

Reactions of Titanium Tetrachloride with Carboxylic Acids. Crystal and Molecular Structure of the Dinuclear Titanium Oxo Compound $[\{\text{TiCl}_2(\text{O}_2\text{CBu}^t)(\text{Bu}^t\text{CO}_2\text{H})\}_2\text{O}]^\dagger$

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Reaction of TiCl_4 (1 mol) with 2,2-dimethylpropanoic acid (2.5 mol) at room temperature yields the dinuclear oxo-bridged species $[\{\text{TiCl}_2(\text{O}_2\text{CBu}^t)(\text{Bu}^t\text{CO}_2\text{H})\}_2\text{O}]$ **1** which has been fully characterised by an X-ray crystal structure analysis. The two metal atoms are bridged by the oxo and two carboxylate groups, which with a co-ordinated acid molecule and two chlorine atoms on each titanium gives a slightly distorted octahedral environment around each metal centre. At 40 °C compound **1** decomposes to the trinuclear species $[\text{Ti}_3\text{Cl}_3(\text{O}_2\text{CBu}^t)_5\text{O}_2]$, and at higher temperatures (100–120 °C) to another dinuclear oxo derivative $[\{\text{TiCl}(\text{O}_2\text{CBu}^t)_2\}_2\text{O}]$ which can also be obtained from the action of 2,2-dimethylpropanoic anhydride on TiCl_4 in refluxing toluene. Acetic acid produces a similar, but less soluble, species to **1**. Aromatic acids react differently; *para*-substituted aryl acids generally yield trinuclear compounds $[\text{Ti}_3\text{Cl}_3(\text{O}_2\text{CC}_6\text{H}_4\text{X}-p)_5\text{O}_2]$ (X = Cl or Br) although the *p*-Bu^t acid forms $[\{\text{TiCl}(\text{O}_2\text{CC}_6\text{H}_4\text{Bu}^t-p)_2\}_2\text{O}]$. In contrast the *ortho*- and *meta*-substituted acids react to give either $[\text{Ti}_3\text{Cl}_4(\text{O}_2\text{CR})_4\text{O}_2]$ (R = C₆H₄Cl-*o* or -*m*) or $[\text{Ti}_4\text{Cl}_5(\text{O}_2\text{CR})_7\text{O}_2]$ (R = C₆H₄Me-*o*) derivatives.

Several recent studies have reported the preparation of titanium oxo derivatives,¹ but many of the species isolated so far contain the cyclopentadienyl group ($\eta\text{-C}_5\text{H}_5$ or $\eta\text{-C}_5\text{Me}_5$),² and most have been obtained by the hydrolysis of metal chloro compounds which often leads to the removal of all the functional M–Cl centres in the starting material. We have previously found that titanium tetrachloride reacts with carboxylic acids RCO_2H (R = alkyl or aryl) using a 1:1 mole ratio to give $[\text{Ti}_2\text{Cl}_7(\text{O}_2\text{CR})(\text{RCO}_2\text{H})]$ at 0–25 °C, and $[\text{TiCl}_3(\text{O}_2\text{CR})]$ at 25–60 °C.³ When a 1:2.5 mole ratio (Ti:acid) is used then above 100 °C metal oxo cluster compounds such as $[\text{Ti}_4\text{Cl}_6(\text{O}_2\text{CPh})_6\text{O}_2]$ ^{4a} and $[\text{Ti}_3\text{Cl}_3(\text{O}_2\text{CC}_6\text{H}_4\text{Me}-p)_5\text{O}_2]$ ^{4b} are formed. These oxo species arise from the aryl acids by oxygen abstraction from the acid, with the concomitant generation of the acid chloride RCOCl . The overall reaction thus affords a clean non-hydrolytic route to titanium oxo derivatives which still retain reactive Ti–Cl bonds.

The above diverse observations have prompted us to examine more closely these reactions using a wider range of acids (alkyl and aryl), with different mole ratios of reactants over the temperature range 25–120 °C. This paper reports the results of such a study, and the crystal structure of the new oxo-bridged intermediate $[\{\text{TiCl}_2(\text{O}_2\text{CBu}^t)(\text{Bu}^t\text{CO}_2\text{H})\}_2\text{O}]$ **1**. A preliminary report of some related compounds has been published previously.⁵

Results and Discussion

The reactions of TiCl_4 with both the alkyl (R = Me or Bu^t) and aryl (R = C₆H₄Prⁱ-*p*, C₆H₄Br-*p*, C₆H₄Cl-*o*, -*m* or -*p*, or C₆H₄Me-*o*) acids were investigated for comparison. Some surprising variations occur depending on both the acid used, and the reaction conditions. Initial experiments were made using a 1:2 (instead of a 1:1) mole ratio (Ti:acid), although subsequently the ratio was modified to 1:2.5 for reasons

outlined below. Thus the dropwise addition of TiCl_4 (1 mol) to a solution of Bu^tCO₂H (2 mol) in light petroleum (b.p. 60–80 °C) at ambient temperature produces a yellow solution initially with the evolution of HCl. After stirring for a short time (1–2 h) a colourless air-reactive crystalline material begins to deposit, and can eventually be isolated in 60–70% yield (based on Ti). The IR spectrum of the solid shows bands at 1525 and 1418 cm⁻¹ from co-ordinated carboxylate groups, with the Δ value [$\Delta = \nu(\text{CO}_2^-)_{\text{asym}} - \nu(\text{CO}_2^-)_{\text{sym}}$] of 107 cm⁻¹ indicating that the carboxylate groups are probably bridging.⁶ In addition a further strong band at 1650 cm⁻¹ [*cf.* a $\nu(\text{C}=\text{O})$ band at 1705 cm⁻¹ in the free acid] together with a weaker broad band at 3200 cm⁻¹ suggests the presence of co-ordinated carboxylic acid ligands, and this is confirmed by the X-ray study given below. Further bands at 405 and 390 cm⁻¹ indicated that the product retains Ti–Cl bonds, and microanalytical data are consistent with the product being the oxo species $[\{\text{TiCl}_2(\text{O}_2\text{CBu}^t)(\text{Bu}^t\text{CO}_2\text{H})\}_2\text{O}]$ **1**.

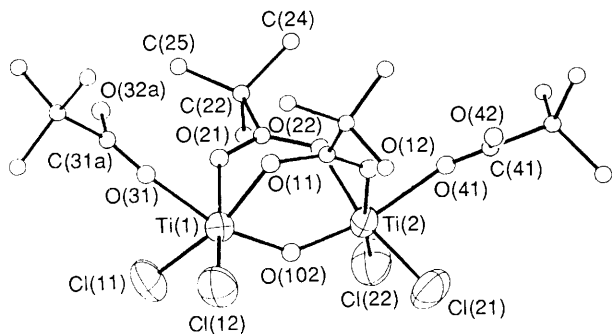
The presence of complexed acid molecules is also indicated by the ¹H NMR spectrum which shows a broad resonance (2 H) at δ 11.3 with a complex multiplet (36 H) between δ 1.20 and 1.36 from the Bu^t protons. The multiplet contains at least nine resonances instead of the one (or two) expected, and is reminiscent of the complex multiplet observed for $[\text{TiCl}_3(\text{O}_2\text{CBu}^t)]^3$. We have suggested tentatively for the latter that this is due to the presence of different conformers being present in the solution, although in both cases we have no convincing explanation for the complexity of this particular resonance. In contrast the ¹³C NMR spectrum of compound **1** is straightforward showing two sets of resonances from the co-ordinated carboxylate and acid moieties at δ 26 and 27, and δ 39 and 40 from the methyl groups and the single carbon atom of the Bu^t groups respectively. The resonance from both the carboxylate carbons occurs at δ 189.5.

The crystal structure of complex **1** (Fig. 1) reveals the presence of the characteristic μ -oxo di- μ -carboxylate dinuclear fragment $\text{M}(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2\text{M}$ which has already been found for a number of other metals.⁷ The titanium centres show a near octahedral co-ordination with the remaining three non-

[†] Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

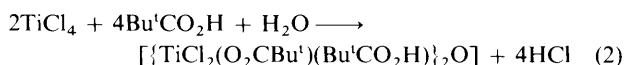
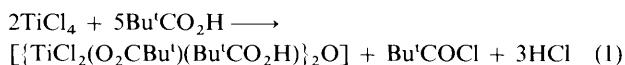
Table 1 Selected bond distances (Å) and angles (°) in $[\{\text{TiCl}_2(\text{O}_2\text{CBu}^*)(\text{Bu}^*\text{CO}_2\text{H})\}_2\text{O}]$ **1** with estimated standard deviations (e.s.d.s) in parentheses

Ti(1)–Cl(12)	2.259(8)	Ti(1)–O(31)	2.085(17)	Ti(2)–O(102)	1.766(15)
Ti(1)–Cl(11)	2.260(8)	Ti(1)–O(21)	2.060(15)	Ti(2)–O(22)	1.991(15)
Ti(2)–Cl(21)	2.275(8)	Ti(1)–O(11)	2.055(14)	Ti(2)–O(12)	2.090(16)
Ti(2)–Cl(22)	2.255(9)	Ti(1)–O(102)	1.772(15)	Ti(2)–O(41)	2.138(18)
Cl(11)–Ti(1)–Cl(12)	97.8(3)	O(11)–Ti(1)–O(21)	83.3(6)	O(11)–C(11)–C(12)	119.4(21)
Cl(11)–Ti(1)–O(102)	100.1(5)	Cl(12)–Ti(1)–O(21)	169.0(5)	Ti(1)–O(21)–C(21)	132.9(15)
Cl(11)–Ti(1)–O(31)	89.2(6)	Cl(12)–Ti(1)–O(11)	87.9(5)	O(21)–C(21)–O(22)	122.1(23)
O(21)–Ti(1)–O(31)	81.5(6)	Ti(1)–O(102)–Ti(2)	138.3(9)	O(11)–C(11)–O(12)	121.6(21)

**Fig. 1** View of $[\{\text{TiCl}_2(\text{O}_2\text{CBu}^*)(\text{Bu}^*\text{CO}_2\text{H})\}_2\text{O}]$ **1** showing the principal atomic numbering. Only the major components of the disordered co-ordinated acid molecules are shown

bridging positions on each metal being occupied by two chlorine atoms and an acid molecule which is *trans* to the μ -oxo group and co-ordinated through the carbonyl group. We have reported the related compounds $[\text{Ti}_2(\mu\text{-O})(\mu\text{-O}_2\text{CPh})_2\text{Cl}_4 \cdot 2\text{L}]$ ($\text{L} = \text{MeCO}_2\text{Et}$ or tetrahydrofuran) which were obtained by hydrolysis reactions,⁵ and these also have the ligand *trans* to the bridging oxygen atom, but **1** now demonstrates that in the absence of other donors the sixth positions of the titanium octahedra can be occupied by donor acid molecules. This particular feature is noteworthy since it is known that TiCl_4 reacts rapidly with carboxylic acids to evolve HCl and form $[\text{TiCl}_3(\text{O}_2\text{CR})]$. Compound **1** therefore provides a further unusual example, in addition to the known $[\text{Ti}_2\text{Cl}_7(\text{O}_2\text{CR})(\text{RCO}_2\text{H})]$,³ of a titanium species containing both a reactive Ti–Cl bond and a co-ordinated acid molecule at the same metal centre. Selected bond distances and angles for compound **1** are given in Table 1. Because of disorder the dimensions are of comparatively low accuracy, but are typical for these dinuclear species. The Ti–O distances are graduated as Ti– μ -O 1.77 Å < Ti– μ -O (acid anion) 1.99–2.09 Å < Ti–O (neutral acid ligand) 2.09–2.14 Å, and the Ti–Cl distances (2.25–2.27 Å) are within the expected values.

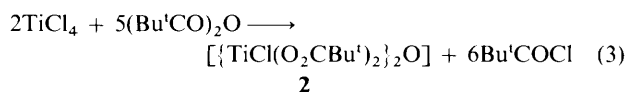
In the present case it appears that compound **1** is formed by a reaction involving oxygen abstraction, similar to that postulated earlier for the oxo clusters, e.g. $[\text{Ti}_4\text{Cl}_6(\text{O}_2\text{CPh})_6\text{O}_2]$,^{4a} even though **1** is obtained at room temperature, and the oxo clusters require 100 °C. Such a process [equation (1)] can be distinguished from a pathway involving hydrolysis [equation (2)] by the appearance of the acid chloride which we have



identified in the mother-liquor from its IR spectrum. Further support for reaction (1) rather than (2) comes from the rigorous precautions taken to exclude all traces of moisture from the

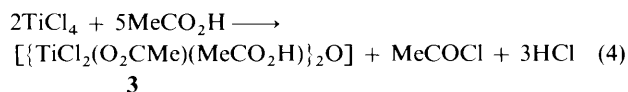
reaction mixture, and from the fact that optimum yields of **1** (~80% based on Ti after work-up) are obtained using a 1:2.5 (Ti:acid) rather than a 1:2 mole ratio of reactants. It has been suggested that the product of this reaction is the bis-(carboxylate) $[\text{TiCl}_2(\text{O}_2\text{CBu}^*)_2]$.⁸ The quoted IR spectrum is identical to that of the present oxo compound, and it would appear therefore that only the oxo derivative is obtained from the reaction at room temperature.

Different products are obtained from the reaction at higher temperatures. Thus when the initial reactants, or even compound **1** itself, are heated in hexane at 40 °C another colourless solid, which is still hydrolysed slowly in air but is more soluble in both hexane and halogenated solvents, is obtained. The IR spectrum of this new solid shows bands at 1558, 1522, 1427 and 1420 cm^{-1} associated with bridging carboxylate groups, but has lost the bands due to the co-ordinated acid present in **1**. The material is best formulated as $[\text{Ti}_3\text{Cl}_3(\text{O}_2\text{CBu}^*)_5\text{O}_2]$, an alkyl acid analogue of other compounds obtained previously using *para*-substituted aryl acids.^{4b} We have no further structural data on this 2,2-dimethylpropanoate derivative since despite repeated attempts we have been unable to obtain crystals suitable for X-ray analysis. At still higher temperatures using a 1:2.5 mole ratio (Ti:acid) mixture in refluxing light petroleum (b.p. 100–120 °C) the IR spectrum of the product is more complex and suggests that it is a mixture of **1** with other unidentified oxo carboxylate species. On prolonged reflux a less soluble product is obtained which from microanalytical data is best formulated as $[\{\text{TiCl}(\text{O}_2\text{-CBu}^*)_2\}_2\text{O}]$ **2**, and an identical solid is formed in the reaction with 2,2-dimethylpropanoic anhydride in refluxing toluene [equation (3)]. We have again confirmed the presence of 2,2-



dimethylpropanoyl chloride in the mother-liquor, and we assume that, in view of the very limited solubility, the product is polymeric containing both bridging oxo and carboxylate groups.

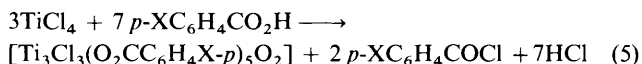
With acetic acid using a $\text{TiCl}_4 : \text{MeCO}_2\text{H}$ mole ratio of either 1:2 or 1:2.5 in light petroleum (b.p. 60–80 °C) at room temperature, or even in refluxing toluene solution, the product has a similar empirical formula to that of **1**. After evolution of HCl a colourless solid precipitates from solution, with acetyl chloride being detected in the mother-liquor from its IR spectrum [equation (4)]. The air-reactive oxo acetate **3** shows



very limited solubility in a range of organic solvents, and the compound probably contains bridging carboxylate groups. The presence of such groups is indicated from the IR spectrum with absorptions at 1540 and 1430 cm^{-1} ($\Delta = 110 \text{ cm}^{-1}$), with bands from the co-ordinated acid occurring at 3200 (hydroxyl)

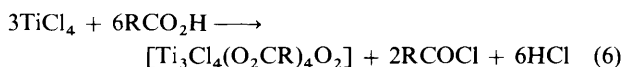
and 1655 cm⁻¹ (carbonyl). A band at 733 cm⁻¹ may be assigned to the Ti–O–Ti group.

Reactions involving the aryl acids are of interest for comparative purposes. We have previously reported briefly that with a 1:2 (Ti:acid) mole ratio at 100–150 °C, benzoic acid yields [Ti₄Cl₆(O₂CPh)₆O₂]^{4a}, while some *para*-substituted acids form [Ti₃Cl₃(O₂CC₆H₄X-*p*)₅O₂] (X = Me, Et, F or I).^{4b} We have therefore extended the range of aryl acids in order to establish whether the pattern of reactivity observed is general. From our results benzoic acid is unique in forming the tetranuclear species. Using a range of *para*-substituted acids, with a mole ratio between 1:2.0 and 1:2.5, reaction at 100–120 °C yields the trinuclear oxo compounds, often in high yields (essentially quantitative for the C₆H₄Me-*p* derivative) according to equation (5) (X = Me, Et, F, Cl, Br or I).

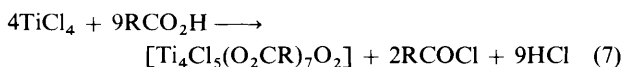


We have confirmed the presence of the acyl chloride in the solution from its IR spectrum. From the similarities in the IR and NMR spectra of these compounds (see Experimental section) to those already reported for the structurally characterised [Ti₃Cl₃(O₂CC₆H₄Me-*p*)₅O₂]^{4b} it seems likely that they all possess closely related structures. It is noteworthy that we have not been able to obtain a pure sample of the trinuclear compound in the case of the *p*-Prⁱ acid, and it is probable that this solid is a mixture especially since the *p*-Bu^t derivative affords a dinuclear [{TiCl(O₂CC₆H₄Bu^t-*p*)₂O}] instead of a trinuclear derivative. Microanalytical and other data not reported previously are given in the Experimental section.

Significant changes in the products occur when the substitution on the phenyl ring is in the *ortho* or *meta* position. For example, when TiCl₄ and *o*- (or *m*-)ClC₆H₄CO₂H are mixed in a 1:2.5 mole ratio and refluxed in light petroleum at 100–120 °C, sparingly soluble air-reactive yellow solids, which analysed as [Ti₃Cl₄(O₂CR)₄O₂], are produced in ~50% yield. Since the acyl chloride is produced as a by-product together with HCl a possible reaction is as shown in equation (6) (R = *o*-



or *m*-ClC₆H₄). Both solids show similar IR spectra which indicate the presence of bridging (or chelating) carboxylate groups, Ti–O–Ti units and terminal Ti–Cl bonds (see Experimental section). When *o*-MeC₆H₄CO₂H is used in the reaction, a sparingly soluble yellow solid product is isolated in essentially quantitative yield (based on Ti). It is empirically formulated as a tetranuclear oxo cluster [Ti₄Cl₅(O₂CC₆H₄Me-*o*)₇O₂]. In view of the lack of other titanium-containing products the reaction shown in equation (7) seems most likely. The IR



spectrum again indicates the presence of bridging carboxylate groups together with Ti–O and Ti–Cl bonds, but unlike the soluble product [Ti₄Cl₆(O₂CPh)₆O₂] with benzoic acid, the insolubility of the present compound has prevented a more complete characterisation.

In conclusion, the above studies demonstrate that a range of functional metal oxo compounds can be conveniently obtained in reasonable yield by treating a metal halide with a carboxylic acid under controlled conditions. This procedure offers an alternative method for preparing such species complementing the hydrolytic and other routes which are currently well established. We are continuing to investigate these oxo abstraction processes in order to understand more fully the relationships between the various oxo derivatives.

Experimental

Infrared spectra (4000–200 cm⁻¹) were recorded from Nujol mulls using CsI plates and either a Perkin-Elmer 1720X FT-IR or 580B spectrophotometer. Proton and ¹³C NMR spectra were run on a Bruker Associates ACF 250 instrument using CDCl₃ solutions with shifts referenced to SiMe₄ (δ 0). Microanalyses were carried out by Butterworth Laboratories, Teddington, or Medac, Brunel University, and titanium was determined using a Pye-Unicam SP6-250 spectrometer and a titanium(IV) peroxo species absorbing at 410 nm. Chloride was estimated with silver nitrate by the Volhard method. The air-sensitive compounds were handled using Schlenk apparatus or in a glove-box under dry nitrogen. All solvents were dried and distilled from calcium hydride or sodium diphenyl ketyl, titanium tetrachloride of reagent grade (BDH) was used without further purification and the carboxylic acids were recrystallised from CH₂Cl₂ or distilled from P₂O₅ or the acid anhydride prior to use. The preparations of the various carboxylates are described below; in all cases rigid precautions were taken to exclude air and moisture from the reaction mixtures and products.

[{TiCl₂(O₂CBu^t)(Bu^tCO₂H)}₂O] **1**.—The compound TiCl₄ (1.1 cm³, 10 mmol) was added dropwise to a stirred solution of 2,2-dimethylpropanoic acid (2.55 g, 25 mmol) in light petroleum (b.p. 60–80 °C, 40 cm³) at room temperature. The resulting yellow solution was stirred for 5 h, within which time a white precipitate was produced. The solid was isolated from the reaction liquor by filtration, washed with light petroleum (3 × 20 cm³) and dried by pumping under vacuum for 5 h. The solid was recrystallised from dichloromethane layered with light petroleum to give colourless plates suitable for X-ray analysis. Yield 2.29 g, 69% (Found: C, 36.40; H, 6.05; Ti, 14.3. C₂₀H₃₈Cl₄O₉Ti₂ requires C, 36.40; H, 5.80; Ti, 14.50%). The ¹H NMR spectrum (CDCl₃) showed resonances at δ 11.3 (2 H) and 1.36–1.20 (36 H, complex multiplet from Bu^t). Major IR bands at 3200 (br)[v(OH)], 1650 [v(O=C)_{coord acid}], 1525 [v(O₂C)_{asym}], 1485, 1418 [v(O₂C)_{sym}], 1281, 1224, 1205, 733 (br)[v(Ti–O–Ti)], 611, 540, 451, 405, 390, 375 and 330 cm⁻¹.

[Ti₃Cl₃(O₂CBu^t)₅O₂].—A suspension of compound **1** (2.0 g, 3.0 mmol) in hexane (40 cm³) was heated gently at 40 °C for 30 min. Some solvent was removed and the precipitate was isolated by filtration, washed with light petroleum (3 × 20 cm³) and dried by pumping under vacuum for 4 h. Yield 1.11 g, 71% (Found: C, 39.60; H, 5.95; Ti, 18.75. C₂₅H₄₅Cl₃O₁₂Ti₃ requires C, 38.10; H, 5.70; Ti, 18.25%). The ¹H NMR spectrum (CDCl₃) showed three resonances at δ 1.28 (18 H), 1.25 (18 H) and 1.20 (9 H). Major IR bands at 1558 [v(O₂C)_{asym}], 1522 [v(O₂C)_{asym}], 1427 [v(O₂C)_{sym}], 1420 [v(O₂C)_{sym}], 1224, 785, 716, 671 [v(Ti–O–Ti)], 611, 490, 375 (sh) and 350 cm⁻¹.

[{TiCl(O₂CBu^t)₂O]}₂O] **2**.—The compound TiCl₄ (1.1 cm³, 10 mmol) was added to a stirred solution of 2,2-dimethylpropanoic anhydride (5.1 cm³, 25 mmol) in toluene or light petroleum (b.p. 100–120 °C, 50 cm³) at room temperature. The resulting yellow solution was refluxed for 3 h within which time a white precipitate was produced. When cool, the solid was isolated from the reaction liquor by filtration, washed with light petroleum (b.p. 60–80 °C, 3 × 20 cm³) and dried by pumping under vacuum for 5 h. Yield 2.61 g, 88.7% (Found: C, 41.20; H, 6.15; Ti, 16.00. C₂₀H₃₆Cl₂O₉Ti₂ requires C, 40.90; H, 6.20; Ti, 16.30%). Major IR bands at 1590 [v(O₂C)_{asym}], 1550 [v(O₂C)_{asym}], 1510 [v(O₂C)_{sym}], 1413 [v(O₂C)_{sym}], 1225, 720 [v(Ti–O–Ti)] 603, 560, 461, 410, 390 and 375 cm⁻¹. The product was too insoluble for any NMR spectra to be obtained.

[{TiCl₂(O₂CMe)(MeCO₂H)}₂O] **3**.—The compound TiCl₄ (1.1 cm³, 10 mmol) was added dropwise to a stirred solution of acetic acid (1.09 cm³, 25 mmol) in toluene (40 cm³) at room temperature. From the resulting red solution a yellow

precipitate formed within a few minutes. The solid was isolated from the reaction liquor by filtration, washed with light petroleum (b.p. 60–80 °C, 3 × 20 cm³) and dried by pumping under vacuum for 5 h. Yield 2.15 g, 87% (Found: C, 19.00; H, 2.95; Ti, 19.20. C₈H₁₄Cl₄O₉Ti₂ requires C, 19.55; H, 2.85; Ti, 19.50%). The ¹H NMR spectrum (CD₃CN solvent) showed resonances at δ 8.8 and 2.2–1.93 (overlap with residual protons from CD₃CN). Major IR bands at 3200 (br)[v(OH)], 1655 [v(O=C)_{coord acid}], 1540 [v(O₂C)_{asym}], 1430 [v(O₂C)_{sym}], 1370, 1244, 1045, 1027, 733 (br)[v(Ti–O–Ti)], 650, 600, 560, 485, 410, 380 and 350 cm⁻¹.

Derivatives using Aryl Acids.—Two preparative routes were used, one without solvent and the other more usual route involving refluxing in light petroleum (b.p. 100–120 °C).

[{TiCl(O₂CC₆H₄Bu^t-*p*)₂]₂O}. The compound TiCl₄ (1.0 cm³, 8.99 mmol) was added to *p*-Bu^tC₆H₄CO₂H (3.2 g, 18 mmol) in the absence of solvent, and the mixture shaken. A brisk effervescence of HCl occurred and a fine yellow powder was produced. This powder was then heated to 150 °C *in vacuo* in a Schlenk tube fitted with a water-cooled cold finger, and was subsequently recrystallised from dichloromethane–hexane. Yield of product 10% based on Ti (Found: C, 59.25; H, 5.85; Cl, 7.95; Ti, 10.75. C₄₄H₅₂O₉Cl₂Ti₂ requires C, 58.15; H, 5.80; Cl, 7.25; Ti, 10.60%). Proton NMR: δ 8.30 and 7.75 (multiplets, each 4 H from C₆H₄ protons), 1.5 (singlet, 18 H, Bu^t). Major IR bands at 1610, 1590, 1550 [v(O₂C)_{asym}], 1510, 1420 [v(O₂C)_{sym}], 1200, 1020, 890, 860, 790 [v(Ti–O–Ti)], 720, 680, 600, 510, 420 and 360 cm⁻¹.

[Ti₃Cl₃(O₂CC₆H₄X-*p*)₅O₂]. A typical procedure for X = Cl is as follows. The compound *p*-ClC₆H₄CO₂H (5.85 g, 37.4 mmol) was stirred in light petroleum (b.p. 100–120 °C, 60 cm³) at 0 °C, and TiCl₄ (1.64 cm³, 14.9 mmol) added by syringe. After warming slowly to room temperature the mixture was heated to reflux for 4 h. The initial orange precipitate dissolved and a yellow solid was slowly precipitated. After cooling and filtration, the yellow solid was washed with hexane (2 × 20 cm³) and dried *in vacuo* for 2 h. Yield 3.15 g, 60% (Found: C, 39.80; H, 1.90; Ti, 13.45. C₃₅H₂₀Cl₈O₁₂Ti₃ requires C, 39.70; H, 1.90; Ti, 13.55%). Proton NMR: δ 8.22 (4 H), 8.10 (4 H), 7.90 (2 H), 7.55 (4 H), 7.42 (4 H) and 7.35 (2 H). Major IR bands at 1600, 1540 [v(O₂C)_{asym}], 1410 [v(O₂C)_{sym}], 1170, 1150, 1090, 1010, 850, 780 [v(Ti–O–Ti)], 720, 670 and 360 [v(Ti–Cl)] cm⁻¹.

The other [Ti₃Cl₃(O₂CC₆H₄X-*p*)₅O₂] derivatives were prepared by the same method, the data being as follows. X = Et, yield 31% (Found: C, 52.80; H, 4.2. C₄₅H₄₅Cl₃O₁₂Ti₃ requires C, 52.60; H, 4.4%). IR bands at 1605, 1580, 1510, 1180, 780, 720, 610, 530, 490 and 370 cm⁻¹. Proton NMR: δ 8.07 (6 H), 7.85 (2 H), 7.40–7.10 (12 H), 2.90–2.55 (10 H), 1.85–1.10 (15 H). X = Br, yield 35% (Found: C, 31.60; H, 1.40; Ti, 11.11. C₃₅H₂₀Br₅Cl₃O₁₂Ti₃ requires C, 32.80; H, 1.55; Ti, 11.20%). IR bands at 1590, 1540, 1380, 1180, 1010, 770, 720, 550 and 430 cm⁻¹. Proton NMR: δ 8.25 (4 H), 8.00 (4 H), 7.80 (2 H), 7.75 (4 H), 7.55 (4 H), 7.43 (1 H), 7.32 (1 H). X = I, yield 44% (Found: C, 27.40; H, 1.30; Ti, 9.40. C₃₅H₂₀Cl₃I₅O₁₂Ti₃ requires C, 27.70; H, 1.30; Ti, 9.45%). IR bands at 1580, 1530, 1170, 765, 720, 660, 540, 520 and 350 cm⁻¹. Proton NMR: δ 8.00, 7.95, 7.75 (2 H, multiplet), 7.60 (10 H), 7.40 (4 H), 7.30 (4 H).

[Ti₄Cl₅(O₂CC₆H₄Me-*o*)₇O₂].—This compound was prepared by the same method as for the trinuclear species above, the yield being essentially quantitative (99%) (Found: C, 49.20; H, 3.60; Cl, 13.25; Ti, 14.20. C₅₆H₄₉Cl₅O₁₆Ti₄ requires C, 49.10; H, 3.65; Cl, 13.15; Ti, 14.20%). IR bands at 1600, 1520, 1160, 740, 720, 630, 560, 500 and 360 cm⁻¹. Insolubility of the sample prevented reliable NMR spectra being obtained.

[Ti₃Cl₄(O₂CC₆H₄Cl-*o* or *m*)₄O₂].—These compounds were prepared as above, yields for the *o*-Cl and *m*-Cl derivatives being 49 and 47% respectively. For *o*-Cl (Found: C, 35.45; H, 1.80; Ti, 15.35. C₂₈H₁₆Cl₈O₁₀Ti₃ requires C, 35.80; H, 1.70;

Table 2 Atomic coordinates (× 10⁴) for [(TiCl₂(O₂CBu^t)(Bu^tCO₂H))₂O] **1** with e.s.d.s in parentheses

Atom	x	y	z
Ti(1)	1411(4)	5000	4973(3)
Ti(2)	2682(4)	5578(5)	2590(3)
Cl(11)	204(7)	3557(6)	4938(6)
Cl(12)	2912(6)	4442(7)	6205(6)
Cl(21)	4737(6)	5082(8)	2555(6)
Cl(22)	2001(7)	4566(7)	1169(6)
O(102)	2229(13)	4827(12)	3732(12)
O(11)	2177(13)	6458(11)	5130(13)
O(12)	3257(14)	6759(12)	3681(12)
C(11)	3010(20)	6931(18)	4669(19)
C(12)	3714(25)	7766(19)	5285(20)
C(13)	3136(34)	7925(28)	6386(30)
C(14)	3636(29)	8745(26)	4659(25)
C(15)	5065(24)	7448(28)	5388(32)
O(21)	42(13)	5762(13)	4035(12)
O(22)	1036(13)	6319(12)	2571(12)
C(21)	36(24)	6176(21)	3085(26)
C(22)	-1227(24)	6486(20)	2543(20)
C(23)	-1486(29)	5619(31)	1764(24)
C(24)	-1040(26)	7518(24)	1951(23)
C(25)	-2265(22)	6587(20)	3299(22)
O(31)	353(13)	5574(16)	6259(13)
O(32a)*	-1567(26)	6027(26)	5817(25)
O(32b)*	1333(69)	5598(71)	7971(60)
C(31a)*	-539(31)	5874(37)	6583(26)
C(31b)*	418(57)	5912(54)	7137(37)
C(32a)*	-977(33)	6204(29)	7692(27)
C(32b)*	-696(57)	6044(51)	7863(49)
C(33a)*	-216(51)	7141(39)	8120(50)
C(33b)*	-199(91)	6577(88)	8923(59)
C(34a)*	-2353(37)	6526(53)	7565(53)
C(34b)*	-1704(77)	6712(77)	7278(88)
C(35a)*	-794(68)	5283(45)	8487(47)
C(35b)*	-1258(89)	4987(61)	8137(85)
O(41)	3097(15)	6772(14)	1431(13)
O(42)	4567(36)	7834(32)	2153(32)
C(41)	3833(34)	7361(28)	1265(26)
C(42)	4216(22)	7938(21)	255(21)
C(43a)†	4682(60)	9023(31)	628(43)
C(43b)†	5491(62)	8467(94)	486(79)
C(44a)†	3082(34)	8115(49)	-546(36)
C(44b)†	3226(61)	8722(62)	-146(65)
C(45a)†	5280(47)	7413(42)	-348(45)
C(45b)†	4379(125)	7129(50)	-666(50)

* (a) and (b) atoms occupancy 0.68(3) and 0.33 respectively. † (a) and (b) atoms occupancy 0.54(8) and 0.46 respectively.

Ti, 15.30%). IR bands at 1590, 1160, 1060, 740, 720, 615, 520 and 380 cm⁻¹. For *m*-Cl (Found: C, 35.90; H, 1.80; Ti, 15.60. C₂₈H₁₆Cl₈O₁₀Ti₃ requires C, 35.80; H, 1.70; Ti, 15.30%). IR bands at 1590, 1540, 1165, 750, 730, 620, 500 and 380 cm⁻¹. Again insolubility in organic solvents prevented NMR data being obtained.

Crystal Structure Analysis.—*Crystal data.* C₂₀H₃₈Cl₄O₉Ti₂, *M* = 660.1, monoclinic, space group *P*2₁, *a* = 10.618(10), *b* = 12.900(9), *c* = 12.076(7) Å, β = 92.05(6)°, *U* = 1653(2) Å³, *Z* = 2, *D*_c = 1.33 g cm⁻³, *F*(000) = 684, Mo-Kα radiation, λ = 0.710 69 Å, μ(Mo-Kα) = 0.84 mm⁻¹, *T* = 290 K, *R* = 0.076 for 1267 unique observed [*I*/σ(*I*) > = 2.0] reflections.

The colourless platy air-sensitive crystals were mounted in Lindemann tubes. Data were collected with a Siemens R3m four-circle diffractometer in the ω–2θ mode. Maximum 2θ was 45° with scan range ± 0.75° (ω) around the Kα1–Kα2 angles, scan speed 2–15° (ω) min⁻¹, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time; *hkl* ranges were 0–11, 0–13 and –12 to 13.

Three standard reflections were monitored every 200 reflec-

tions, and showed no change during data collection. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($15 < 2\theta < 18^\circ$). Reflections were processed using profile analysis to give 2273 unique reflections ($R_{\text{int}} = 0.030$), of which 1267 were considered observed [$I/\sigma(I) > = 2.0$]. These were corrected for Lorentz, polarisation and absorption effects (by the Gaussian method); minimum and maximum transmission factors were 0.82 and 0.93. Crystal dimensions were $0.09 \times 0.23 \times 0.78$ mm.

Systematic reflection conditions $0k0$ ($k = 2n$) indicate either $P2_1$ or $P2_1/m$ as the space group. With a predicted Z of 2, the latter would require the molecule to have a mirror plane or a centre of inversion. As this was considered unlikely, $P2_1$ was initially selected. Although in principle the molecular structure as finally revealed could contain a mirror plane, it does not do so.

Heavy atoms were located by the Patterson interpretation section of SHELXTL and the light atoms then found on successive Fourier syntheses.⁹ Both singly co-ordinated 2,2-dimethylpropanoic acid ligands are disordered. One was modelled with two part occupancy molecules sharing a common co-ordinated oxygen atom, with coplanar carboxylic acid groups approximately as mirror images of each other; refined occupancies were in the ratio 0.68:0.32. For the other ligand, the three methyl groups took up two orientations about the C–C bond, with approximately equal occupancies (0.54:0.46). In both ligands, the C=O, C–C and non-bonded C...C distances were constrained to chemically reasonable values. The high thermal parameters and residual electron density in the areas of these ligands indicate that the modelling does not represent the full extent of the disorder.

Anisotropic thermal parameters were used for all non-H atoms, apart from those of the disordered ligands. Hydrogen atoms were given fixed isotropic thermal parameters, $U = 0.08 \text{ \AA}^2$. Those defined by the molecular geometry were inserted at calculated positions and not refined; methyl groups were treated as rigid CH_3 units, though the hydrogen atoms on the disordered ligands were omitted. The absolute structure of the individual crystal chosen was checked by refinement of a $\delta f''$ multiplier. The y coordinate of Ti(1) was fixed to define the origin. Final refinement was on F by least-squares methods refining 294 parameters; refinement was stable, despite the rather low parameter:reflection ratio. Largest positive and negative peaks on a final Fourier-difference synthesis were of heights 0.6 and -0.5 e \AA^{-3} .

A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.005$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.076$, $R' = 0.094$, $S = 1.08$. Maximum shift/error in final cycle 0.4. Computing was with SHELXTL PLUS⁹ on a DEC Microvax-II computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from International Tables.¹⁰ Final atomic coordinates are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters and remaining bond lengths and angles.

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References

- 1 T. Carofiglio, C. Floriani, A. Sgamellotti, M. Rossi, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Dalton Trans.*, 1992, 1081; V. W. Day, T. A. Eberspacher, W. G. Klemperer, C. W. Park and F. S. Rosenberg, *J. Am. Chem. Soc.*, 1991, **113**, 8190; R. Schmid, A. Mosset and J. Galy, *J. Chem. Soc., Dalton Trans.*, 1991, 1999.
- 2 F. Bottomley and L. Sutin, *Adv. Organomet. Chem.*, 1988, **28**, 339; F. Palacios, P. Royo, R. Serrano, J. L. Balcazar, I. Fonseca and F. Florencio, *J. Organomet. Chem.*, 1989, **375**, 51.
- 3 N. W. Alcock, D. A. Brown, T. F. Illson, S. M. Roe and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1991, 873.
- 4 (a) N. W. Alcock, D. A. Brown, S. M. Roe and M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, 1992, 846; (b) A. Bashall, D. A. Brown, M. McPartlin and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1992, 2529.
- 5 N. W. Alcock, P. N. Bartlett, D. Gordon, T. F. Illson and M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, 1986, 614.
- 6 G. B. Deacon, F. Huber and R. J. Phillips, *Inorg. Chim. Acta*, 1985, **104**, 41.
- 7 R. Hotzelmann, K. Wieghardt, J. Enslin, H. Romstedt, P. Gütlich, E. Bill, U. Flörke and H.-J. Haupt, *J. Am. Chem. Soc.*, 1992, **114**, 9470 and refs. therein.
- 8 J. Amaudrut, *Bull. Soc. Chim. Fr.*, 1977, 7–8, 624.
- 9 G. M. Sheldrick, SHELXTL PLUS User's manual, Nicolet Instrument Co., Madison, WI, 1986.
- 10 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974.

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