

The preparation, molecular structure and catalytic relevance of $\text{Ti}(\text{OSiPh}_3)_4$ and $\text{Ti}(\text{OGePh}_3)_4$

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Abstract

The preparation, spectroscopic characterisation and molecular structures of the four-coordinate, tetrahedral and monomeric compounds $\text{Ti}(\text{OSiPh}_3)_4$ and $\text{Ti}(\text{OGePh}_3)_4$ are presented and discussed. The catalytic inactivity of both of these compounds may be rationalised on the basis of the steric inaccessibility of the substrates to the Ti(IV) active sites, which are effectively shrouded by the bulky triphenyl groups. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

In previous efforts [1–11] to understand the factors, especially stereochemical ones [12,13], that influence the catalytic performance of titanium in the selective oxidation of hydrocarbons (particularly in the epoxidation of alkenes), it has been found that two features are particularly important. First, the central Ti(IV) ion, irrespective of whether it be in a continuous solid (such as the titanasilicate TS-1) [14–16] or in a grafted and isolated state on the inner walls of mesoporous silica (such as $\text{Ti}\uparrow\text{MCM-41}$) [1,17], has to be initially in the four coordinated state. Secondly, access to the central ion by a reactant alkene and the sacrificial oxidant (usually an alkyl hydroperoxide such as TBHP), must be relatively unhindered so that, as proven by in situ X-ray absorption spectroscopy [1,4,5], the coordination shell can expand from four to six during catalysis. We have demonstrated recently [12,13] that the same ideas apply

when isolated Ti(IV) centres are incorporated into incompletely condensed silsesquioxane frameworks. In such a way, the resulting titanosilsesquioxane complexes can act as effective homogeneous molecular models for the purported Ti(IV) active sites in the above-mentioned heterogeneous titanasilicate catalysts. As a consequence of our investigations into Group 14-derivatised titanosilsesquioxanes that can serve as homogeneous model systems for the active sites present in the heterogeneous catalytic materials $\text{Ti}\uparrow\text{Ge}\uparrow\text{MCM-41}$ and $\text{Ti}\uparrow\text{Sn}\uparrow\text{MCM41}$ [18], we here wish to report on the synthesis, characterisation and catalytic performance in the epoxidation of alkenes, of two Ti(IV) precursor molecular compounds $\text{Ti}(\text{OSiPh}_3)_4$ and $\text{Ti}(\text{OGePh}_3)_4$.

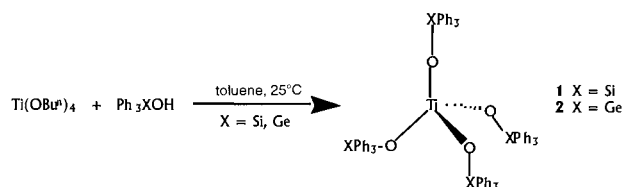


Fig. 1. The synthesis of the Group 14-derivatised molecular compounds 1 and 2.

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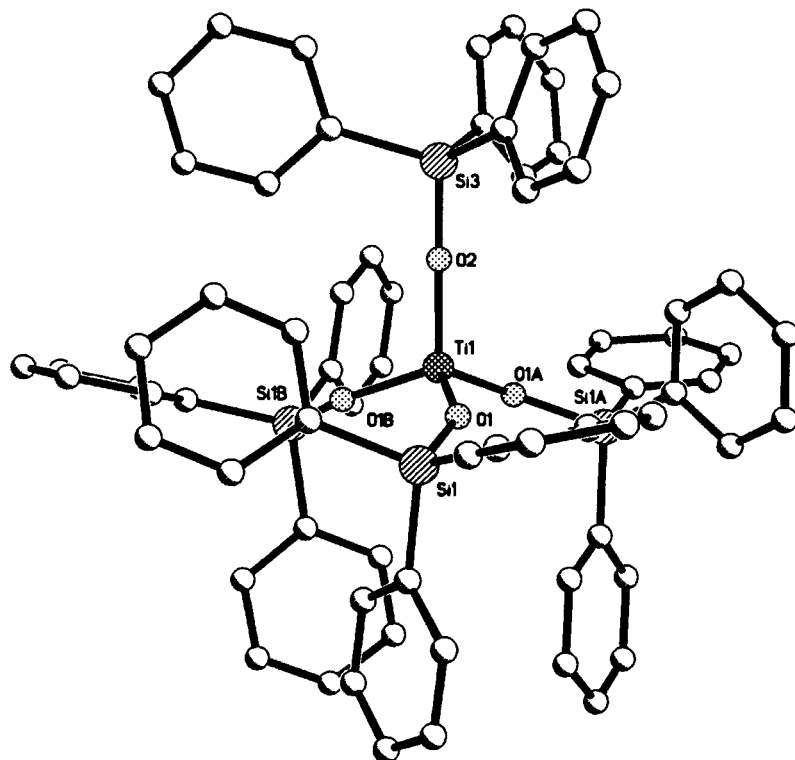


Fig. 2. Crystal structure of molecular compound **1**, showing the atomic labelling scheme (H atoms are omitted for clarity).

2. Results and discussion

Following the literature procedure developed for one of these compounds [19], the reaction of an excess of Ph_3XOH ($\text{X} = \text{Si}, \text{Ge}$ [20]) with $\text{Ti}(\text{OBU}^n)_4$ in toluene at 25°C leads to the isolation of both the Ti(IV) compounds $\text{Ti}(\text{OSiPh}_3)_4$ (**1**) or $\text{Ti}(\text{OGePh}_3)_4$ (**2**), as white microcrystalline powders in relatively high yields (see Fig. 1). In the case of compound **1**, minute single crystals could be isolated and the molecular structure solved successfully by microdiffraction using a synchrotron source, as has been described previously [21] (see Fig. 2). For compound **2**, it was also possible to isolate a single crystal suitable for X-ray diffractive analysis so that its molecular structure may thus be compared with that of compound **1** (see Fig. 3). Some of the more important bond lengths and angles for both compounds are given in Tables 1 and 2; full lists are provided as supplementary material.

Each Ti(IV) atom in **1** and **2** has an almost regular tetrahedral geometry, as is demonstrated by the O–Ti–O angles of 109.2 – 109.7° , confirming the results obtained from recent X-ray absorption studies that we have performed on both compounds [18]. Each of these titanium atoms is further coordinated to four oxygen atoms which are subsequently bonded to a XPh_3 moiety (where $\text{X} = \text{Si}$ for **1** and $\text{X} = \text{Ge}$ for **2**). (This combination of four coordination and regular tetrahedral geometry is relatively rare for sterically unhindered

Ti(IV)–O complexes, which have a strong tendency to exist as oligomers in both the solid and solution state.) Evidence for strong π -bonding is also provided by the relatively short Ti–O distances in both molecules: $1.7822(4)$ – $1.798(7)$ Å, and the high thermal stability of both compounds **1** and **2** when contrasted with titanosilsesquioxanes [22]. Curiously, both molecules also possess one linear and unique Ti–O–X bond, having a slightly shorter O–X bond distance than that found for the remaining three bent Ti–O–X bonds: Si(2)–O(2) is $1.613(7)$ Å cf. Si(1)–O(1) being $1.650(4)$ Å in **1**; Ge(2)–O(2) is $1.752(9)$ Å cf. Ge(1)–O(1) being $1.777(5)$ Å in **2**. Furthermore, the three C–X bond distances and O–X–C bond angles arising from this unique X atom in both compounds are found to be identical: Si(2)–C(19A,B,C) is $1.858(6)$ Å and O(2)–Si(2)–C(19A,B,C) is $107.3(2)^\circ$ in **1**; Ge(2)–C(19a,b,c) is $1.957(8)$ Å and O(2)–Ge(2)–C(19a,b,c) is $105.1(3)^\circ$ in **2**. This is not apparent for the remaining X atoms, where both the C–X bond distances and O–X–C bond angles are now different from one another.

Such a linear bonding arrangement is what would be expected for all the Ti–O–X bonds in both compounds, since bent bonds would preclude the formation of three-centre partial $p\pi$ – $d\pi$ bonding between the empty d orbitals of the Ti(IV) and X atoms and the filled 2p orbitals of the O atoms. Indeed, such linear bonding has been reported in the crystal structures of the ti-

tanosilsesquioxane complex $[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}\text{TiOSiMe}_3]$ [23] and the titanatrane complex $[\text{N}(\text{C}_2\text{H}_4\text{O})_3\text{-TiOSiPh}_3]$ [24]. However, it seems that the steric constraints of the 12 phenyl rings in both compounds prevent all but one of the bonds from being able to adopt this linear arrangement. Such distortions from linearity are also evidenced in related, sterically hindered complexes that contain a Ti–O–Si bond [25–27]. Furthermore, the larger Ge atoms in compound **2** are apparently unable to compensate sufficiently for this steric strain in order to allow more than one linear Ti–O–Ge bond to form.

In an effort to investigate the effect of whether the catalytic performance of isolated Ti(IV) active sites is significantly enhanced if more than one silicon atom juxtaposed to the Ti(IV) site were replaced by a germanium atom, we endeavoured to compare the catalytic activity of both compounds **1** and **2** towards epoxidation. However, despite the coordinative unsaturation present in both compounds, each is found to be totally inactive in the epoxidation of a variety of alkene substrates using TBHP as the sacrificial oxidant. These substrates range from terminal alkenes, including styrene and 1-octene, to allylic alcohols such as crotyl alcohol and *trans*-cinamyl alcohol, as well as other,

more reactive alkenes such as cyclohexene and 1-methylstyrene. We have established using molecular modelling studies [18] that unlike the corresponding tanosilsesquioxane species, where access to the single-site, catalytically active centre is unimpaird, there is now considerable atomic congestion surrounding the Ti(IV) ion in both compounds **1** and **2**. Such steric congestion, we believe, is responsible for the total inactivity of both compounds towards epoxidation and their monomeric natures in both the solution (as evidenced by ^1H - and ^{13}C -NMR data) and solid states. Additional evidence for the inaccessibility of the Ti(IV) active sites is provided by the lack of hygroscopicity of both compounds when exposed to atmospheric moisture. In addition, unlike the accessible Ti(IV) ions present in alkoxy-derived tanosilsesquioxane complexes [12], UV–vis studies give no indication for the formation of yellow η^2 peroxy-complexes when both compounds **1** and **2** are reacted with TBHP. We propose that such steric congestion is also likely to be responsible for the catalytic inactivity of other severely hindered Ti(IV) species, such as [26,27] $\text{Ti}[\text{OSiPh}_2\text{-OSiPh}_2\text{OSiPh}_2\text{O}]_2$, which we have also found to show no activity towards alkene epoxidation, under the same conditions employed for both **1** and **2**.

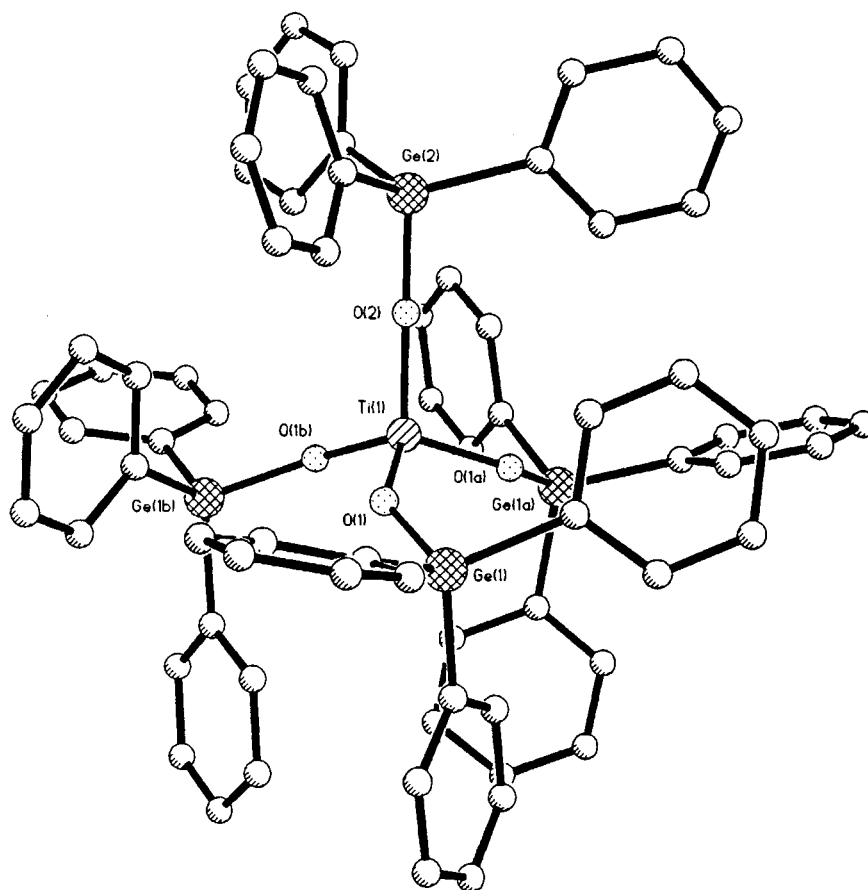


Fig. 3. Crystal structure of molecular compound **2**, showing the atomic labelling scheme (H atoms are omitted for clarity).

Table 1
Selected bond lengths (Å) and angles (°) for compound **1**, with estimated standard deviations in parentheses

Bond lengths			
Ti(1)–O(1)	1.782(4)	Ti(1)–O(2)	1.798(7)
Si(1)–O(1)	1.650(4)	Si(2)–O(2)	1.613(7)
Si(1)–C(1)	1.857(6)	Si(2)–C(19A)	1.858(6)
Si(1)–C(7)	1.851(6)	Si(2)–C(19B)	1.858(6)
Si(1)–C(13)	1.866(6)	Si(2)–C(19C)	1.858(6)
Mean C–C	1.38(9)		
Bond angles			
O(1)–Ti(1)–O(1)	109.18(14)	O(2)–Ti(1)–O(1)	109.76(13)
Si(1)–O(1)–Ti(1)	148.2(3)	Si(2)–O(2)–Ti(1)	180.0
O(1)–Si(1)–C(1)	108.1(2)	O(2)–Si(2)–C(19A)	107.3(2)
O(1)–Si(1)–C(7)	107.5(3)	O(2)–Si(2)–C(19B)	107.3(2)
O(1)–Si(1)–C(13)	107.3(3)	O(2)–Si(2)–C(19C)	107.3(2)
C(1)–Si(1)–C(7)	111.8(3)	C(19A)–Si(2)–C(19A)	111.6(2)
C(1)–Si(1)–C(13)	112.5(3)	C(19A)–Si(2)–C(19C)	111.6(2)
C(7)–Si(1)–C(13)	109.4(3)	C(19B)–Si(2)–C(19C)	111.6(2)

Table 2
Selected bond lengths (Å) and angles (°) for compound **2**, with estimated standard deviations in parentheses

Bond lengths			
Ti(1)–O(1)	1.796(5)	Ti(1)–O(2)	1.788(10)
Ge(1)–O(1)	1.777(5)	Ge(2)–O(2)	1.752(9)
Ge(1)–C(1)	1.935(8)	Ge(2)–C(19a)	1.957(8)
Ge(1)–C(7)	1.938(8)	Ge(2)–C(19b)	1.957(8)
Ge(1)–C(13)	1.926(8)	Ge(2)–C(19c)	1.957(8)
Mean C–C	1.38(13)		
Bond angles			
O(1)–Ti(1)–O(1)	109.2(2)	O(2)–Ti(1)–O(1)	109.7(2)
Ge(1)–O(1)–Ti(1)	142.3(3)	Ge(2)–O(2)–Ti(1)	180.0
O(1)–Ge(1)–C(1)	106.5(3)	O(2)–Ge(2)–C(19a)	105.1(3)
O(1)–Ge(1)–C(7)	107.8(3)	O(2)–Ge(2)–C(19b)	105.1(3)
O(1)–Ge(1)–C(13)	105.7(3)	O(2)–Ge(2)–C(19c)	105.1(3)
C(1)–Ge(1)–C(7)	110.5(3)	C(19a)–Ge(2)–C(19b)	113.5(2)
C(1)–Ge(1)–C(13)	113.1(3)	C(19a)–Ge(2)–C(19c)	113.5(2)
C(7)–Ge(1)–C(13)	112.8(3)	C(19b)–Ge(2)–C(19c)	113.5(2)

The reactions of these compounds with incompletely condensed silsesquioxanes and their investigation using X-ray absorption spectroscopy is presented elsewhere [18].

3. Experimental

Unless otherwise stated, all experiments were performed under an atmosphere of dry, oxygen-free nitrogen using conventional Schlenk techniques and solvents that were freshly distilled before use. Ph_3GeOH was synthesised following the method of Dannley and Farant [20]. All other reagents were used as obtained commercially.

3.1. Synthesis of compounds **1** and **2**

Both $\text{Ti}(\text{OSiPh}_3)_4$ (**1**) and $\text{Ti}(\text{OGePh}_3)_4$ (**2**) were synthesised by adopting the procedure of Zeitler and Brown [24], using Ph_3SiOH (2.00 g, 7.25 mmol) or Ph_3GeOH (2.32 g, 7.25 mmol) and $\text{Ti}(\text{OBu}^n)_4$ (0.47 ml, 1.45 mmol) in toluene (50 ml) at 25°C. The products precipitated out as analytically pure, white crystalline compounds $\text{Ti}(\text{OSiPh}_3)_4$ (1.55 g, 93%) and $\text{Ti}(\text{OGePh}_3)_4$ (1.85 g, 96%).

3.2. Selected spectroscopic data for **1**

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C, TMS): $\delta = 7.63$ (d, $^3J(\text{H,H}) = 10$ Hz, 24H; SiPh_3), 7.42 (dd, $^3J(\text{H,H}) = 10$ Hz, 7.5 Hz, 12H; SiPh_3), 7.38 (t, $^3J(\text{H,H}) = 7.5$ Hz, 24H; SiPh_3); $^{13}\text{C-NMR}$ (400 MHz, CDCl_3 , 25°C, TMS): $\delta = 134.92$ (s, CH, SiPh_3), 129.59 (s, CH, SiPh_3), 127.94 (s, C, SiPh_3), 127.71 (s, CH, SiPh_3); m/z (FAB⁺): 873 [$\text{M}^+ - \text{OSiPh}_3$]; Anal. Calc. for $\text{C}_{72}\text{H}_{60}\text{O}_4\text{Si}_4\text{Ti}$ (found): C, 75.2 (73.9); H 5.23 (5.24)%. Crystal data: $\text{C}_{72}\text{H}_{60}\text{O}_4\text{Si}_4\text{Ti}$, colourless plates, $M = 1149.46$, $T = 100(2)$ K, hexagonal, space group $R\bar{3}$, $a = 18.930(5)$ Å, $b = 18.930(5)$ Å, $c = 29.014(8)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 9004(4)$ Å³, $F(000) = 3612$, $Z = 6$, $D_{\text{calc.}} = 1.27$ g cm⁻³, $\mu(\text{synchrotron}) = 0.273$ mm⁻¹, specimen $0.04 \times 0.04 \times 0.04$ mm³, Siemens SMART CCD diffractometer equipped with a silicon (111) crystal monochromator and a palladium-coated focusing mirror, on the single crystal diffraction station no. 9.8 at the Daresbury Laboratory Synchrotron Radiation Source, ω rotation with narrow frames; coverage of a hemisphere of reciprocal space was achieved by 0.2° frame increments in ω ; multiscan corrections were applied to account for incident beam decay and absorption effects, synchrotron radiation $\lambda = 0.6890$ Å, $\omega/2\theta$ scans; h , -13 to 18; k , -18 to 21; l , -26 to 32; 2865 unique reflections for $1.82 < \theta < 22.49^\circ$, $R_1 = 0.1170$ for 2865 reflections with $I > 2\sigma(I)$, $wR_2 = 0.1649$, refinements carried out on F^2 using 4744 reflections, SHELXS 86 [28] used for structure solution and SHELXL 93 [29] for refinement, hydrogen atoms added in calculated positions ($\text{C-H} = 0.95$, $B = 1.2 \times B_{\text{eq}}$ of the carrying carbon atoms) and refined riding on their respective C atoms.

3.3. Selected spectroscopic data for **2**

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C, TMS): $\delta = 7.64$ (d, $^3J(\text{H,H}) = 10$ Hz, 24H; GePh_3), 7.44 (dd, $^3J(\text{H,H}) = 10$ Hz, 7.5 Hz, 12H; GePh_3), 7.38 (t, $^3J(\text{H,H}) = 7.5$ Hz, 24H; GePh_3); $^{13}\text{C-NMR}$ (400 MHz, CDCl_3 , 25°C, TMS): $\delta = 135.91$ (s, CH, GePh_3), 134.09 (s, C, GePh_3), 130.07 (s, CH, GePh_3), 128.47 (s, CH, GePh_3); m/z (FAB⁺): 547 [$\text{M}^+ - \text{OGePh}_3 - 6\text{Ph}$], 460 [$\text{M}^+ - 2\text{OGePh}_3 - 3\text{Ph}$]; Anal. Calc. for $\text{C}_{72}\text{H}_{60}\text{O}_4\text{Ge}_4\text{Ti}$

(found): C, 65.1 (65.1); H 4.52 (4.64)%. Crystal data: $C_{72}H_{60}O_4Ge_4Ti$, colourless plates, $M = 1327.46$, $T = 180$ K, trigonal, space group $R\bar{3}$, $a = 19.131(2)$ Å, $b = 19.1312(14)$ Å, $c = 29.3810(14)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 9312.8(12)$ Å³, $F(000) = 4044$, $Z = 6$, $D_{\text{calc.}} = 1.42$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 2.086$ mm⁻¹, specimen $0.12 \times 0.12 \times 0.12$ mm⁻³, Rigaku R-Axis II-c imaging plate system equipped with a rotating anode graphite monochromator and an Oxford Cryosystem device for the low-temperature collection, Mo-K α radiation $\lambda = 0.71073$ Å, $\omega/2\theta$ scans; h , -23 to 22 ; k , -22 to 23 ; l , -35 to 2997 ; 15 126 unique reflections for $1.41 < \theta < 25.41^\circ$, $R_1 = 0.1170$ for 3671 reflections with $I > 2\sigma(I)$, $wR_2 = 0.1648$, refinements carried out on F^2 using all reflections, SHELXS 86 [28] used for structure solution and SHELXL 93 [29] for refinement, hydrogen atoms added in calculated positions ($C-H = 0.95$ Å, $B = 1.2 \times B_{\text{eq}}$ of the carrying carbon atoms) and refined riding on their respective C atoms.

3.4. Catalytic studies

Tests were performed under argon using catalyst that was pre-dried at 80°C, 10^{-4} Torr for 12 h, using one equivalent of catalyst to 70 equivalents of alkene, TBHP and TMS (internal standard), in 0.5 ml of $CDCl_3$ at 45°C in sealed vials that were magnetically stirred. Catalytic activity was evaluated using ¹H-NMR spectroscopy.

4. Supplementary material

Crystal data and details of measurement, tables of atomic coordinates, tables of anisotropic thermal parameters and tables of bond lengths and angles are available as supplementary material and have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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