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Synthesis, characterization and thermal behaviour of four homoleptic titanium silanolates

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Four titanium silanolates $Ti(OSiR_2R')_4$ (1, R = Ph, R′ = ^{t}Bu; 2, R = R′ = Ph; 3, R = R′ = ^{i}Pr; 4, R = Me, R′ = ^{t}Bu) were synthesised starting from $Ti(O^iPr)_4$ and the corresponding silanol, and their thermally induced decomposition was studied. Colourless single crystals of $Ti(OSiPh_2{}^tBu)_4\cdot\frac{2}{3}CHCl_3\cdot\frac{1}{3}C_7H_8$ ($1\cdot\frac{2}{3}CHCl_3\cdot\frac{1}{3}C_7H_8$) were obtained from a mixture of chloroform and toluene (1:1) at −20 °C. The compound crystallizes in the space group $R\bar{3}c$ with $Z = 18$. The metal atom shows an almost ideal tetrahedral coordination, as is demonstrated by the O–Ti–O angles of 108.4(1)–111.1(1)°. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: titanium; silanolate; thermolysis; crystal structure

INTRODUCTION

Titanium silanolates were among the first metal silanolates, and have been studied as potential precursors for novel materials.[1–6] Since the discovery of silica-supported titania epoxidation catalysts there has been growing interest in molecular titanium silanolates, and a large number of diverse compounds, such as cyclic, spirocyclic and cubic titanasiloxanes, as well as titanium silsesquioxanes, have been the subject of a variety of research projects.[7–20] We became interested in titanium silanolates in a research project aimed at the synthesis of molecular heterobimetallic bismuth–titanium precursors for bismuth titanates, which are of interest because of their electronic properties, such as ferroelectricity.[21–24] However, simple titanium silanolates might also serve as molecular precursors for titanium silicates. Tilley and co-workers[25] have shown that thermolysis of $Ti[OSi(O^tBu)_3]_4$ gave mixed SiO_2–TiO_2 materials that are highly active epoxidation catalysts. More recently it was claimed in a patent that compounds of the general type $[Ti(OSiR_1R_2R_3)_4L_y]$ (L = ligand) produce thin titanium silicate films upon thermal decomposition using techniques such as chemical vapour deposition (CVD) or atomic layer deposition (ALD).[26] Here, we report the synthesis of four titanium silanolates $Ti(OSiR_2R')_4$ (**1**, R = Ph, R′ = ^{t}Bu; **2**, R = R′ = Ph; **3**, R = R′ = ^{i}Pr; **4**, R = Me, R′ = ^{t}Bu) and compare their thermal behaviour.

RESULTS AND DISCUSSION

The title compounds **1**–**4** were obtained in good yields by the reaction of $Ti(O^iPr)_4$ with the corresponding silanols in tetrahydrofuran (THF) at room temperature. The synthesis and structural characterization of compound **2** have been reported previously,[1,13,27] but to the best of our knowledge the synthesis and characterization of **1, 3** and **4** have not been reported so far.

$$
\begin{aligned}
Ti(O^iPr)_4 + 4R_2R'SiOH \xrightarrow{\text{THF}} & Ti(OSiR_2R')_4 + 4HO^iPr \\
& \mathbf{1}, R = Ph, R' = {}^tBu \qquad (1) \\
& \mathbf{2}, R = R' = Ph \\
& \mathbf{3}, R = R' = {}^iPr \\
& \mathbf{4}, R = Me, R' = {}^tBu
\end{aligned}
$$

The titanium silanolate **1** was crystallized from a mixture of chloroform and toluene (1:1) at −20 °C to give single crystals of the composition $Ti(OSiPh_2{}^tBu)_4\cdot\frac{2}{3}CHCl_3\cdot\frac{1}{3}C_7H_8$ ($1\cdot\frac{2}{3}CHCl_3\cdot\frac{1}{3}C_7H_8$). The compound crystallizes in the space group $R\bar{3}c$ with $Z = 18$. The silanolate **1** is monomeric and its molecular structure (Fig. 1) is composed of a titanium atom

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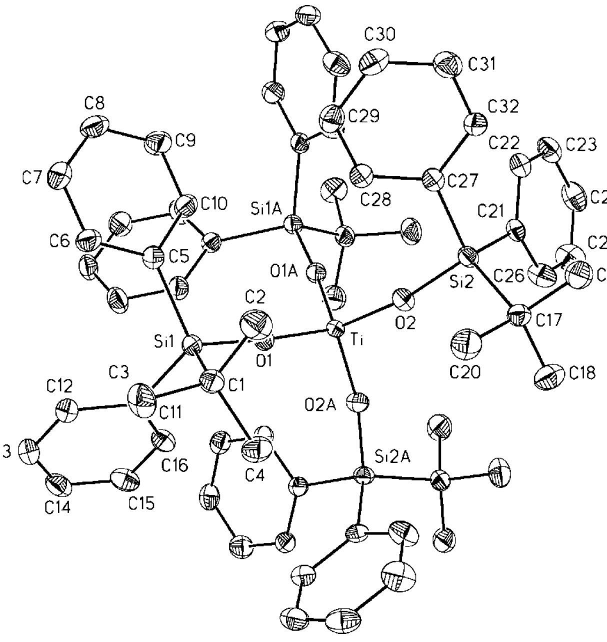

Figure 1. Molecular structure of Ti(OSiPh$_2{}^t$Bu)$_4$ (**1**) showing 30% probability displacement ellipsoids and the atom labelling scheme; hydrogen atoms omitted for clarity. Ti–O(1) 1.786(2) Å, Ti–O(2) 1.783(2) Å, Si(1)-O(1) 1.656(2) Å, Si(2)-O(2) 1.647(2) Å, Si(1)-C(1) 1.893(4) Å, Si(1)-C(5) 1.873(3) Å, Si(1)-C(11) 1.868(4) Å; O(1)-Ti–O(2) 108.4(1)°, O(1)-Ti–O(1A) 108.9(1)°, O(2)-Ti–O(1A) 111.1(1)°, O(2)-Ti–O(2A) 109.1(2)°, Ti–O(1)-Si(1) 175.4(2)°, Ti–O(2)-Si(2) 166.5(2)°. Symmetry operation A: $-x + 1/2, y, z$.

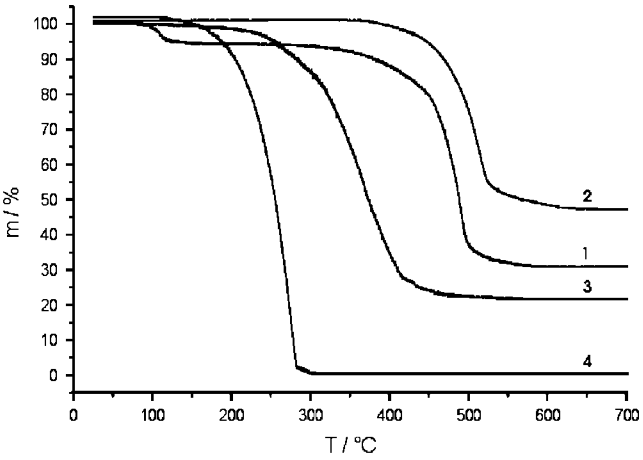

Figure 2. TGA curves of **1**–**4** obtained in an inert atmosphere of flowing argon. A heating rate of 4 °C min^{-1} to 700 °C was used.

with an almost ideal tetrahedral coordination. The O–Ti–O angles are in the range 108.4(1)–111.1(1)°. The Ti–O(1)–Si(1) and the Ti–O(2)–Si(2) angles amount to 175.4(2)° and 166.5(2)° respectively, and thus differ significantly from those reported for Ti(OSiPh$_3$)$_4$ (148.2–180.0°).[13] Most likely, steric hindrance precludes the formation of linear Ti–O–Si bonds, demonstrating the flexibility of this bond type. The experimental values of the Ti–O, Si–C and Si–O distances, with averages of 1.79 Å, 1.88 Å and 1.65 Å respectively, compare well with standard Ti–O, Si–C and Si–O bond lengths.

Differential thermal analysis (DTA)–thermogravimetric analysis (TGA) measurements for compounds **1**–**4** were carried out with a heating rate of 4 °C min^{-1} under inert atmosphere to a maximum temperature of 700 °C. The TGA diagrams are given in Fig. 2. All compounds exhibit a higher thermal stability than was reported for Ti[OSi(O^{t}Bu)$_3$]$_4$,[25] which showed an onset temperature for its decomposition of ~250 °C. The thermal stability is highest for the triphenylsiloxy compound **2**, which shows a melting point of 371 °C and an onset temperature for its decomposition of ~400 °C. In contrast, the trialkylsilanolate Ti(OSiMe$_2{}^t$Bu)$_4$ (**4**) was completely evaporated in the temperature range 150–280 °C. The weight loss observed for $\mathbf{1}\cdot\frac{2}{3}\mathrm{CHCl_3}\cdot\frac{1}{3}\mathrm{C_7H_8}$ proceeds in two steps, which is consistent with the loss of solvent molecules in the temperature range 80–120 °C and thermolysis of **1** in the temperature range 350–520 °C. The ceramic yield of 30.9% is significantly higher than calculated for TiO$_2$·SiO$_2$ (11.8%). An energy-dispersive X-ray (EDX) analysis of the black residue gave a Ti : Si ratio of approximately 1 : 3 and a carbon content of approximately 39%. Similarly, thermolysis of Ti(OSiPh$_3$)$_4$ gave a high ceramic yield of 46.6%. The black residue shows a Ti : Si ratio of approximately 1 : 3 and a carbon content of 41%.

For compound **3**, which decomposes in the temperature range 280–420 °C, a ceramic yield of 21.7% was observed. The carbon content in the black residue amounts to only 1% and the Ti : Si ratio was determined by EDX analysis to be approximately 1 : 1. These results are in agreement with the formation of TiO$_2$·SiO$_2$ (calculated ceramic yield 18.9%) showing some carbon contamination.

The scanning electron microscope (SEM) images of **1**–**3** are shown in Fig. 3. The decomposition products are isolated in the form of thin vitreous-looking plates showing a large number of cracks in the case of **2**. A relatively smooth surface results from thermolysis of Ti(OSi^{i}Pr$_3$)$_4$ (**3**).

Our attempts to prepare heterobimetallic bismuth–titanium (oxo)silanolates by partial hydrolysis of titanium and bismuth silanolates failed. However, hydrolysing a 3 : 4 mixture of Ti(OSiMe$_2{}^t$Bu)$_4$ (**4**) and Bi(OSiMe$_2{}^t$Bu)$_3$,[28] as required for the synthesis of Bi$_4$Ti$_3$O$_{12}$, followed by calcination of the precipitate at 700 °C gave a mixture of Bi$_4$Ti$_3$O$_{12}$ (JCPDS No. 80–2143) and Bi$_2$Ti$_2$O$_7$ (JCPDS No. 32–0118) as crystalline phases, together with some amorphous material.

CONCLUSIONS

In a recent patent, the potential of simple titanium silanolates for the manufacture of thin titanium silicate films using

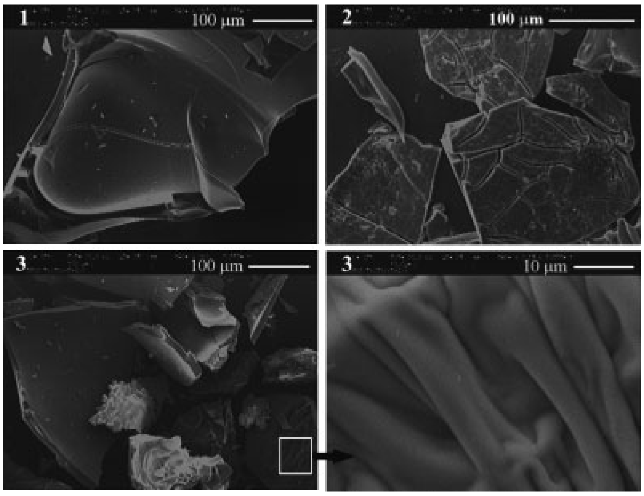

Figure 3. SEM images of the thermolysis products of compounds **1**–**3**.

techniques such as CVD or ALD was proposed.[26] Our study reveals some problems, which might result from the high thermal stability of the titanium silanolates reported in this paper. Substantial decomposition is achieved only by applying very high temperatures. As might be expected, thermolysis of arylsilanolates under argon gave products with a very high carbon content, whereas the decomposition product of Ti(OSi^{i}Pr$_3$)$_4$ (**3**) showed only minor carbon contamination. However, Tilley and co-workers'[25] Ti[OSi(O^{t}Bu)$_3$]$_4$ is much better suited to preparing mixed TiO_2–SiO_2 materials via thermolysis in the solid state; but, in contrast to compounds of the type Ti(OSiR$_3$)$_4$, it is not volatile and thus not suited for CVD applications.

EXPERIMENTAL

The commercially available starting materials Ti(O^{i}Pr)$_4$ (Aldrich) and HOSi^{i}Pr$_3$ (ABCR) were used as received. The silanols Ph$_3$SiOH,[29] ^{t}BuPh$_2$SiOH,[30] and ^{t}BuMe$_2$SiOH[31] were prepared according to literature procedures. Solvents were distilled from appropriate drying agents prior to use. ^{1}H, ^{13}C and ^{29}Si NMR spectra were measured at room temperature on DPX 200, DPX 300 and DRX 400 spectrometers from Bruker. Chemical shifts δ (ppm) are referenced against Me$_4$Si. Elemental analyses were performed on a LECO-CHNS-Analyser. For the melting point measurements, a Büchi SMP-20 instrument was used. Thermal analyses were recorded using a TA1 thermoanalyser (Mettler Instrumente AG). The DTA–TGA measurements were performed at a heating rate of 4 °C min^{-1} to a maximum temperature of 700 °C in an atmosphere of flowing argon using Al_2O_3 as reference material. The residues were analysed by EDX analysis and SEM images were recorded using a Stereoscan electron microscope (Cambridge Instruments).

Synthesis of Ti(OSiPh$_2$^{t}Bu)$_4$ (1)

A solution of HOSiPh$_2$^{t}Bu (5.03 g, 19.61 mmol) in 100 ml THF was added dropwise to a solution of Ti(O^{i}Pr)$_4$ (1.39 g, 4.90 mmol) in 50 ml THF at room temperature. The reaction mixture was stirred for 12 h. The solvent was removed *in vacuo* at 40 °C and the solid material was crystallized from a mixture of hexane and toluene (1 : 1) at −20 °C. Compound **1** was separated as a colourless solid (5.98 g, 60%) with a melting point of 153 °C. Single crystals suitable for X-ray crystal structure analysis were obtained by crystallization from a mixture of $CHCl_3$ and toluene (1 : 1) at −20 °C.

^{1}H NMR (200.13 MHz, C_6D_6): δ 1.20 (s, 36H, CH_3), 7.01 (tt, 8H, *para*-H_{Ph}), 7.03 (dd, 16H, *meta*-H_{Ph}), 7.84 (dd, 16H, *ortho*-H_{Ph}). ^{13}C{^{1}H} NMR (100.63 MHz, C_6D_6): δ 20.1 (CCH$_3$), 27.33 (CH$_3$), 127.9 (C_o), 129.7 (C_{ipso}), 135.5 (C_m), 135.6 (C_p). ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6): δ −4.6. Anal. Found: C, 71.8; H, 7.3. Calc. for $C_{64}H_{76}O_4Si_4Ti$: C, 71.9; H, 7.2%.

Synthesis of Ti(OSiPh$_3$)$_4$ (2)

The compound was prepared according to a literature procedure[27] from Ti(O^{i}Pr)$_4$ (2.14 g, 7.53 mmol) and HOSiPh$_3$ (8.33 g, 30.13 mmol) in toluene to give a colourless precipitate of **2** (7.71 g, 77%) with a melting point of 371 °C.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.37–7.64 (complex pattern, H_{Ph}). Anal. Found: C, 75.1; H, 5.1. Calc. for $C_{72}H_{60}O_4Si_4Ti$: C, 75.2; H, 5.2%.

Synthesis of Ti(OSi^{i}Pr$_3$)$_4$ (3)

A solution of HOSi^{i}Pr$_3$ (4.96 g, 28.47 mmol) in 120 ml THF was added dropwise to a solution of Ti(O^{i}Pr)$_4$ (2.00 g, 7.05 mmol) in 50 ml THF at room temperature. The reaction mixture was stirred for 12 h. The solvent was removed *in vacuo* at 40 °C and the solid material dried to give compound **3** (4.24 g, 81%), which starts to decompose at 276 °C.

^{1}H NMR (200.13 MHz, C_6D_6): δ 0.95 (sep, 1H, CH), 1.23 (d, 6H, CH_3). ^{13}C{^{1}H} NMR (100.63 MHz, C_6D_6): δ 13.6 (SiCH$_3$), 18.4 (CCH$_3$), 26.1 (CCH$_3$). ^{29}Si{^{1}H} NMR (59.62 MHz, C_6D_6): δ 14.8. Anal. Found: C, 58.7; H, 11.9. Calc. for $C_{36}H_{84}O_4Si_4Ti$: C, 58.3; H, 11.4%.

Synthesis of Ti(OSiMe$_2$^{t}Bu)$_4$ (4)

A solution of HOSiMe$_2$^{t}Bu (9.28 g, 70.32 mmol) in 150 ml THF was added dropwise to a solution of Ti(O^{i}Pr)$_4$ (5.00 g, 17.58 mmol) in 60 ml THF at room temperature. The reaction mixture was stirred for 12 h. The solvent was removed *in vacuo* at 40 °C and the solid material dried to give **4** (9.23 g, 91%) with a melting point of 99 °C.

^{1}H NMR (200.13 MHz, C_6D_6): δ 0.21 (s, 6H, SiCH_3), 1.05 (s, 9H, CCH_3). ^{13}C{^{1}H} NMR (100.63 MHz, C_6D_6): δ 1.4 (SiCH$_3$), 19.0 (CCH$_3$), 26.1 (CCH$_3$). ^{29}Si{^{1}H} NMR (59.62 MHz, C_6D_6): δ 17.1. Anal. Found: C, 49.6; H, 11.1. Calc. for $C_{24}H_{60}O_4Si_4Ti$: C, 50.3; H, 10.6%.

Crystallography

The moisture-sensitive compound Ti(OSiPh$_2$^{t}Bu)$_4$$\cdot\frac{2}{3}$CHCl$_3$$\cdot\frac{1}{3}C_7H_8$ (**1**$\cdot\frac{2}{3}$CHCl$_3$$\cdot\frac{1}{3}C_7H_8$) was directly transferred from the mother liquid to the diffractometer using the oil-drop technique. Intensity data were collected at 173 K on a Nonius KappaCCD diffractometer for a colourless block of dimensions 0.14 × 0.14 × 0.16 mm^3. $C_{67}H_{79.33}Cl_2O_4Si_4Ti$, $M = 1179.80$, trigonal, $R\overline{3}c$, $a = 23.826(3)$ Å, $c = 59.492(12)$ Å, $V = 29249(8)$ Å^3, $Z = 18$, 5910 unique data (θ_{max} 25.3°), 3059 data with $I \geq 2\sigma(I)$, $R = 0.052$ (obs. data), $wR = 0.138$ (all data). Programs used: SHELXS-97, SHELXL-97 and ORTEP. CCDC deposition no. 269 343 ($\mathbf{1}\cdot\frac{2}{3}CHCl_3\cdot\frac{1}{3}C_7H_8$).

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