes, using a Hitachi U-3300 spectrophotometer, or in the reflectance mode (TS-1) using a Perkin-Elmer LS-50 spectrometer. In the latter case the vacuum dried solids were measured in air. Elemental analyses were performed by Analytische Laboratorien, D-5270 Gummersbach, Germany, or by the analytical group at Shell Research and Technology Centre, Amsterdam. The oxide WO_3 was routinely added to samples to aid combustion and suppress the formation of silicon carbide.

Preparations

[Ti(CH$_2$Ph){(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$}] 5. Pentane (20 ml) was added to a solid mixture of [Ti(CH$_2$Ph)$_4$] (0.500 g, 1.21 mmol) and silasesquioxane **2** (1.179 g, 1.21 mmol). Stirring at room temperature for 30 min afforded a deep yellow solution, which was filtered and reduced to dryness under vacuum. The residue was dissolved in toluene and acetonitrile added dropwise to give a precipitate of **5**. The yellow microcrystalline solid was isolated by filtration, washed with acetonitrile (3 × 5 ml) and dried under vacuum (1.194 g, 89%). ^{1}H NMR (C$_6$D$_6$, 250.1 MHz): δ 7.31–7.03 (m, 5 H, C$_6$H$_5$), 3.10 (s, 2 H, C*H*$_2$Ph) and 2.20–0.97 (m, 77 H, *c*-C$_6$H$_{11}$). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ 142.98 (s, *ipso*-C of Ph), 124.33 (s, Ph, other signals obscured by solvent), 81.17 (s, *C*H$_2$Ph), 27.77, 27.70, 27.60, 27.32, 27.30, 27.27, 27.21 (s, CH$_2$), 23.75, 23.72, 23.51 (s, 3 : 1 : 3 for CH). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −65.55, −67.67 and −68.73 (s, 3 : 1 : 3). Found: C, 52.79; H, 7.68. Calc. for $C_{49}H_{84}O_{12}Si_7Ti$: C, 53.11; H, 7.64%.

[Ti(NMe$_2$){(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$}] 6. The compound [Ti(NMe$_2$)$_4$] (0.20 g, 0.89 mmol) was added *via* syringe to a stirred solution of **2** (0.833 g, 0.86 mmol) in pentane–diethyl ether 1 : 1 (60 ml). Work-up of the resulting solution (as for **5**) afforded **6** as a yellow powder (0.882 g, 97%). ^{1}H NMR (C$_6$D$_6$, 250.1 MHz): δ 3.05 (s, 6 H, NMe$_2$), 2.12–0.97 (m, 77 H, *c*-C$_6$H$_{11}$). ^{13}C NMR (C$_6$D$_6$, MHz): δ 44.97 (s, NMe$_2$), 27.97, 27.88, 27.83, 27.69, 27.52, 27.37, 27.33 (s, CH$_2$), 24.15, 24.09, 23.91 (s, 3 : 1 : 3 for CH). ^{29}Si NMR (C$_6$D$_6$, MHz): δ −65.1, −67.1 and −68.1 (s, 3 : 1 : 3). Found: C, 48.15; H, 7.61; N, 1.19. Calc. for $C_{44}H_{83}NO_{12}Si_7Ti$: C, 49.73; H, 7.87; N, 1.32%.

[Ti(OSiMe$_3$){(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$}] 7. Addition of [Ti(OSiMe$_3$)$_4$] (1.08 g, 2.67 mmol) to compound **2** (2.595 g, 2.67 mmol), followed by work-up as above, afforded **7** as a white microcrystalline solid (2.817 g, 95%). ^{1}H NMR (C$_6$D$_6$, 250.1 MHz): δ 2.13–0.97 (m, 77 H, *c*-C$_6$H$_{11}$) and 0.21 (s, 9 H, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ 27.80, 27.76, 27.42, 27.40, 27.32, 27.25, 27.18 (s, CH$_2$), 23.88, 23.85, 23.61 (s, 3 : 1 : 3 for CH) and 1.59 (s, SiMe$_3$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ 16.52 (s, OSiMe$_3$), −65.80, −67.90 and −68.85 (s, 3 : 1 : 3). Mass spectrum (FD): *m*/*z* 1969.9 (100, [Ti{(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$}]$_2$O$^+$) and 1107.6 (15%, M$^+$). Found: C, 48.56; H, 7.69. Calc. for $C_{45}H_{86}O_{13}Si_8Ti$: C, 48.79; H, 7.82%.

[Ti(OPr^i){(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$}] 8. Addition of [Ti(OPr^i)$_4$] (0.62 g, 2.18 mmol) to compound **2** (2.050 g, 2.11 mmol), followed by work-up as above, afforded **8** as a white microcrystalline solid (2.240 g, 99%). ^{1}H NMR (C$_6$D$_6$, 250.1 MHz): δ 4.41 (septet, 1 H, C*H*(CH$_3$)$_2$, *J* = 6.1), 2.15–1.00 (m, 77 H, *c*-C$_6$H$_{11}$) and 1.20 (d, 6 H, CH(C*H*$_3$)$_2$, *J* = 6.1 Hz). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ 80.09 (s, *C*H(CH$_3$)$_2$), 27.83, 27.81, 27.48, 27.44, 27.33, 27.28, 27.22 (s, CH$_2$), 25.80 (s, CH$_3$), 23.91, 23.85 and 23.78 (s, 3 : 1 : 3 for CH). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −66.24, −68.09, −69.08 (s, 3 : 1 : 3, monomer); −67.24, −68.08, −68.36, −69.01 and −70.00 (5 × s, 1 : 1 : 2 : 1 : 2, dimer). Mass spectrum (FD): *m*/*z* 1969.9 (100%, [Ti{(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$}]$_2$O$^+$). Found: C, 49.93; H, 7.70. Calc. for $C_{45}H_{84}O_{13}Si_7Ti$: C, 50.16; H, 7.86%.

[Ti(OBu^t){(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$}] 9. Addition of [Ti(OBu^t)$_4$] (0.99 g, 2.72 mmol) to a solution of compound **2** (2.66 g, 2.74 mmol) in toluene (100 ml), followed by work-up as above, afforded **9** as a white microcrystalline solid (1.72 g, 57%). ^{1}H NMR (C$_6$D$_6$, 300.2 MHz): δ 2.15–1.24 (m, 77 H, *c*-C$_6$H$_{11}$) and 1.30 (s, 9 H, OC(CH$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ 85.22 (s, O*C*(CH$_3$)$_3$), 31.44 (s, OC(*C*H$_3$)$_3$), 27.92, 27.72, 27.53, 27.50, 27.33, 27.19, 27.15, 26.95 (s, CH$_2$), 23.83, 23.75 and 23.64 (s, 3 : 1 : 3 for CH). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −68.32, −70.36 and −71.36 (s, 3 : 1 : 3). Found: C, 50.52; H, 7.88. Calc. for $C_{46}H_{86}O_{13}Si_7Ti$: C, 50.61; H, 7.94%.

Repetition of the above procedure using THF instead of toluene afforded compound **9** as a mixture of monomer and dimer (and containing THF of crystallisation). ^{1}H NMR (C$_6$D$_6$, 300.2 MHz): δ 3.54 (m, THF, α-CH$_2$), 2.14–0.86 (m, Cy; THF, β-CH$_2$), 1.30 (s, OC(CH$_3$)$_3$) and 1.05 (s, μ-OC(CH$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ 85.29 (s, O*C*(CH$_3$)$_3$), 67.85 (s, THF, α-CH$_2$), 31.48 (s, OC(*C*H$_3$)$_3$), 31.31 (s, μ-OC(*C*H$_3$)$_3$), 27.98, 27.86, 27.82, 27.78, 27.69, 27.59, 27.57, 27.42, 27.40, 27.34, 27.28, 27.24, 27.20, 27.11 (s, CH$_2$), 25.76 (s, THF, β-CH$_2$), 24.72, 24.31, 23.89, 23.82, 23.71 and 23.44 (s, CH). ^{29}Si NMR (C$_6$D$_6$, 97.5 MHz): δ −68.29, −70.31, −71.36 (3 : 1 : 3, monomer), −69.49, −70.36, −70.60, −71.27 and −72.27 (1 : 1 : 2 : 1 : 2, dimer).

[Ti(OPh){(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$}] 10. A solution of phenol (0.082 g, 0.87 mmol) in diethyl ether (30 ml) was added dropwise, using a flexible stainless steel cannula, to a stirred solution of compound **8** (0.844 g, 0.78 mmol) in diethyl ether over a period of 30 min. The resulting mixture was stirred for 1 h at room temperature. The volume of solvent was then reduced under vacuum (to *ca.* 30 ml) and acetonitrile (30 ml) added. The resulting white precipitate was isolated by filtration, washed with acetonitrile (5 × 20 ml) and dried under vacuum to afford **10** (0.800 g, 92%). ^{1}H NMR (C$_6$D$_6$, 250.1 MHz): δ 7.50 (m, 2 H, *o*-H of C$_6$H$_5$), 7.41 (m, 2 H, *m*-H of C$_6$H$_5$), 6.98 (m, 1 H, *p*-H of C$_6$H$_5$), 2.08–0.94 (m, 77 H, *c*-C$_6$H$_{11}$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −66.40, −67.60, −68.34 (s, 3 : 1 : 3, monomer); −66.68, −67.50, −67.79, −68.43 and −69.43 (5 × s, 1 : 1 : 2 : 1 : 2, dimer). Mass spectrum (FD): *m*/*z* 1110.3 (100, M$^+$) and 555.3 (10%, M^{2+}). Found: C, 50.10; H, 7.51. Calc. for $C_{48}H_{82}O_{13}Si_7Ti$: C, 51.86; H, 7.43%.

Repetition of the above procedure using THF instead of diethyl ether afforded compound **10** as a mixture of monomer and dimer, containing co-ordinated THF. ^{1}H NMR (C$_6$D$_6$, 300.2 MHz): δ 7.50 (m, 2 H, *o*-H of C$_6$H$_5$), 7.41 (m, 2 H, *m*-H of C$_6$H$_5$), 6.98 (m, 1 H, *p*-H of C$_6$H$_5$), 3.75 (s, co-ordinated THF, α-CH$_2$), 2.19–0.92 (m, 77 H, *c*-C$_6$H$_{11}$; THF, β-CH$_2$). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ 166.20 (*ipso*-C of C$_6$H$_5$), 129.07 (C$_6$H$_5$), 122.00 (C$_6$H$_5$), 121.71 (C$_6$H$_5$), 69.71 (s, co-ordinated THF, α-CH$_2$), 27.98, 27.91, 27.86, 27.78, 27.70, 27.55, 27.44, 27.33, 27.27, 27.21, 27.12 (s, CH$_2$), 25.66 (s, THF, β-CH$_2$), 24.73, 24.32, 23.89, 23.85, 23.82, 23.72, 23.70, 23.49, 23.45 (s, CH). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −66.97, −67.10, −67.51, −67.85, −68.08 (2 signals), −68.70 and −69.76.

[Ti(OC$_6$H$_4$F-*p*){(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$}] 11. Dropwise addition of a solution of 4-fluorophenol (0.142 g, 1.27 mmol) in diethyl ether (30 ml) to compound **8** (1.285 g, 1.19 mmol) dissolved in diethyl ether (30 ml) as described for **10**, followed by the same work-up procedure, afforded **11** as a pale yellow powder (1.14 g, 85%). ^{1}H NMR (C$_6$D$_6$, 250.1 MHz): δ 7.42 (m, 2 H, *o*-H of C$_6$H$_5$), 7.15 (m, 2 H, *m*-H of C$_6$H$_5$) and 2.10–0.95 (m, 77 H, *c*-C$_6$H$_{11}$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −66.34, −67.55, −68.28 (s, 3 : 1 : 3, monomer); −66.68, −67.50, −67.79, −68.44 and −69.44 (5 × s, 1 : 1 : 2 : 1 : 2, dimer). Mass spectrum (FD): *m*/*z* 1129.6 (100, M$^+$) and 564.5 (8%, M^{2+}). Found: C, 52.12; H, 7.37. Calc. for C$_{48}$H$_{81}$FO$_{13}$Si$_7$Ti: C, 51.04; H, 7.23%.

Repetition of the above procedure using THF instead of diethyl ether afforded compound **11** as a mixture of monomer and dimer, containing co-ordinated THF. ^{1}H NMR (C$_6$D$_6$, 300.2 MHz): δ 7.46 (m, 2 H, *o*-H of C$_6$H$_5$), 7.15 (m, 2 H, *m*-H of C$_6$H$_5$), 3.86 (m, co-ordinated THF, α-CH$_2$) and 2.09–0.91 (m, 77 H, *c*-C$_6$H$_{11}$; THF, β-CH$_2$). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ 162.08 (s, *ipso*-C of C$_6$H$_5$), 158.57 (d, *p*-C of C$_6$H$_5$, $^1J_{\text{C-F}} = 239$), 122.39 (s, *o*-C of C$_6$H$_5$), 115.38 (d, *m*-C of C$_6$H$_5$, $^2J = 21$ Hz), 69.41 (s, co-ordinated THF, α-CH$_2$), 27.95, 27.89, 27.85, 27.80, 27.77, 27.71, 27.68, 27.57, 27.54, 27.41, 27.31, 27.24, 27.16 and 27.09 (s, CH$_2$), 25.68 (s, THF, β-CH$_2$), 24.71, 24.30, 23.87, 23.78 (2 signals), 23.71, 23.67 and 23.43 (s, CH). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −66.95, −67.33, −67.80 (2 signals), −68.06, −68.58, −68.73 and −69.73.

[Ti(OC$_6$H$_4$NO$_2$-*p*){(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$}] 12. Dropwise addition of a solution of 4-nitrophenol (0.400 g, 2.88 mmol) in diethyl ether (30 ml) to compound **8** (2.969 g, 2.76 mmol) dissolved in diethyl ether (30 ml) as described for **10**, followed by the same work-up procedure, afforded **12** as a bright yellow powder (2.90 g, 91%). ^{1}H NMR (C$_6$D$_6$, 250.1 MHz): δ 8.47 (m, 2 H, *o*-H of C$_6$H$_5$), 7.53 (m, 2 H, *m*-H of C$_6$H$_5$) and 2.11–0.95 (m, 77 H, *c*-C$_6$H$_{11}$). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −66.39, −67.48, −68.18 (s, 3 : 1 : 3, monomer); −66.68, −67.50, −67.79, −68.43 and −69.44 (5 × s, 1 : 1 : 2 : 1 : 2, dimer). Mass spectrum (FD): *m*/*z* 1155.6 (100, M$^+$) and 577.9 (8%, M^{2+}). Found: C, 50.20; H, 7.09; N, 0.87. Calc. for C$_{48}$H$_{81}$NO$_{15}$Si$_7$Ti: C, 49.84; H, 7.06; N, 1.21%.

Repetition of the above procedure using THF instead of diethyl ether afforded compound **12** as a mixture of monomer and dimer, containing co-ordinated THF. ^{1}H NMR (C$_6$D$_6$, 300.2 MHz): δ 8.46 (m, 2 H, *o*-H of C$_6$H$_5$), 7.52 (m, 2 H, *m*-H of C$_6$H$_5$), 4.26 (m, co-ordinated THF, α-CH$_2$) and 2.10–0.90 (m, 77 H, *c*-C$_6$H$_{11}$; THF, β-CH$_2$). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ 169.79 (*ipso*-C of C$_6$H$_5$), 143.50 (C$_6$H$_5$), 125.64 (C$_6$H$_5$), 121.88 (C$_6$H$_5$), 72.31 (s, co-ordinated THF, α-CH$_2$), 28.02, 27.92, 27.84, 27.77, 27.70, 27.65, 27.41, 27.33, 27.26, 27.21, 27.16, 26.98 (s, CH$_2$), 25.58 (s, THF, β-CH$_2$), 24.78, 24.37, 23.94, 23.72, 23.62 and 23.48 (s, CH).

Alternatively, a solution of 4-nitrophenol (0.108 g, 0.78 mmol) in diethyl ether (15 ml) was added dropwise to a slurry of compound **5** (0.862 g, 0.78 mmol) in diethyl ether (15 ml). The resulting deep orange solution was stirred for 30 min and then filtered. The volume of solvent was reduced under vacuum (to *ca.* 15 ml) and acetonitrile (25 ml) added to afford a precipitate. The solid was isolated by filtration, was washed with acetonitrile (5 × 10 ml) and dried under vacuum to afford **12** (0.436 g, 48%), identified by ^{1}H and ^{29}Si NMR spectroscopy.

[Ti(CH$_2$Ph){(*c*-C$_5$H$_9$)$_7$Si$_7$O$_{12}$}] 13. A solution of [Ti(CH$_2$Ph)$_4$] (0.919 g, 2.23 mmol) in diethyl ether (20 ml) was added dropwise to a vigorously stirred suspension of compound **1** (1.950 g, 2.23 mmol) in ether (100 ml). The resulting deep yellow solution was stirred for 2 h. The volume of solvent was then reduced under vacuum (to *ca.* 15 ml) and acetonitrile (15 ml) added to afford **13** as a yellow precipitate. The solid was isolated by filtration, washed with acetonitrile (3 × 10 ml) and dried under vacuum (1.85 g, 82%). ^{1}H NMR (C$_6$D$_6$, 500.1 MHz): δ 7.18–7.15 (m, 4 H, *o*-, *m*-H of C$_6$H$_5$), 6.87 (m, 1 H, *p*-H of C$_6$H$_5$, *J* = Hz), 3.02 (s, 2 H, C*H*$_2$Ph) and 1.99–1.13 (m, 63 H, *c*-C$_5$H$_9$). ^{13}C NMR (C$_6$D$_6$, 125.8 MHz): δ 142.90 (s, *ipso*-C of Ph), 124.34 (s, Ph, other signals obscured by solvent), 81.53 (*C*H$_2$Ph), 27.92, 27.90, 27.87, 27.78, 27.46 (s, CH$_2$), 22.73, 22.65 and 22.40 (s, 3 : 1 : 3 for CH). ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ −62.72, −64.74 and −65.88 (s, 3 : 1 : 3). Found: H, 6.80. Calc. for C$_{42}$H$_{70}$O$_{12}$Si$_7$Ti: H, 6.98%; satisfactory carbon analysis could not be obtained.

[Ti(OPr^i){(*c*-C$_5$H$_9$)$_7$Si$_7$O$_{12}$}] 14. The compound [Ti(OPr^i)$_4$] (0.48 g, 1.69 mmol) was added dropwise *via* syringe to a vigorously stirred suspension of **1** (1.350 g, 1.54 mmol) in ether (120 ml). The mixture was stirred at room temperature for 20 h, after which time work-up (as described for **13**) afforded **14** as a white microcrystalline solid (1.291 g, 85%). ^{1}H NMR (C$_6$D$_6$, 500.1 MHz): δ 4.40 (septet, 1 H, CH(C*H*$_3$)$_2$, *J* = 6.0), 1.94–1.11 (m, 63 H, *c*-C$_5$H$_9$) and 1.18 (d, 6 H, CH(C*H*$_3$)$_2$, *J* = 6.0 Hz). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ 80.09 (s, *C*H(CH$_3$)$_2$), 28.05, 27.97, 27.87, 27.51, 27.44 (s, CH$_2$), 25.67 (s, CH$_3$), 22.84, 22.77 and 22.64 (s, 3 : 1 : 3 for CH). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −63.81, −65.80, −66.83 (s, 3 : 1 : 3). Found: C, 45.79; H, 6.96. Calc. for C$_{38}$H$_{70}$O$_{13}$Si$_7$Ti: C, 46.60; H, 7.20%.

[Zr(OBu^t){(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$}] 15. A solution of [Zr(OBu^t)$_4$] (1.29 g, 3.36 mmol) in THF (20 ml) was added dropwise *via* cannula to a stirred solution of compound **2** (2.99 g, 3.07 mmol) in THF (70 ml) and stirring continued for 90 min. The volume of liquid was then reduced to 10 ml and acetonitrile (80 ml) added. The resulting precipitate was isolated by filtration, washed with acetonitrile (3 × 10 ml) and dried under vacuum to afford **15** (3.15 g, 92%) as a mixture of monomer and dimer. ^{1}H NMR (C$_6$D$_6$, 300.2 MHz): δ 2.29–1.03 (m, *c*-C$_6$H$_{11}$, μ-OC(CH$_3$)$_3$) and 1.07 (s, OC(CH$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ 78.74 (O*C*(CH$_3$)$_3$), 76.45 (μ-O*C*(CH$_3$)$_3$), 32.11 (OC(*C*H$_3$)$_3$), 31.55 (μ-OC(*C*H$_3$)$_3$), 28.48–27.30 (m, CH$_2$), 25.54, 24.90, 24.72, 24.54, 24.23, 24.15 and 24.02 (s, CH). ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ −70.06, −70.24, −70.36, −71.82, −72.03 (dimer, 1 : 1 : 2 : 1 : 2), −70.19, −71.03 and −71.77 (monomer, 3 : 1 : 3). Found: C, 48.84; H, 7.65. Calc. for C$_{46}$H$_{86}$O$_{13}$Si$_7$Zr: C, 48.68; H, 7.64%.

[Ti(OPr^i)$_2${(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{11}$(OSiMe$_3$)}] 16. A solution of compound **4** (2.500 g, 2.39 mmol) in diethyl ether (50 ml) was added dropwise (*via* cannula) over a period of 2 h to a vigorously stirred solution of [Ti(OPr^i)$_4$] (1.38 g, 4.85 mmol) in diethyl ether (50 ml). Stirring was continued for 30 min, after which time the volume of liquid was reduced under vacuum until *ca.* 10 ml remained. Acetonitrile (15 ml) was then added, resulting in the precipitation of **16** as a white microcrystalline solid. The product was isolated by filtration, washed with acetonitrile (4 × 10 ml) and dried under vacuum (2.622 g, 91%). ^{1}H NMR (C$_6$D$_6$, 500.1 MHz): δ 4.62 (septet, 1 H, C*H*(CH$_3$)$_2$, *J* = 6.1), 4.57 (septet, 1 H, C*H*(CH$_3$)$_2$, *J* = 6.1), 2.17–1.05 (m, 77 H, *c*-C$_6$H$_{11}$), 1.32 (d, 6 H, CH$_3$, *J* = 6.1), 1.30 (d, 6 H, CH$_3$, *J* = 6.1 Hz) and 0.47 (s, 9 H, Si(CH$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$, 125.8 MHz): δ 79.32 (s, OCH), 79.05 (s, OCH), 28.12, 28.08, 28.03, 27.87, 27.81, 27.79, 27.71, 27.67, 27.63, 27.54, 27.48, 27.40, 27.36, 27.32, 27.23 (s, CH$_2$), 26.29 (br s, CH$_3$), 25.67, 25.13, 24.96, 24.11, 23.86 (s, 1 : 2 : 2 : 1 : 1, CH) and 2.19 (s, Si(CH$_3$)$_3$). ^{29}Si NMR (C$_6$D$_6$, 99.4 MHz): δ 10.94 (s, Si(CH$_3$)$_3$), −65.64, −66.37, −66.58, −67.49 and −68.86 (s, 1 : 1 : 1 : 2 : 2). Found: C, 50.36; H, 8.21. Calc. for C$_{51}$H$_{100}$O$_{14}$Si$_8$Ti: C, 50.63; H, 8.33%.

[Ti{(*c*-C$_6$H$_{11}$)$_7$Si$_7$O$_{11}$(OSiMe$_3$)}$_2$] 17. Diethyl ether (30 ml) was added to a solid mixture of [Ti(CH$_2$Ph)$_4$] (0.316 g, 0.77 mmol) and compound **4** (1.601 g, 1.53 mmol). Work-up of the resulting solution (as above) afforded **17** as a white microcrystalline solid (1.590 g, 97%). ^{1}H NMR (C$_6$D$_6$, 250.1 MHz): δ 2.14–1.00 (m, 154 H, *c*-C$_6$H$_{11}$) and 0.52 (s, 18 H, Si(CH$_3$)$_3$). ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ 28.04, 27.93, 27.80, 27.74, 27.60,

Table 6 Crystal and other structural data for compounds **7** and **17**·C_6H_5Me

	7	**17**·C_6H_5Me
Empirical formula	$C_{45}H_{86}O_{13}Si_8Ti$	$C_{97}H_{180}O_{24}Si_{16}Ti$
M	1107.76	2227.75
Crystal system	Rhombohedral	Triclinic
Space group (no.)	$R\bar{3}$ (148)	$P\bar{1}$ (2)
a/Å	16.955(4)	21.085(8)
b/Å	16.955(4)	22.498(8)
c/Å	17.853(6)	27.786(10)
α/°		73.86(3)
β/°		77.13(3)
γ/°		87.37(3)
V/Å^3	4445(2)	12342(8)
Z	3	4
μ/mm^{-1}	0.360	0.286
Reflections collected	1448	32278
Independent reflections	1296	32278
R_{int}	0.022	—
Final $R1$ [$I > 2\sigma(I)$]	0.107	0.134

27.47, 27.34, 27.27, 27.18 (s, CH_2), 25.62, 25.23, 24.87, 24.85, 24.51, 23.80, 23.78 (s, CH) and 2.42 (s, $Si(CH_3)_3$). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ 10.42 (s, $Si(CH_3)_3$), −66.35, −66.79, −66.92, −68.22, −69.26, −69.50 and −69.72 (s, all × 1). Found: C, 50.39; H, 7.96. Calc. for $C_{90}H_{172}O_{24}Si_{16}Ti$: C, 50.69; H, 8.13%.

Structural analyses of compounds 7 and 17·C_6H_5Me

Suitable crystals of compound **7** were obtained by vapour diffusion of acetonitrile into a diethyl ether solution of the titanium complex cooled to 4 °C. Crystals of **17** were prepared by vapour diffusion of acetonitrile into a pentane solution of **17**·C_6H_5Me cooled to 4 °C. All diffraction measurements were made at 200 K on a Siemens R3m/V diffractometer fitted with an LT-1 crystal cooling device, using graphite monochromated Mo-Kα X-radiation.

Crystal data and other details of the structure analyses are presented in Table 6. Standard four-circle diffractometry and data analysis procedures were used with unusual features as detailed below.

Careful inspection of symmetry equivalent reflections for this crystal of compound **7** (and for other samples of **7** and of $[Ti(OPr^i)\{(SiR)_7O_{12}\}]$ **8**, which also crystallises in space group $R\bar{3}$ with similar cell dimensions to those of **7**) revealed no evidence for lower diffraction symmetry. Attempts to refine **7** in a lower symmetry space group (*e.g.* $R3$) led to much less reasonable molecular geometries and very unstable refinements, as might be expected. Similar behaviour (with worse outcome) was noted for data collected on the pseudo-isostructural **8**. The final model (of many employed) for **7** (see Fig. 1) has the molecule disordered about a site of crystallographic -3 symmetry. Pairs of atoms related by disorder across the inversion centre [Ti(1) and Si(1); C(9) and C(10); O(3) and C(7)] were constrained to have identical positional and displacement parameters. Atoms Ti(1), Si(1), O(3), C(7) and Si(4) all lie on the crystallographic 3-fold axis. All non-hydrogen atoms (except C(11)) were assigned anisotropic displacement parameters. The atoms within the cyclohexyl group [C(1)–C(6)] were restrained to have similar displacement parameter components along the C–C bond directions and to have C–C bond lengths following C_2 local symmetry (the DELU and SAME restraints in SHELXL 93).[75] The other single-site atoms [O(1), O(2), Si(2)] were refined without constraints on their positional parameters. The cyclohexyl group [C(7), C(8), C(10), C(11)] attached to Si(1) is disordered about the crystallographic 3-fold axis. Models including merohedral twinning with twin plane (0001) gave no improvement to the residuals, as might be expected given the R_{int} value for $6/m$ Laue symmetry (0.388).

For compound **17** three cyclohexyl groups suffered disorder (those attached to Si(6), Si(7) and Si(31)) and were refined with two site models in which some carbons were common to both ring conformations and the occupancies of the two orientations were refined. One trimethylsilyl group was also disordered (50 : 50 by refinement) and modelled in a similar way with two silicon positions (Si(32) and Si(33)) and having one methyl carbon position in common (C(180)). All ordered non-hydrogen atoms were assigned anisotropic displacement parameters and restraints (ISOR in the terminology of SHELXL 93)[75] applied ensuring that the parameters of Si, O and C were reasonably near to isotropic. Disordered and solvate Si or C atoms were assigned freely refined isotropic displacement parameters. All Si–Me distances were weakly restrained to be close to 1.9 Å, and C–C bond distances in the disordered cyclohexyl rings and those attached to Si(3), Si(5), and Si(19) were also weakly restrained to be close to 1.5 Å. The toluene solvate molecules were assigned rigid fixed geometries. Finally a correction was applied for unassigned solvent scattering density (SWAT in the terminology of SHELXL 93,[75] parameter value = 1.71(13)). The relatively high residuals (although they are quite low by macromolecule standards; there are 276 non-hydrogen atoms in this structure) are in part a consequence of reflection overlap problems noted during data collection. Other factors include the difficulties in treatment of the less well ordered cyclohexyl groups and the solvate molecules.

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See http://www.rsc.org/suppdata/dt/1999/3791/ for crystallographic files in .cif format.

Epoxidation of oct-1-ene

Epoxidation tests were performed batchwise in a magnetically stirred 250 ml glass reactor, equipped with a condenser, thermometer probe and septum for withdrawing samples. All runs were performed under an atmosphere of dry nitrogen. Typically, toluene (3 g, 0.03 mol as internal standard), oct-1-ene (73 g, 0.6 mol), a quantity of catalyst (equivalent to 0.2 mmol of Ti) and a stirrer bar were placed in the reactor. The mixture was warmed to 80 °C and 10 ml of TBHP solution were added *via* syringe. Immediately a sample was taken for analysis (GLC and iodometric titration), further samples for analysis being taken at regular intervals. GLC Analyses were performed on a Hewlett-Packard HP 5890 instrument, with flame ionisation detection (FID), a 25 m × 0.32 mm (0.52 mm film thickness) HP-1 (cross linked methyl silicone gum) fused silica capillary column, and helium as carrier gas. An injection temperature of 140 °C was employed, which was found to be sufficiently low to avoid the occurrence of secondary reactions in the injection port. The TBHP was determined by iodometric titration with sodium thiosulfate. Rate constants for TBHP consumption (k_1, $k_2 = k_1/[Ti]$) were determined from pseudo-first order rate plots ($-\ln[TBHP]$ *versus* t).

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