Synthesis and Solid-State Characterization of Isopropoxy Carboxylate Clusters of Ti^{IV}

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Reaction of $Ti(OiPr)_4$ with chloroacetic acids (1:1 and 1:2 stoichiometric ratio) in toluene gives the corresponding mono- and bis-substituted products in quantitative yield. The products $Ti(OiPr)_3(OOCR)$ (R = CH_2Cl **1a,** $CHCl_2$ **1b**, CCl_3 **1c**) are proposed to have a dimeric structure on the basis of ^1H,^{13}C NMR and IR spectroscopy. On standing in toluene, solutions of **1c** form the trinuclear species $Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OiPr)_2(OiPr)_5(\mu\text{-}O_2CCCl_3)_3$ (**2**) with the three titanium atoms forming an isosceles triangle and the μ_3-O moiety at the center. On standing in toluene, solutions of **1b** form a hexanuclear product $Ti_6(\mu_3\text{-}O)_6(OiPr)_6(\mu\text{-}O_2CCHCl_2)_6$ (**3**), the structure of which consists of two stacked six-membered [Ti-μ_3-O]$_3$ rings connected by Ti–O bonds. Under comparable conditions, the *bis-substituted* product $Ti(OiPr)_2(O_2CCCl_3)_2$ (**4c**) forms the dinuclear species $Ti_2(\mu\text{-}O)(OiPr)_2(HOiPr)_2(\mu\text{-}O_2CCCl_3)_2(O_2C\text{–}CCl_3)_2$ (**5**) in which the two symmetric octahedral titanium centers are bonded to a common oxygen atom.

Introduction

Metal alkoxides [1–4] are the preferred precursors in the sol-gel process of preparing ceramic materials. However, their high hydrolytic instability needs to be overcome by the incorporation of hydroxylated nucleophilic ligands[5] such as carboxylic acids[6–15] and β-diketones[16,17] to produce new molecular precursors. Titanium oxoalkoxy carboxylates have received considerable attention in recent years. These precursors generally consist of four to six titanium atoms with one of six[6–14] types of metal-oxygen core skeletons. Recently,[18] a nonanuclear product was isolated. These highly condensed oxo species are usually generated by a secondary process i.e. esterification. For alkoxides, ether elimination[19–21] and naturally controlled hydrolysis[22] are other routes to oxo products.

Acetic acid[6–9,13,14] has been used most often for preparing the above oxoalkoxy carboxylates, perhaps because addition of acetic acid to sol-gel processes with titanium alkoxides prevents precipitation and increases the gelation time.[23] We wanted to examine the structural changes caused by gradually increasing both the acidity and steric bulk of the carboxylic acid. Therefore, we examined the reactions of chloroacetic acids with titanium isopropoxide. Initially, to produce smaller amounts of condensed/uncondensed species, these reactions were performed in excess solvent (toluene) at room temperature. Surprisingly, these toluene solutions of the simple substitution products formed oxo species on standing, which were characterized by X-ray crystallography. The extent of condensation seems to be dependent on the time the solution is left standing.

We report here the first simple di- and trinuclear oxoalkoxytitanium carboxylates. A hexanuclear species having a Ti_6O_6 core was also obtained.

Results and Discussion

Structurally characterized carboxylic acid-modified titanium alkoxides have generally been reported to contain four to six titanium atoms with one of six[6–14] metal-oxygen core skeletons. Most of these products have been obtained from either neat[9] reaction mixtures or very small solvent volumes.[12–14] Some of the products are obtained from excess solvent, but only at high temperatures[10] or under reflux[15] conditions. In excess solvent, at room temperature, the reaction of $Ti(OEt)_4$ with $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ was recently reported[11] to give the single product $Ti_6O_4(OEt)_{12}\{\mu\text{-}(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_4$.

Since both the absence of solvent and high temperatures of reflux facilitate condensation *by* esterification, we have examined the reactions of $Ti(OiPr)_4$ with chloroacetic acids in solvent at room temperature (25 °C). Initially $Ti(OiPr)_4$ was dissolved in toluene and then a toluene solution of the acid was added to it dropwise while stirring.

The products of the reactions of $Ti(OiPr)_4$ with mono-, di-, and trichloroacetic acids in 1:1 stoichiometric ratio in toluene are $Ti(OiPr)_3(O_2CR)$ (R = CH_2Cl **1a**, $CHCl_2$ **1b**, CCl_3 **1c**), which were obtained in quantitative yields (Equation 1). The liberated 2-propanol was determined by chromic acid oxidation.[24]

$$Ti(OiPr)_4 + RCOOH \rightarrow Ti(OiPr)_3(OOCR) + HOiPr \quad (1)$$

The ambient-temperature ^1H NMR spectrum of **1a** shows two doublets and two septets (intensity ratio 1:2) for the *gem*-dimethyl protons corresponding to the bridging

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and terminal isopropoxy groups respectively. The ^{13}C NMR spectrum also shows the presence of two types of isopropoxy group and one type of carboxylate group. In the IR spectrum of **1a** the difference between the antisymmetric (1580 cm^{-1}) and symmetric (1460 cm^{-1}) stretching bands of the carboxylate group ($\Delta\tilde{\nu}$ = 120 cm^{-1}) suggests[25] a bridging bidentate bonding mode. The bridging and terminal isopropoxy groups are accounted for by the bands at 1020 cm^{-1} and 1090 cm^{-1} respectively. The IR and ^{13}C NMR spectra of the products **1b** and **1c** are similar to those of **1a** but their ambient temperature ^1H NMR spectra show one doublet for the methyl protons, which is probably due to fast exchange of the O*i*Pr groups at the probe temperature. Attempts to grow single crystals of compounds **1** were not successful. Therefore, on the basis of the available spectral evidence, and in accordance with a report of Doeuff and Sanchez,[26] compounds **1** may have dimeric structures.

An attempt to crystallize **1c** by leaving the reaction mixture for two days in toluene (at –15 °C) led to a white crystalline product which was shown to be $Ti_3(\mu_3\text{-}O)(\mu\text{-}O\text{-}iPr)_2(OiPr)_5(\mu_3\text{-}O_2C\text{–}CCl_3)_3$ (**2**) by X-ray crystallographic analysis (Equation 2).

$$3\ Ti(OiPr)_3(OOCCCl_3) \rightarrow Ti_3O(OiPr)_7(OOCCCCl_3)_3 + OiPr_2 \quad (2)$$

We were able to obtain crystalline material of **1b** from the reaction mixture of $Ti(OiPr)_4$ with $CHCl_2COOH$ in toluene. When the mother liquor was left for a few days, a small crop of crystals was obtained, which were characterized as $Ti_6(\mu_3\text{-}O)_6(OiPr)_6(\mu\text{-}O_2CCHCl_2)_6$ (**3**) by X-ray crystallographic analysis. The formation of this highly condensed product may also be accounted for by ether elimination (Equation 3).

$$6\ Ti(OiPr)_3(OOCCHCl_2) \rightarrow Ti_6(O)_6(OiPr)_6(OOCCHCl_2)_6 + 6\ OiPr_2 \quad (3)$$

The bis-substituted products $Ti(OiPr)_2(O_2CR)_2$ (R = CH_2Cl **4a**, $CHCl_2$ **4b**, CCl_3 **4c**) are obtained quantitatively from the reaction of $Ti(OiPr)_4$ with chloroacetic acids (1:2 stoichiometric ratio) according to Equation 4.

$$Ti(OiPr)_4 + 2\ RCOOH \rightarrow Ti(OiPr)_2(OOCR)_2 + 2\ HOiPr \quad (4)$$

The IR spectrum of **4c** shows four absorptions due to the carboxylate group. The two $\tilde{\nu}_{CO2}$ bands at 1766 cm^{-1} (antisymmetric) and 1377 cm^{-1} (symmetric) ($\Delta\tilde{\nu}$ = 389 cm^{-1}) were assigned as a unidentate carboxylate group while those at 1658 cm^{-1} (antisymmetric) and 1462 cm^{-1} (symmetric) ($\Delta\tilde{\nu}$ = 120 cm^{-1}) were assigned as a bridging bidentate carboxylate group. The peaks at 1015 cm^{-1} and 1089 cm^{-1} were assigned as bridging and terminal isopropoxy groups, respectively.[25] However, the ambient temperature ^1H and ^{13}C NMR spectra of **4c** were not structurally informative. The IR and the ambient temperature ^1H and ^{13}C NMR spectra of **4a** and **4b** are similar to those of **4c**. We were unable to structurally characterize **4** since we could not obtain single crystals of these compounds. As before, we tried to crystallize **4c** by leaving the reaction mixture to stand for two days, and obtained the white crystalline dinuclear species $Ti_2(\mu\text{-}O)(OiPr)_2(HOiPr)_2(\mu\text{-}O_2C\text{–}Cl_3)_2(O_2C\text{–}Cl_3)_2$ (**5**) (Equation 5).

$$2\ Ti(OiPr)_4 + 4\ CCl_3COOH \rightarrow Ti_2(O)(OiPr)_2(HOiPr)_2(OOCCCl_3)_4 + OiPr_2 + 2\ HOiPr \quad (5)$$

The IR spectra of the volatiles from reactions (2), (3) and (5) showed strong absorptions around 1165 cm^{-1}, characteristic of isopropyl ether. No absorptions were observed in the carbonyl region. Therefore, ester formation does not appear to take place under the mild conditions of these reactions. A similar observation has been reported[10] in the reaction of $Ti(OiPr)_4$ with $(CO)_9Co_3(\mu_3\text{-}C\text{–}CO_2H)$.

X-ray Crystallographic Structures

The X-ray structure (Figure 1, Table 1) of **2** shows the three titanium atoms sitting at the corners of an isosceles triangle with the triply bridged oxo group at the center.

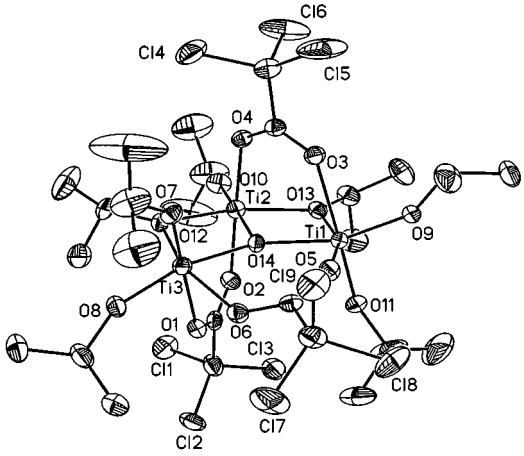

Figure 1. Molecular structure of compound **2** in ORTEP description; hydrogen atoms omitted for the sake of clarity; thermal ellipsoids represent a 25 % probability

All three trichloroacetate groups are bidentate and symmetrically bridge the three titanium centers with a propeller arrangement. All three titanium atoms are six coordinate with two of the atoms (Ti1, Ti3) in a similar coordination environment. The third titanium atom (Ti2) has one terminal O*i*Pr group, making the structure asymmetric. The bridging O*i*Pr groups are also asymmetrical with one O*i*Pr group bridging Ti1 and Ti2, and the other Ti2 and Ti3; there is no bridge between Ti1 and Ti3. This Ti_3O skeletal arrangement is the first[12] of its type reported for titanium oxo alkoxy carboxylates. It is interesting to note that if the fourth coordination site (the one generating the cubic framework) of the μ_4-O group in the structure of $Ti_4(\mu\text{-}O)(\mu_4\text{-}O)(O_2CH)_2(\mu\text{-}OiPr)_4(OiPr)_6$[12] was removed, a Ti_3O_3 core similar to **2** would be obtained.

The geometry around the μ_3-O group is remarkable as the sum of the angles is 360°, making it perfectly planar. The constraints of the two four-membered rings (Ti2, O13,

Table 1. Selected bond lengths [Å] and angles [°] for **2**

Bond lengths					
Ti(1)–O(11)	1.765(3)	Ti(1)–O(9)	1.783(3)	Ti(1)–O(14)	1.921(3)
Ti(1)–O(13)	2.025(3)	Ti(1)–O(5)	2.087(3)	Ti(1)–O(3)	2.276(3)
Ti(1)–Ti(2)	3.0633(13)	Ti(2)–O(10)	1.760(3)	Ti(2)–O(14)	1.920(3)
Ti(2)–O(13)	1.971(3)	Ti(2)–O(12)	1.976(3)	Ti(2)–O(4)	2.024(3)
Ti(2)–O(2)	2.056(3)	Ti(2)–Ti(3)	3.07088(12)	Ti(3)–O(7)	1.771(3)
Ti(3)–O(8)	1.780(3)	Ti(3)–O(14)	1.932(3)	Ti(3)–O(12)	2.026(3)
Ti(3)–O(6)	2.099(3)	Ti(3)–O(1)	2.261(3)	Ti(3)–O(6)	2.099(3)
Ti(3)–O(1)	2.261(3)				
Bond angles					
O(11)–Ti(1)–O(9)	101.16(13)	O(11)–Ti(1)–O(14)	100.92(13)	O(9)–Ti(1)–O(14)	157.43(13)
O(11)–Ti(1)–O(13)	96.28(13)	O(9)–Ti(1)–O(13)	105.91(12)	O(14)–Ti(1)–O(13)	76.21(11)
O(11)–Ti(1)–O(5)	91.90(13)	O(9)–Ti(1)–O(5)	91.66(12)	O(14)–Ti(1)–O(5)	82.96(11)
O(13)–Ti(1)–O(5)	158.71(11)	O(11)–Ti(1)–O(3)	177.87(13)	O(9)–Ti(1)–O(3)	80.48(12)
O(14)–Ti(1)–O(3)	77.58(11)	O(13)–Ti(1)–O(3)	81.92(11)	O(5)–Ti(1)–O(3)	89.41(11)
O(10)–Ti(2)–O(13)	102.06(14)	O(14)–Ti(2)–O(13)	77.51(11)	O(10)–Ti(2)–O(12)	102.90(14)
O(14)–Ti(2)–O(12)	77.53(11)	O(13)–Ti(2)–O(12)	155.03(12)	O(10)–Ti(2)–O(4)	94.17(13)
O(14)–Ti(2)–O(4)	88.90(11)	O(13)–Ti(2)–O(4)	87.87(11)	O(12)–Ti(2)–O(4)	91.11(12)
O(10)–Ti(2)–O(2)	89.88(13)	O(14)–Ti(2)–O(2)	87.05(12)	O(13)–Ti(2)–O(2)	91.75(12)
O(12)–Ti(2)–O(2)	87.51(12)	O(7)–Ti(3)–O(14)	100.61(13)	O(7)–Ti(3)–O(12)	98.00(13)
O(8)–Ti(3)–O(12)	103.60(13)	O(14)–Ti(3)–O(12)	76.06(11)	O(7)–Ti(3)–O(6)	91.46(13)
O(8)–Ti(3)–O(6)	93.71(12)	O(14)–Ti(3)–O(6)	83.41(11)	O(12)–Ti(3)–O(6)	158.64(11)
O(8)–Ti(3)–O(1)	81.65(13)	O(14)–Ti(3)–O(1)	78.79(11)	O(12)–Ti(3)–O(1)	82.71(11)
O(6)–Ti(3)–O(1)	87.61(11)	Ti(2)–O(12)–Ti(3)	100.24(12)	Ti(2)–O(13)–Ti(1)	100.07(12)
Ti(2)–O(14)–Ti(3)	105.70(12)	Ti(2)–O(14)–Ti(1)	105.79(12)	Ti(1)–O(14)–Ti(3)	148.52(14)

Ti1, O14 and Ti2, O14, Ti3, O12) cause the angle Ti3–O14–Ti1 (148.5°) to open up, while the other two angles (105.8°) are equal. The $Ti(2)O_6$ octahedron shares two of its edges with the other two octahedra, while the tricoordinate oxygen atom O14 is the only common point between $Ti(1)O_6$ and $Ti(3)O_6$. The three octahedra are distorted with angles ranging from 76.2° to 105.9°.

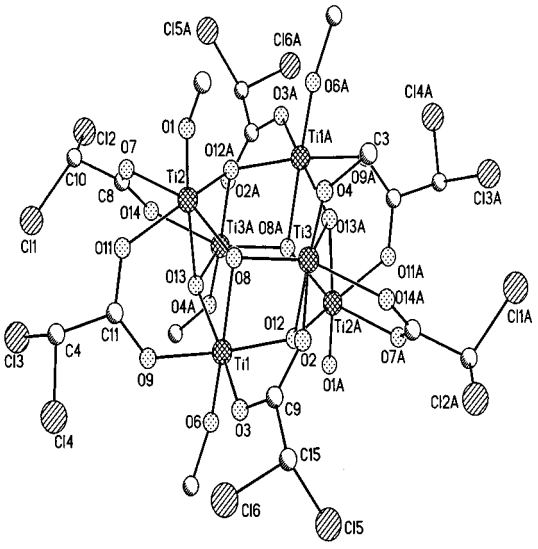

Figure 2. Stick-and-ball model of the molecular structure of the hexatitanium hexaoxo complex **3**; hydrogen atoms and the methyl carbon atoms are omitted for clarity

The X-ray crystal and molecular structure (Figure 2) of **3** shows two stacked six-membered rings consisting of alternating titanium and oxygen atoms. The rings are connected through Ti–O bonds. There is one terminal isopropoxy group attached to each titanium atom. Six dichloroacetate groups bridge the six titanium centers in a bidentate fashion, one from the upper and one from the lower ring. The angles at the alternating titanium and oxygen atoms of the hexagonal rings average 102.6° and 133.7°, respectively, showing considerable distortion in the hexagons. These angles are within the range recently reported.[12] The angles at the atoms binding the upper ring to the lower average 100.4°. While this work was in progress two oxo alkoxy carboxylates with a Ti_6O_6 core i.e. $Ti_6O_6(OiPr)_6(O_2CR)_6$ and $Ti_6O_6(OEt)_6(O_2CR)_6$ (R = H,[12] C_6H_4-*o*-OPh[15]) were reported, with their formation being attributed to ester elimination reactions. It has been ar-

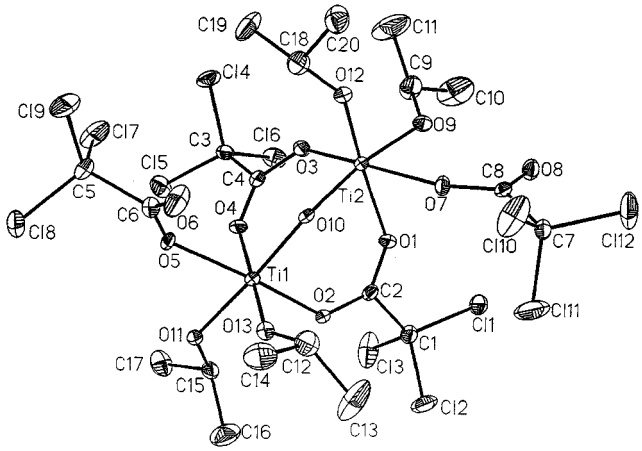

Figure 3. Molecular structure of the dititanoxane complex **5** in ORTEP description; hydrogen atoms omitted; thermal ellipsoids represent a 25 % probability

gued[12] that the sterically less demanding nature of R and increased acidity may be the reasons for the formation of highly condensed species. However, almost isostructural systems are obtained from either dichloroacetic acid (present work) or 2-phenoxybenzoic acid,[14] which does not substantiate this observation. In fact a number of oxo alkoxy carboxylates with Ti_6O_4 core, $Ti_6O_4(O_2CMe)_4(OR)_{12}$ (R = CH_2Me,[11] $CHMe_2$[14]), $Ti_6O_4(O_2CMe)_8(OR)_8$ [R = $CHMe_2$,[7] $(CH_2)_3CH_3$[9]] and $Ti_6O_4(O_2C_6H_4)_4\{\mu$-$(CO)_9Co_3(\mu_3$-$O_2CC)\}_4(OiPr)_4$[11] have been found to retain their basic structural skeleton irrespective of the steric bulk of the alkoxide and/or the carboxylic acid.

The structure of **5** (Figure 3) consists of two symmetrical, octahedral titanium centers Ti1 and Ti2 with a common μ-oxo group O10, thereby forming a novel Ti_2O core.

Each titanium atom is bound to three terminal oxygens, one each from 2-propanol, an isopropoxy and a monodentate trichloroacetate group. The two octahedrons are joined by two bridging bidentate trichloroacetate groups which are slightly distorted. The angles for the octahedrons range from 78.5° to 100.5°. Compound **5** is the first oxo alkoxy carboxylate with an alcohol attached by a dative bond. This may be due to its low nuclearity relative to other complexes. At both titanium atoms the HO*i*Pr groups are *trans* to the oxo group. The terminal groups give rise to intermolecular interactions (Cl···Cl and O–H···O contacts). Both octahedrons show a hydrogen-bonding interaction between the carbonyl oxygen of the terminal trichloroacetate group and the hydrogen of 2-propanol. Also observed are chlorine–oxygen and chlorine–titanium interactions.

Table 2. Selected bond lengths [Å] and angles [°] for **3**

Bond lengths					
Ti(1)–O(6)	1.740(5)	Ti(1)–O(13)	1.886(5)	Ti(1)–O(12)	1.891(5)
Ti(1)–O(9)	2.066(5)	Ti(1)–O(3)	2.092(6)	Ti(1)–O(8)	2.176(5)
Ti(2)–O(1)	1.747(5)	Ti(2)–O(12A)	1.899(5)	Ti(2)–O(8)	1.906(5)
Ti(2)–O(11)	2.062(5)	Ti(2)–O(7)	2.082(5)	Ti(2)–O(13)	2.156(5)
Ti(3)–O(4)	1.751(5)	Ti(3)–O(8)	1.873(5)	Ti(3)–O(13A)	1.891(5)
Ti(3)–O(2)	2.063(6)	Ti(3)–O(14A)	2.070(5)	Ti(3)–O(12)	2.180(5)
Bond angles					
O(6)–Ti(1)–O(13)	102.1(2)	O(6)–Ti(1)–O(12)	103.5(2)	O(13)–Ti(1)–O(12)	102.1(2)
O(6)–Ti(1)–O(9)	92.7(2)	O(13)–Ti(1)–O(9)	88.4(2)	O(12)–Ti(1)–O(9)	158.2(2)
O(6)–Ti(1)–O(3)	93.1(3)	O(13)–Ti(1)–O(3)	160.2(2)	O(12)–Ti(1)–O(3)	86.4(2)
O(9)–Ti(1)–O(3)	78.1(2)	O(8)–Ti(1)–O(13)	76.9(2)	O(12)–Ti(1)–O(8)	78.17(19)
O(9)–Ti(1)–O(8)	85.9(2)	O(3)–Ti(1)–O(8)	87.6(2)	O1)–Ti(2)–O(12A)	101.6(2)
O(1)–Ti(2)–O(8)	97.8(2)	O(12A)–Ti2)–O(8)	102.8(2)	O(1)–Ti(2)–O(11)	94.6(2)
O(12A)–Ti2–O(11)	158.4(2)	O(11)–Ti(2)–O(8)	88.9(2)	O(1)–Ti(2)–O(7)	95.7(2)
O(12A)–Ti2–O(7)	87.5(2)	O(11)–Ti2–O(7)	76.6(2)	O(12A)–Ti2–O(13)	77.8(2)
O(13)–Ti(2)–O(8)	77.0(2)	O(11)–Ti(2)–O(13)	87.5(2)	O(7)–Ti(2)–O(13)	89.8(2)
O(1)–Ti(2)–O(3A)	144.2(2)	O(4)–Ti(3)–O(8)	104.0(2)	O(4)–Ti3–O(13A)	100.3(2)
O(8)–Ti3–O(13A)	102.9(2)	O(4)–Ti(3)–O(2)	94.6(3)	O(2)–Ti(3)–O(8)	89.4(2)
O(4)–Ti3–O(14A)	90.9(2)	O(8)–Ti3–O(14A)	159.8(2)	O14A)–Ti3–O13A)	87.3(2)
O(2)–Ti3–O(14A)	75.8(2)	O(12)–Ti(3)–O(8)	78.5(2)	O(12)–Ti3–O(13A)	77.3(2)
O(12)–Ti3–O(14A)	87.05(19)	O(2)–Ti(3)–O(12)	87.2(2)	Ti(3)–O(8) –Ti(2)	133.3(3)
Ti(3)–O(8)–Ti(1)	100.2(2)	Ti(1)–O(8)–Ti(2)	100.2(2)	Ti(1)–O12–Ti(2A)	133.9(3)
Ti(1)–O(12)–Ti(3)	99.5(2)	Ti(3)–O12–Ti(2A)	99.9(2)	Ti(1)–O13–Ti(3A)	134.0(3)
Ti(1)–O13–Ti(2)	101.6(2)	Ti(2)–O13–Ti(3A)	101.0(2)		

Table 3. Selected bond lengths [Å] and angles [°] for **5**

Bond lengths					
Ti(1)–O(13)	1.745(5)	Ti(1)–O(10)	1.813(4)	Ti(1)–O(5)	1.960(4)
Ti(1)–O(2)	2.054(4)	Ti(1)–O(11)	2.109(4)	Ti(1)–O(4)	2.198(4)
Ti(2)–O(12)	1.740(5)	Ti(2)–O(10)	1.809(4)	Ti(2)–O(7)	1.977(4)
Ti(2)–O(3)	2.008(4)	Ti(2)–O(9)	2.111(5)	Ti(2)–O(1)	2.192(5)
Bond angles					
O(13)–Ti(1)–O(10)	97.3(2)	O(13)–Ti(1)–O(5)	100.5(2)	O(5)–Ti(1)–O(10)	98.89(19)
O(13)–Ti(1)–O(2)	94.13(19)	O(2)–Ti(1)–O(10)	91.04(18)	O(13)–Ti(1)–O(11)	97.74(19)
O(11)–Ti(1)–O(5)	83.17(17)	O(11)–Ti(1)–O(2)	82.99(17)	O(4)–Ti(1)–O(10)	86.13(18)
O(5)–Ti(1)–O(4)	82.58(18)	O(2)–Ti(1)–O(4)	82.06(18)	O(11)–Ti(1)–O(4)	78.52(17)
O(12)–Ti(2)–O(7)	97.1(2)	O(10)–Ti(2)–O(7)	98.31(19)	O(12)–Ti(2)–O(3)	94.9(2)
O(10)–Ti(2)–O(3)	91.86(19)	O(12)–Ti(2)–O(9)	96.0(2)	O(9)–Ti(2)–O(7)	83.9(18)
O(3)–Ti(2)–O(9)	82.88(19)	O(10)–Ti(2)–O(1)	86.05(18)	O(1)–Ti(2)–O(7)	81.69(18)
O(3)–Ti(2)–O(1)	85.41(19)	O(9)–Ti(2)–O(1)	79.96(17)	Ti(2)–O(10)–Ti(1)	139.6(3)

Table 4. Preparation, analytical and spectroscopic data for the complexes

Reactants [g, mol]		Product yield [g, %]	Nature	Analysis (%) (calculated values in parentheses) Ti	O*i*Pr	HO*i*Pr in volatiles
$Ti(OiPr)_4$ + $CH_2ClCOOH$ (1.220, 4.29) (0.406, 4.29)	**1a**	$Ti(OiPr)_3(OOCCH_2Cl)$ (1.352, 98.9)	Light yellow solid	15.09 (15.04)	55.51 (55.55)	0.22 (0.25)
$Ti(OiPr)_4$ + $CHCl_2COOH$ (1.251, 4.40) (0.526, 4.40)	**1b**	$Ti(OiPr)_3(OOCCHCl_2)$ (1.541, 99.9)	White solid	13.59 (13.57)	50.10 (50.15)	0.26 (0.27)
$Ti(OiPr)_4$ + CCl_3COOH (1.119, 3.94) (0.644, 3.93)	**1c**	$Ti(OiPr)_3(OOCCCl_3)$ (1.518, 99.5)	Light yellow solid	12.38 (12.33)	45.67 (45.68)	0.25 (0.24)
$Ti(OiPr)_4$ + $2CH_2ClCOOH$ (0.919, 3.23) (0.611, 6.46)	**4a**	$Ti(OiPr)_2(OOCCH_2Cl)_2$ (1.404, 98.7)	White solid	13.59 (13.56)	33.90 (33.43)	0.37 (0.39)
$Ti(OiPr)_4$ +$2CHCl_2COOH$ (0.894, 3.14) (0.812, 6.29)	**4b**	$Ti(OiPr)_2(OOCCHCl_2)_2$ (1.318, 99.3)	Light yellow solid	11.41 (11.35)	27.95 (27.96)	0.34 (0.36)
$Ti(OiPr)_4$ + $2CCl_3COOH$ (0.911, 3.20) (1.049, 6.41)	**4c**	$Ti(OiPr)_2(OOCCCl_3)_2$ (1.575, 99.9)	White solid	9.90 (9.75)	24.01 (24.03)	0.37 (0.39)

Selected bond lengths and angles for **2**, **3** and **5** are given in Table 1, Table 2 and Table 3. The Ti–O*i*$Pr_{terminal}$ distances [**2** (av. 1.772 Å), **3** (av. 1.745 Å), **5** (av. 1.742 Å)] for the three complexes are in accordance with reported[14,17] values. The Ti–HO*i*Pr (Ti1–O13, Ti2–O9) distances (av. 2.110 Å) are, as expected, longer than the isopropoxy distances. The Ti–μ-O*i*Pr lengths (av. 1.997 Å), which are present only in **2**, are shorter than the terminal Ti–O*i*Pr lengths.[12] For **2** the Ti–μ_3-O distances (av. 1.920 Å) and for **5** the Ti–μ-O distances (av. 1.811 Å) are consistent with literature[13] values.

However, for **3** the Ti–μ_3-O distances (av. 1.885 Å) are somewhat shorter than values recently reported.[12]

For **2** the distances Ti1···Ti2 and Ti2···Ti3 (av. 3.066 Å) correspond to two octahedra sharing an edge[15] while for **3** the distances from upper to lower hexagonal rings (av. 2.176 Å) are consistent with those recently reported.[10] The center of the molecule **3** is empty, resulting in a hole.

The Ti–μ-OAc distances [**2** (av. 2.115 Å), **3** (av. 2.070 Å) and **5** (av. 2.113 Å)] are also in accordance with literature values while for **5** the Ti–OAc lengths (av. 1.968 Å) are shorter than the bridging carboxylate distances.

Conclusions

The reaction of $Ti(OiPr)_4$ with chloroacetic acids in excess toluene at room temperature prevents esterification, thereby giving simple substitution products. However the propensity of the metal atoms to achieve higher coordination numbers through oxo ligands is so strong that it can even be achieved through ether elimination reactions. In this way the formation of products **2** and **5** can be accounted for. The generation of **3** from **1b** on standing in toluene suggests that the extent of the ethereal loss is directly proportional to length of time in solution. In the process significant structural changes are observed. However, due to our limited findings, no conclusions regarding effects of increasing acidity and steric bulk of carboxylic acids on the structures could be drawn.

Experimental Section

All reactions were performed under a dry argon atmosphere, using standard Schlenk and glovebox techniques. Toluene and $CDCl_3$ were dried by standard procedures. Titanium isopropoxide was obtained from $TiCl_4$ (Aldrich) by the ammonia method[27] and purified by vacuum distillation. Mono-, di- and trichloroacetic acids were distilled before use. Infrared spectra were recorded on a JASCO FT-IR-5300 as Nujol mulls between NaCl plates. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with a JEOL-FX 90Q spectrometer with $SiMe_4$ as internal reference. Ti was determined as TiO_2 and isopropoxy analysis by the method of Bradley[24] et al.

Synthesis

General Method for the Complexes 1a–c, and 4a–c (Table 4): A solution of the acid in toluene (ca. 20 mL) was added dropwise with stirring to a solution of $Ti(OiPr)_4$ in toluene (ca. 25 mL) over 1/2 h at room temperature (ca. 25 °C). The reaction mixture (colorless) was stirred for six hours to give a light red solution. The volatiles were removed in vacuo to give a solid residue.

1a: ^1H NMR: δ = 1.26 (d), 1.35 (d, *gem*-Me_2 of O*i*Pr), 4.80 (sept), 5.30 (sept, CH of O*i*Pr), 4.00 (s, CH_2 of the acid, 18:3:2). – ^{13}C NMR: δ = 192.91 (CO of acid), 63.43, 64.45 (CH of O*i*Pr), 41.49 (CH_2Cl of acid), 23.62, 24.32 (*gem*-Me_2 of O*i*Pr). – IR: $\tilde{\nu}$ = 1580 (ν_{as} CO_2), 1460 (ν_s CO_2), 1120 (terminal O*i*Pr), 1010 (bridging O*i*Pr).

1b: ^1H NMR: δ = 1.40 (d, *gem*-Me_2 of O*i*Pr), 4.16, 5.00 (sept, CH of O*i*Pr), 6.08 (s, CH_2 of acid, 18:3:1). – ^{13}C NMR: δ = 191.97 (CO of acid), 67.43, 68.21 (CH of O*i*Pr), 55.49 ($CHCl_2$ of acid), 23.32, 24.35 (*gem*-Me_2 of O*i*Pr). – IR: $\tilde{\nu}$ = 1589 (ν_{as} CO_2), 1460 (ν_s CO_2), 1119 (terminal O*i*Pr), 1011 (bridging O*i*Pr).

1c: ^1H NMR: δ = 1.31 (d, *gem*-Me_2 of O*i*Pr), 4.10, 5.10 (sept, CH of O*i*Pr). – ^{13}C NMR: δ = 180.97 (CO of acid), 63.43, 65.10 (CH of O*i*Pr), 86.58, (CCl_3 of acid), 23.51, 24.21 (*gem*-Me_2 of O*i*Pr). – IR: $\tilde{\nu}$ = 1658 (ν_{as} CO_2), 1460 (ν_s CO_2), 1112 (terminal O*i*Pr), 1009 (bridging O*i*Pr).

4a: ^1H NMR: δ = 1.15 (d, *gem*-Me_2 of O*i*Pr), 4.80 (sept, CH of O*i*Pr), 4.00 (CH_2 of acid) (6:1:2). – ^{13}C NMR: δ = 189.97 (CO of acid), 63.46 (CH of O*i*Pr), 43.58 (CH_2Cl of acid), 23.59 (*gem*-Me_2 of O*i*Pr). – IR: $\tilde{\nu}$ = 1769, 1654 (ν_{as} CO_2), 1378, 1460 (ν_s CO_2), 1112 (terminal O*i*Pr), 1009 (bridging O*i*Pr).

4b: ^{1}H NMR: δ = 1.40 (d, *gem*-Me_2 of O*i*Pr), 5.02 (sept, CH of O*i*Pr), 6.00 (s, CH_2 of acid) (6:1:1). – ^{13}C NMR: δ = 190.57 (CO of acid), 67.79 (CH of O*i*Pr), 57.48 ($CHCl_2$ of acid), 24.35 (*gem*-Me_2 of O*i*Pr). – IR: $\tilde{\nu}$ = 1777, 1589 (ν_{as} CO_2), 1380, 1460 (ν_s CO_2), 1110 (terminal O*i*Pr), 1010 (bridging O*i*Pr).

4c: ^{1}H NMR: δ = 1.39 (d, *gem*-Me_2 of O*i*Pr), 4.85 (sept, CH of O*i*Pr). – ^{13}C NMR: δ = 192.97, (CO of acid), 70.26 (CH of O*i*Pr), 87.81 (CCl_3 of acid), 23.29 (*gem*-Me_2 of O*i*Pr).

Ti(μ$_3$-O)(μ-O*i*Pr)$_2$(O*i*Pr)$_5$(μ-O$_2$C–CCl$_3$)$_3$ (2): A solution of Cl_3C–C(O)OH (1.295 g, 7.92 mmol) in toluene (ca. 20 mL) was added dropwise with stirring to a solution of Ti(O*i*Pr)$_4$ (2.245 g, 7.91 mmol) in toluene (ca. 25 mL) over 30 min at room temperature (30 °C). The reaction mixture (colorless) was stirred for 6 h to give a dark yellow solution. It was concentrated to half of its volume and kept at –15 °C. After 2 d, a white crystalline product (1.932 g of **2**, 65%) was obtained. – $C_{27}H_{49}Cl_9O_{14}Ti_3$ (1060.4): calcd. Ti 13.55, O*i*Pr 39.01; found Ti 13.91, O*i*Pr 38.91. – ^{1}H NMR (25 °C): δ = 1.31 (d, CH_3 of O*i*Pr), 4.11, 5.01 (sept, CH of O*i*Pr). – ^{13}C{^{1}H} NMR: δ = 180.99 (CO of acid), 90.85 (CCl_3 of acid), 63.92 (CH of O*i*Pr), 23.51, 24.21 (CH_3 of O*i*Pr). – FT-IR (Nujol): $\tilde{\nu}$ = 1658 (ν_{as} CO_2), 1460 (ν_s CO_2), 1112 (terminal O*i*Pr), 1009 (bridging O*i*Pr) cm^{-1}. – Single crystals were grown in toluene at –15° C.

Ti(O*i*Pr)$_3$(O$_2$C–CHCl$_2$ (1b) and Ti$_6$(μ$_3$-O)$_6$(O*i*Pr)$_6$(μ-O$_2$C–CHCl$_2$)$_6$ (3): White crystalline **1b** (1.110 g, 65%) was obtained by concentrating the reaction mixture of Ti(O*i*Pr)$_4$ (1.158 g, 4.07 mmol) and dichloroacetic acid (0.526 g, 4.07 mmol) in toluene by the general method. – $C_{11}H_{22}Cl_2O_5Ti_2$ (353.1): calcd. Ti 13.56, O*i*Pr 50.20; found Ti 13.89, O*i*Pr 50.01. – ^{1}H NMR (25 °C): δ = 1.42 (m, CH_3 of O*i*Pr), 4.16, 5.01 (sept, CH of O*i*Pr), 6.08 (s, CH_2 of acid). – ^{13}C{^{1}H} NMR: δ = 192.91 (CO of acid), 63.43 (CH of O*i*Pr), 55.51 ($CHCl_2$ of acid), 23.91, 24.38 (CH_3 of O*i*Pr). – FT-IR (Nujol): $\tilde{\nu}$ = 1589 (ν_{as} CO_2), 1458 (ν_s CO_2), 1120 (terminal O*i*Pr), 1006 (bridging O*i*Pr) cm^{-1}. – The mother liquor upon standing for 5 days at –15 °C gave a small batch of crystals which was shown to be **3** by X-ray crystallography.

Ti$_2$(μ-O)(HO*i*Pr)$_2$(O*i*Pr)$_2$(O$_2$C–CCl$_3$)$_2$(μ-O$_2$C–CCl$_3$)$_2$ (5): A reaction mixture comprising Ti(O*i*Pr)$_4$ (1.362 g, 4.80 mmol) and trichloroacetic acid (1.57 g, 9.60 mmol) in toluene was stirred for six hours. It was then concentrated to half of its volume and kept at –15 °C. After 2 d, a white crystalline product was obtained. – Yield: 1.651 g of **5** (72 %). – $C_{20}H_{30}Cl_{12}O_{13}Ti_2$ (999.6): calcd. Ti 9.56, O*i*Pr 23.64; found Ti 9.57, O*i*Pr 23.91. – ^{1}H NMR (25 °C): δ = 1.39 (d, CH_3 of O*i*Pr), 4.85 (sept, CH of O*i*Pr). – ^{13}C{^{1}H} NMR: δ = 192.31, 181.37 (CO of acid), 87.91 (CCl_3 of acid), 70.26 (CH of O*i*Pr), 23.29 (CH_3 of O*i*Pr). – FT-IR (Nujol): $\tilde{\nu}$ = 1787 (ν_{as} CO_2), 1378(ν_s CO_2), 1649 (ν_{as} CO_2), 1460 (ν_s CO_2) 1090 (terminal O*i*Pr), 1012 (bridging O*i*Pr) cm^{-1}. – Single crystals were obtained from toluene.

Crystallography

The structure determinations were performed using a Siemens P4 diffractometer equipped with a CCD area detector. Mo-K_α radiation (λ = 0.71013 Å) was used and the samples cooled to 193 K (**2**, **3**) and 183 K (**4**) respectively. Data reduction was achieved with the program SAINT and absorptions by SADABS (**2**, **3**) and semi-empirical methods (**4**). Computer calculations were carried out using the SHELXS-97 (Sheldrick, 1997) program package and the structures were solved by direct methods. Refinements were performed by SHELXL-97 (Sheldrick, 1997) using anisotropic thermal parameters for the non hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined with a riding model. The crystallographic data for **2**, **3** and **5** are given in Table 5. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138443 (**2**), -138445 (**5**), -138444 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 5. Data collection for (**2**), (**3**), (**5**)

Compound	**2**	**3**	**5**
Empirical formula	$C_{27}H_{49}Cl_9O_{14}Ti_3$	$C_{30}H_{48}Cl_{12}O_{24}Ti_6$	$C_{20}H_{30}Cl_{12}O_{13}Ti_2$
Molecular mass	1060.4	1505.4	999.6
Crystal size [mm]	0.40 × 0.20 × 0.18	0.20 × 0.24 × 0.33	0.2 × 0.4 × 0.45
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	*Pbca*	*C*2/*c*	*P*2(1)2(1)(1)
a [Å]	21.990(6)	14.7192(2)	10.645(5)
b [Å]	17.628(4)	21.7216(5)	18.146(7)
c [Å]	24.323(7)	19.7550(4)	20.782(7)
α [°]	90	90	90
β [°]	90	107.230(1)	90
γ [°]	90	90	90
V [Å^3]	9429(4)	6032.7(2)	4014(3)
Z	8	4	4
ρ(calcd.) [Mg/m^3]	1.493	1.658	1.651
μ [mm^{-1}]	1.059	1.356	1.248
F(000)	4336	3024	2008
Index range	$-28 \le h \le 28$	$-15 \le h \le 15$	$-13 \le h \le 13$
	$-20 \le k \le 19$	$-23 \le k \le 23$	$-23 \le k \le 23$
	$-31 \le l \le 31$	$-21 \le l \le 21$	$-22 \le l \le 27$
2θ [°]	54.98	46.52	58.58
Temp [K]	193	193	183
Refl. collected	49114	12136	23244
Refl. unique	9668	4113	8058
Refl. observed (4σ)	5296 (2σ)	2612	6029
R(int.)	0.0574	0.0728	0.0598
No. of variables	520	320	424
Weighting scheme[a] *x*/*y*	0.0865/0.000	0.11074/0.000	0.0468/8.2523
GOOF	0.981	1.046	1.144
Final *R*(4σ)	0.0531	0.0759	0.0701
Final *wR*2	0.1357	0.1904	0.1342
Largest. resid. peak [e/Å^3]	0.960	0.909	0.833

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = F_o^2 + 2F_c^2)/3$.

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