

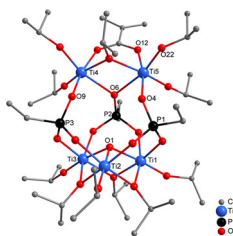
Titanium oxo/alkoxo clusters with both phosphonate and methacrylate ligands

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Received: 6 October 2014 / Accepted: 19 February 2015 / Published online: 8 April 2015
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Abstract The clusters $\text{Ti}_5\text{O}(\text{O}i\text{Pr})_{11}(\text{OMc})(\text{O}_3\text{PR})_3$ (OMc = methacrylate; R = Et, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$) and $\text{Ti}_{10}(\text{O}i\text{Pr})_{16}(\text{OMc})_4(\text{O}_3\text{PCH}_2\text{CH}=\text{CH}_2)_{10}$ were obtained when $\text{Ti}(\text{O}i\text{Pr})_4$ was reacted with the corresponding bis(trimethylsilyl) phosphonate and methacrylic acid. Oxo clusters of the composition $\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_{10}(\text{OMc})_2(\text{O}_3\text{PR})_2$, with a variety of groups R (Et, Ph, $\text{CH}=\text{CH}_2$, CH_2Ph , $\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, $\text{CH}_2\text{CH}_2\text{CN}$, $\text{CH}_2\text{C}(\text{O})\text{Me}$, $\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{Me})=\text{CH}_2$), were formed instead, when a stoichiometric amount of water was added to the reaction mixture.

Graphical abstract



Keywords Titanium alkoxides · Methacrylate ligands · Phosphonate ligands · Structure analysis

Introduction

We have recently obtained phosphonate/acetate-substituted titanium oxo/alkoxo clusters from $\text{Ti}(\text{O}i\text{Pr})_4$ and

bis(trimethylsilyl) phosphonates in the presence of acetic acid (AcOH), which served for in situ water generation through ester formation with eliminated *i*PrOH. Oxo clusters of the composition $\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_{10}(\text{OAc})_2(\text{O}_3\text{PR})_2$ were obtained with a large variety of functional and non-functional substituents R (Et, CH_2Ph , $\text{CH}_2\text{C}_{10}\text{H}_7$, $\text{CH}=\text{CH}_2$, $\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$), and also when the reaction conditions were varied [1]. This cluster type, which is also retained in solution, therefore appears to be very robust. Other clusters were only obtained in two exceptional cases (see below).

We extended these investigations by using methacrylic acid (McOH) instead of acetic acid. Methacrylic acid could also produce water through in situ ester formation, but would additionally provide reactive ligands in the obtained clusters and thus allow incorporating such clusters in organic polymers by polymerization with organic comonomers (see review articles on cluster-crosslinked polymers [2, 3]). Especially the combination of ligands with different organic functionalities in one cluster appeared attractive. In this article, we report the outcome of these reactions.

Results and discussion

The cluster $\text{Ti}_5(\mu_3\text{-O})(\mu_2\text{-O}i\text{Pr})_4(\text{O}i\text{Pr})_7(\text{OMc})(\text{O}_3\text{PEt})_3$ (**1**) was formed when bis(trimethylsilyl) ethylphosphonate was reacted with methacrylic acid (McOH) and $\text{Ti}(\text{O}i\text{Pr})_4$ in a 1:1:3 molar ratio (Fig. 1). This cluster type was previously obtained, as an exception from general outcome of the reactions with acetic acid mentioned in the “Introduction”, when bis(trimethylsilyl) 3-bromopropylphosphonate was reacted with acetic acid and $\text{Ti}(\text{O}i\text{Pr})_4$ in a 1:1:2 ratio at room temperature. The asymmetric unit of crystalline **1**

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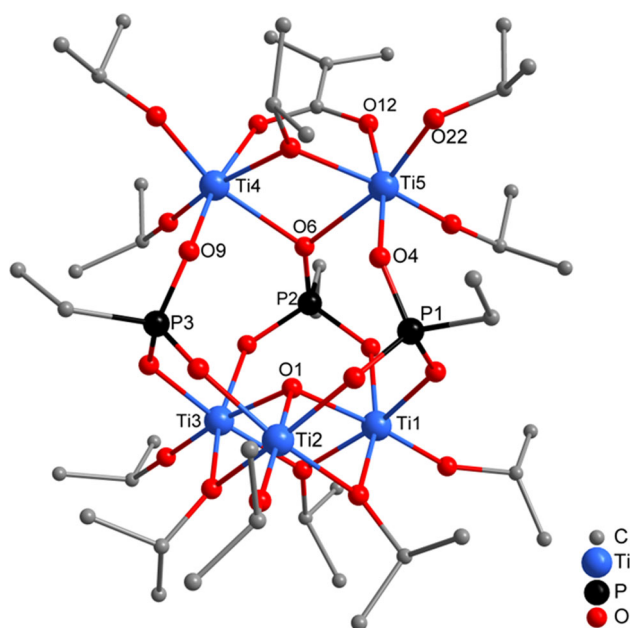


Fig. 1 Molecular structure of $\text{Ti}_5(\mu_3\text{-O})(\mu_2\text{-OiPr})_4(\text{OiPr})_7(\text{OMc})(\text{O}_3\text{PET})_3$ (**1**). Hydrogen atoms are omitted for clarity. Selected bond lengths/pm and angles/ $^\circ$: Ti(1)–O(1) 195.98(19), Ti(1)–O(3) 196.97(19), Ti(1)–O(13) 202.08(19), Ti(1)–O(17) 178.0(2), Ti(2)–O(1) 194.0(2), Ti(2)–O(2) 195.5(2), Ti(2)–O(13) 204.4(2), Ti(3)–O(1) 196.5(2), Ti(3)–O(19) 176.8(2), Ti(4)–O(6) 218.4(2), Ti(4)–O(9) 195.4(2), Ti(5)–O(4) 195.3(2), Ti(5)–O(6) 221.2(2), Ti(5)–O(12) 208.8(2), Ti(5)–O(22) 179.8(2), P(1)–O(2) 153.8(2), P(1)–O(4) 151.5(2), P(2)–O(6) 153.9(2), P(3)–O(9) 151.8(2); Ti(2)–O(1)–Ti(1) 105.18(8), Ti(4)–O(6)–Ti(5) 98.03(7)

contains two independent molecules with very similar bond distances and angles.

The structure of **1** is related to that of the clusters $\text{Ti}_4(\mu_3\text{-O})(\mu_2\text{-OiPr})_3(\text{OiPr})_5(\text{O}_3\text{PR})_3\text{L}$ ($\text{L} = \text{neutral ligand}$) [4–7], which consist of a symmetrical $\text{Ti}_3(\mu_3\text{-O})(\mu_2\text{-OiPr})_3(\text{OiPr})_3$ unit (Ti(1)–Ti(3) in Fig. 1) to which a $\text{Ti}(\text{OiPr})_2\text{L}$ group is connected by means of three phosphonate ligands. In **1**, the capping $\text{Ti}(\text{OiPr})_2\text{L}$ group is replaced by a $\text{Ti}_2(\mu_2\text{-OiPr})(\text{OiPr})_4(\mu_2\text{-OMc})$ moiety (Ti(4) and Ti(5) in Fig. 1). Two of the phosphonate ligands are coordinated to only one Ti atom of the Ti_2 unit and have a 3.111 binding mode (w.xyz refers to the number of metal atoms to which the phosphonate ligand is coordinated [w], and the number of metal atoms to which each oxygen is coordinated [x, y, z] [8]), while the third bridges both of them and has a binding mode of 4.211. The degree of condensation of **1** is 0.2 (O/Ti ratio of the cluster core), while it is 0.67 for the clusters $\text{Ti}_6\text{O}_4(\text{OiPr})_{10}(\text{OAc})_2(\text{O}_3\text{PR})_2$ obtained with acetic acid under the same conditions. This indicates that ester + water formation of methacrylic acid, relative to the rate of substitution [9], is slower than that of acetic acid.

^1H , ^{13}C , and ^{31}P NMR spectra of re-dissolved crystals of **1** in C_6D_6 showed numerous signals. In the ^{31}P NMR

spectrum, for example, eight resonances were observed, while two signals are expected if the solid-state structure of **1** was retained in solution. We therefore assume that **1** is in equilibrium with other compounds.

Isostructural $\text{Ti}_5(\mu_3\text{-O})(\mu_2\text{-OiPr})_4(\text{OiPr})_7(\text{OMc})(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{Br})_3$ (**2**) was obtained from the reaction of bis(trimethylsilyl) bromopropylphosphonate, methacrylic acid, and $\text{Ti}(\text{OiPr})_4$ in a ratio of 1:2:3. The higher proportion of MeOH thus did not influence the outcome of the reaction. $\text{Ti}_2(\text{OMc})_2(\text{OiPr})_6\text{iPrOH}$ [8] was formed as a by-product, as proven by single crystal XRD. The ^1H and ^{31}P NMR spectra of the solid residue correspondingly showed numerous signals. Therefore, it can be assumed that a mixture of products was obtained and/or several species are in equilibrium with each other.

When a 1:2:3 mixture of bis(trimethylsilyl) allylphosphonate, methacrylic acid, and $\text{Ti}(\text{OiPr})_4$ was heated to reflux, the complex $\text{Ti}_{10}(\mu_2\text{-OiPr})_2(\text{OiPr})_{14}(\text{OMc})_4(\text{O}_3\text{PCH}_2\text{CH}=\text{CH}_2)_{10}$ (**3**) (Fig. 2) was obtained after crystallization from CH_2Cl_2 . It is noteworthy that **3** contains no oxo groups, but more OiPr groups were substituted by OMc or O_3PR ligands compared to **1** and **2**. The different outcome of this reaction, compared to **1** and **2**, may be due to the higher reaction temperature. We have previously shown that higher reaction temperatures favor substitution over ester formation [9].

The structure of **3** consists of two $\text{Ti}_5(\text{OiPr})_8(\text{OMc})_2(\text{O}_3\text{P-allyl})_5$ units, which are bridged by two (3.111) phosphonate ligands. The Ti_5 units are composed of methacrylate-bridged dimers $\text{Ti}_2(\mu_2\text{-OiPr})(\text{OiPr})_3(\text{OMc})$ (Ti(2), Ti(5)) and $\text{Ti}_2(\text{OiPr})_3(\text{OMc})$ (Ti(3), Ti(4)), respectively, which are connected through phosphonate ligands among each other as well as to the fifth titanium atom (Ti(1)). Each of the octahedrally coordinated titanium atoms is at least bound to two different phosphonate ligands; Ti(1) is coordinated by five different oxygen atoms of phosphonate ligands and one OiPr ligand. The complexity of the structure of **3** is also reflected in the different binding modes of the phosphonate ligands, of which six are 3.111, two are 3.211, and two are 4.211.

The reactions leading to **1**, **2**, and **3** show that clusters with a noticeably lower degree of condensation were formed compared to analogous reactions with acetic acid [1]. This is most probably due to the lower reaction rate of ester formation between methacrylic acid and isopropyl alcohol compared to that of acetic acid [10]. This assumption was proven by the deliberate addition of water to the reaction mixture. Thus, when bis(trimethylsilyl) 3-bromopropylphosphonate, methacrylic acid, $\text{Ti}(\text{OiPr})_4$, and water were reacted in a 1:1:3:2 ratio, the cluster $\text{Ti}_6\text{O}_4(\text{OiPr})_{10}(\text{OMc})_2(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{Br})_2$ (**4**) (Fig. 3) was obtained. The cluster **4** is isostructural to $\text{Ti}_6\text{O}_4(\text{OiPr})_{10}(\text{OAc})_2(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{Br})_2$ obtained with acetic acid [1].

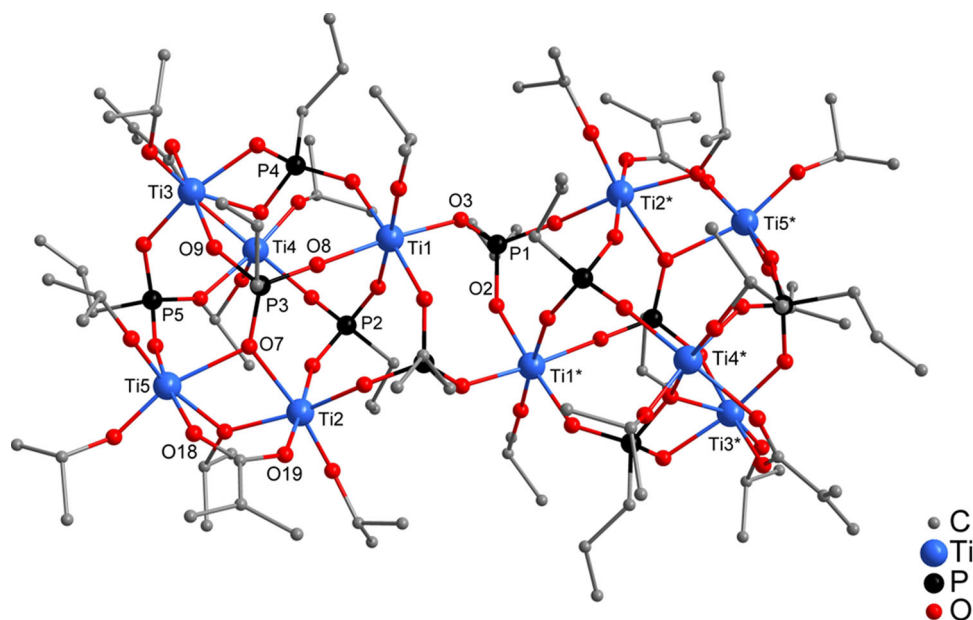


Fig. 2 Molecular structure of $\text{Ti}_{10}(\mu_2\text{-OiPr})_2(\text{OiPr})_{14}(\text{OMc})_4(\text{O}_3\text{PCH}_2\text{CH}=\text{CH}_2)_{10}$ (**3**). Hydrogen atoms are omitted for clarity. Selected bond lengths/pm and angles/ $^\circ$: Ti(1)–O(2) 193.6(2), Ti(1)–O(3) 195.9(2), Ti(1)–O(4) 202.1(2), Ti(1)–O(8) 195.8(2), Ti(1)–O(12) 200.9(2), Ti(1)–O(20) 175.6(2), Ti(2)–O(7) 216.5(2), Ti(2)–O(19) 206.3(3), Ti(3)–O(9) 193.5(2), Ti(3)–O(10) 221.1(2),

Ti(4)–O(5) 193.1(2), Ti(5)–O(7) 217.4(2), Ti(5)–O(18) 206.8(3); Ti(2)–O(7)–Ti(5) 99.38(9), Ti(2)–O(21)–Ti(5) 110.3(1), Ti(3)–O(10)–Ti(4) 126.8(1), O(1)–P(1)–O(2) 110.7(1), O(1)–P(1)–C(1A) 107.3(2), O(10)–P(4)–O(11) 99.1(1), O(10)–P(4)–O(12) 114.6(1), O(11)–P(4)–O(12) 115.6(1)

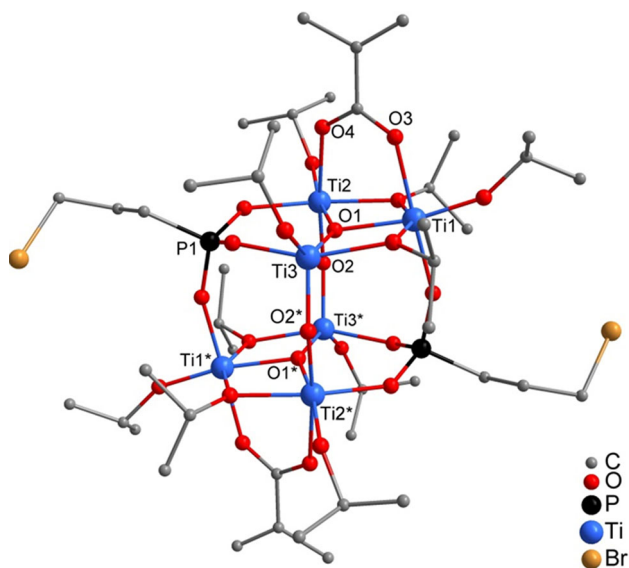


Fig. 3 Molecular structure of $\text{Ti}_6\text{O}_4(\text{OiPr})_{10}(\text{OMc})_2(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{Br})_2$ (**4**). Hydrogen atoms are omitted for clarity. Selected bond lengths/pm and angles/ $^\circ$: Ti(1)–O(1) 197.1(1), Ti(1)–O(3) 208.8(1), Ti(1)–O(5) 199.0(1), Ti(1)–O(6) 196.1(1), Ti(1)–O(7) 177.7(1), Ti(1)–O(12) 192.9(1), Ti(2)–O(1) 199.2(1), Ti(2)–O(2) 187.3(1), Ti(2)–O(10) 196.5(1), Ti(3)–O(1) 189.9(1), Ti(3)–O(2)* 175.0(1), Ti(3)–O(6) 204.7(1), Ti(3)–O(9) 180.9(1); Ti(3)–O(1)–Ti(1) 105.83(6), Ti(3)–O(1)–Ti(2) 149.36(7), Ti(1)–O(1)–Ti(2) 104.15(6), Ti(3)–O(2)–Ti(2) 148.49(8), Ti(1)–O(5)–Ti(2) 102.48(6), Ti(1)–O(6)–Ti(3) 100.75(5)

The centrosymmetric cluster **4** is isostructural to the previously reported acetate-substituted clusters $\text{Ti}_6\text{O}_4(\text{OiPr})_{10}(\text{OAc})_2(\text{O}_3\text{PR})_2$ [1]. The cluster core is formed by two parallel, unsymmetrically substituted $\text{Ti}_3(\mu_3\text{-O})(\mu_2\text{-OiPr})_2(\text{OiPr})_3(\mu_2\text{-OMc})$ units connected by μ_2 -oxo (O(2) and O(2)*, * denotes symmetry-related atoms) and phosphonate bridges. Ti(1) and Ti(2) are bridged by both an OiPr and a methacrylate ligand and are octahedrally coordinated while Ti(3) has a distorted trigonal bipyramidal coordination sphere. The central Ti_3O unit is unsymmetrical, with one short (Ti(3)–O(1) 189.9(1) pm) and two long Ti–O distances (Ti(1)–O(1) 197.1(1), Ti(2)–O(1) 199.2(2) pm), as in the acetate derivatives $\text{Ti}_6\text{O}_4(\text{OiPr})_{10}(\text{OAc})_2(\text{O}_3\text{PR})_2$.

NMR data show that the structure of **4**, especially also their inversion symmetry is retained in solution. Thus, one signal was observed in the ^{31}P NMR spectrum at 27.34 ppm. In the ^1H NMR spectrum five doublets for the methyl groups of the OiPr ligands were observed and three signals for the CH groups (at 4.86, 4.97, and 5.33 ppm) the latter two with double intensity. One singlet at 2.08 ppm and two multiplets at 5.41 and 6.36 ppm can be assigned to the two OMc ligands. In the ^{13}C NMR spectrum only one doublet for each P- CH_2 group was found and one set of signals for the OMc ligands. The signals of the OiPr ligands were partly overlapping.

The clusters **5–12** with a great variety of functional or non-functional phosphonate ligands were obtained according to Scheme 1 by the same synthesis procedure as that for **4**. The ^1H , ^{31}P , and ^{13}C NMR spectra of **5–12** are similar to that of **4**.

Conclusions

The first step in reactions of metal alkoxides with carboxylic or phosphonic acids is the substitution of an OR ligand by a carboxylate or phosphonate ligand. The thus liberated alcohol can undergo ester formation with the carboxylic or phosphonic acid, which produces water that hydrolyzes part or all of the remaining M–OR groups. Thus two reactions, viz. substitution and ester formation, compete with each other, and their relative rate is one of the decisive parameters influencing the outcome of such reactions. How the clusters are formed from the initially formed $\text{M}(\text{OR})_x(\text{carboxylate/phosphonate})_y$ derivatives has not been elucidated in any case. The situation becomes even more complex when two different metal alkoxides or, as in the present case, two different acids are involved.

In previous work, we had preferentially obtained phosphonate/acetate-substituted titanium oxo/alkoxo clusters of the composition $\text{Ti}_6\text{O}_4(\text{OiPr})_{10}(\text{OAc})_2(\text{O}_3\text{PR})_2$ from $\text{Ti}(\text{OiPr})_4$ and bis(trimethylsilyl) phosphonates in the presence of acetic acid (AcOH) [1]. The results of the work reported in this article show that the degree of condensation of the obtained clusters (**1** and **2**) was lower when acetic acid was replaced by methacrylic acid. In one case, the product (compound **3**) contained no oxo groups at all. This can be taken as evidence that the rate of esterification of methacrylic acid is lower than that of acetic acid.

The lower esterification rate can be compensated, however, by controlled addition of a stoichiometric amount

of “external” water. The thus obtained methacrylate/phosphonate-substituted clusters **4–12**, with a very wide variety of phosphonate ligands, are isostructural to the acetate-substituted clusters $\text{Ti}_6\text{O}_4(\text{OiPr})_{10}(\text{OAc})_2(\text{O}_3\text{PR})_2$ obtained in earlier experiments [1]. Incorporation of the polymerizable OMc ligands is a very interesting option for the preparation of cluster-crosslinked polymers [2, 3], especially because this allows the combination (a) of reactive and non-reactive ligands as well as (b) ligands with different organic functionalities in a controlled manner in one cluster.

Experimental

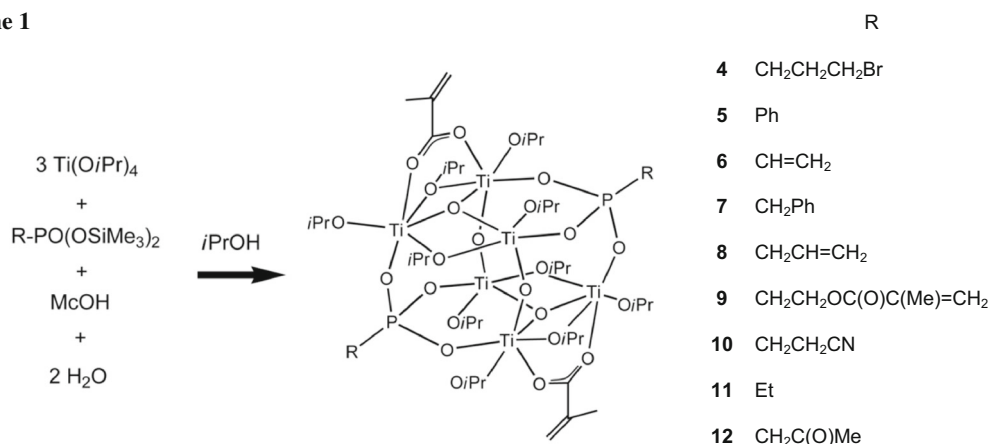
All operations were carried out in a moisture- and oxygen-free argon atmosphere using Schlenk techniques. Isopropyl alcohol was dried by refluxing twice over sodium metal and distillation. The bis(trimethylsilyl) phosphonates were prepared as reported before [1].

Methacrylate-phosphonate-substituted Ti_5 oxo clusters

$\text{Ti}_5\text{O}(\text{OiPr})_{11}(\text{OMc})(\text{O}_3\text{PET})_3$ (**1**): 1.6 cm^3 of $\text{Ti}(\text{OiPr})_4$ (5.42 mmol) was added to a solution of 500 mm^3 of bis(trimethylsilyl) ethylphosphonate (1.81 mmol) and 153 mm^3 of methacrylic acid (1.81 mmol) in 2 cm^3 of isopropyl alcohol. Crystals of **1** were obtained from this solution after 8 weeks. Yield 410 mg (35 %).

$\text{Ti}_5\text{O}(\text{OiPr})_{11}(\text{OMc})(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{Br})_3$ (**2**): 1.2 cm^3 of $\text{Ti}(\text{OiPr})_4$ (4.1 mmol) was added to a solution of 400 mm^3 of bis(trimethylsilyl) 3-bromopropylphosphonate (1.34 mmol) in 2 cm^3 of *i*PrOH, followed by addition of 113 mm^3 of methacrylic acid (1.34 mmol). Crystals of **2** were obtained from this solution after 3 weeks. Yield 620 mg (mixture of compounds).

Scheme 1



Methacrylate-phosphonate-substituted Ti₁₀ oxo cluster
Ti₁₀(OiPr)₁₆(OMc)₄(O₃PCH₂CHCH₂)₁₀ (3):

7.1 cm³ of Ti(OiPr)₄ (24 mmol) was added to a solution of 2 cm³ of bis(trimethylsilyl) allylphosphonate (8 mmol) and 1.35 cm³ of methacrylic acid (16 mmol) in 12 cm³ of isopropyl alcohol. The solution was heated to reflux for 16 h, and a suspension was formed. The solid was separated by filtration and recrystallized from CH₂Cl₂. Yield 120 mg (5 %). The crystals could not be re-dissolved in CD₂Cl₂ or another non-coordinating organic solvent and therefore no NMR measurements were performed.

Methacrylate-phosphonate-substituted Ti₆ oxo clusters:
Ti₆O₄(OiPr)₁₀(OMc)₂(O₃PCH₂CH₂CH₂Br)₂ (4) and
Ti₆O₄(OiPr)₁₀(OMc)₂(O₃PPh)₂ (5)

Ti(OiPr)₄ (1.17 cm³, 4 mmol) was quickly added to a solution of 400 mm³ of bis(trimethylsilyl) 3-bromopropylphosphonate (1.3 mmol) [or 225 mg of bis(trimethylsilyl) phenylphosphonate (0.82 mmol)] in 2 cm³ of 2-propanol followed by addition of 110 mm³ of methacrylic acid (1.3 mmol). Finally, 48 mm³ of water (2.7 mmol) diluted in 1 cm³ of 2-propanol was injected quickly directly into the solution. Crystals were obtained after 1 week.

4: yield 420 mg (43 %); ¹H NMR (C₆D₆, 250 MHz): δ = 1.31 (d, ³J_{H,H} = 6.09 Hz, 12H, CHMe), 1.41 (d, ³J_{H,H} = 6.24 Hz, 12H, CHMe), 1.48 (d, ³J_{H,H} = 6.09 Hz, 12H, CHMe), 1.74 (d, ³J_{H,H} = 6.24 Hz, 12H, CHMe), 1.82 (d, ³J_{H,H} = 6.24 Hz, 12H, CHMe), 1.72–1.88 (m, 2H, PCH₂), 2.08 (s, 6H, =CCH₃), 2.36 (m, ³J_{P,H} = 15.84 Hz, ³J_{H,H} = 7.31 Hz, 2H, CH₂CH₂P), 3.46 (t, ³J_{H,H} = 7.16 Hz, CH₂Br), 4.86 (m, ³J_{H,H} = 6.17 Hz, 2H, OCH), 4.97 (m, ³J_{H,H} = 6.13 Hz, 4H, OCH), 5.33 (m, ³J_{H,H} = 6.20 Hz, 4H, OCH), 5.39–5.43 (m, 2H, =CH₂), 6.34–6.38 (m, 2H, =CH₂) ppm; ³¹P NMR (C₆D₆, 101.2 MHz): δ = 27.34 ppm; ¹³C NMR (C₆D₆, 62.9 MHz): δ = 18.63 (CHMe), 23.89 (CHMe), 24.20 (CHMe), 24.81 (CHMe), 25.20 (CHMe), 25.67 (d, ¹J_{P,C} = 157 Hz, PCH₂), 27.68 (d, ²J_{P,C} = 4.53 Hz, CH₂CH₂P), 33.81 (d, ³J_{P,C} = 14.96 Hz, CH₂Br), 77.83 (OCH), 78.69 (OCH), 79.40 (OCH), 123.41 (=CH₂), 140.02 (=CMe–), 173.39 (COO) ppm.

5: yield 160 mg (27 %); ¹H NMR (C₆D₆, 250 MHz): δ = 1.26 (d, ³J_{H,H} = 6.13 Hz, 12H, CHMe), 1.43 (d, ³J_{H,H} = 6.08 Hz, 24H, CHMe), 1.82 (d, ³J_{H,H} = 6.40 Hz, 12H, CHMe), 1.84 (d, ³J_{H,H} = 6.40 Hz, 12H, CHMe), 2.14 (s, 6H, CH₃ (OMc)), 4.88 (m, ³J_{H,H} = 6.17 Hz, 2H, CH (OiPr)), 4.99 (m, ³J_{H,H} = 6.13 Hz, 4H, CH (OiPr)), 5.36–5.58 (m, 6H, CH (OiPr) + CH₂ (OMc)), 6.43–6.46 (m, 2H, CH₂ (OMc)), 7.10–7.28 (m, 2H, CH (Ph)), 7.34–7.44 (m, 4H, Ph), 8.33–8.44 (m, 4H, Ph) ppm; ³¹P NMR (C₆D₆, 101.2 MHz): δ = 16.03 ppm; ¹³C NMR (C₆D₆, 62.9 MHz): δ = 18.64 (CHMe), 24.06 (CHMe),

24.26 (CHMe), 24.83 (CHMe), 25.17 (CHMe), 77.93 (OCH), 78.78 (OCH), 79.48 (OCH), 123.28 (=CH₂), 130.25 (d, ¹J_{P,C} = 2.99 Hz, Ph), 130.99 (d, ¹J_{P,C} = 9.36 Hz, Ph), 131.80 (d, ¹J_{P,C} = 9.97 Hz, Ph), 134.50 (d, ¹J_{P,C} = 208.43 Hz, Ph), 140.25 (=CMe–), 173.46 (COO) ppm.

Ti₆O₄(OiPr)₁₀(OMc)₂(O₃P–CH=CH₂)₂ (6), Ti₆O₄(OiPr)₁₀(OMc)₂(O₃PCH₂Ph)₂ (7), Ti₆O₄(OiPr)₁₀(OMc)₂(O₃PCH₂–CH=CH₂)₂ (8), Ti₆O₄(OiPr)₁₀(OMc)₂(O₃PCH₂–CH₂–OMc)₂ (9), Ti₆O₄(OiPr)₁₀(OMc)₂(O₃PCH₂CH₂–C≡N)₂ (10), Ti₆O₄(OiPr)₁₀(OMc)₂(O₃PCH₂CH₃)₂ (11), Ti₆O₄(OiPr)₁₀(OMc)₂(O₃PCH₂COCH₃)₂ (12).

Compared to **4** and **5**, the synthesis was slightly modified. In the synthesis of **6** 660 mm³ of Ti(OiPr)₄ (2.27 mmol) was added to a mixture of 200 mm³ of bis(trimethyl)silyl vinylphosphonate (0.76 mmol) and 64 mm³ of methacrylic acid (0.76 mmol) in 2 cm³ of 2-propanol. Immediately afterwards, 27.3 mm³ of water (1.52 mmol) diluted in 0.5 cm³ of 2-propanol was added. Crystals of **6** were obtained after 3 days. The syntheses of **7–11** were analogous. The synthesis of **12** was done analogously, but the precursor solution was additionally heated after addition of water until a clear solution was obtained.

6: yield 70 mg (14 %); ¹H NMR (C₆D₆, 250 MHz): δ = 1.33 (d, ³J_{H,H} = 6.09 Hz, 12H, OCHMe), 1.41 (d, ³J_{H,H} = 6.09 Hz, 12H, OCHMe), 1.51 (d, ³J_{H,H} = 5.94 Hz, 12H, OCHMe), 1.79 (d, ³J_{H,H} = 6.24 Hz, 12H, OCHMe), 1.84 (d, ³J_{H,H} = 6.09 Hz, 12H, OCHMe), 2.09 (s, 6H, =CMe), 4.87 (m, ³J_{H,H} = 6.13 Hz, 2H, OCH), 5.02 (m, ³J_{H,H} = 5.90 Hz, 4H, OCH), 5.30–5.45 (m, 6H, OCH + =CH₂), 5.74 (ddd, ²J_{H,H} = 3.50 Hz, ³J_{H,H} = 12.03 Hz, ³J_{P,H} = 49.42 Hz, 4H, OCH), 6.21–6.57 (m, 6H, CH₂(vinyl) + CH(vinyl) + =CH₂ (OMc)) ppm; ³¹P NMR (C₆D₆, 101.2 MHz): δ = 14.25 ppm; ¹³C NMR (C₆D₆, 62.9 MHz): δ = 18.58 (=CMe), 23.93 (OCHMe), 24.23 (OCHMe), 24.78 (OCHMe), 25.17 (OCHMe), 77.82 (OCH), 78.65 (OCH), 79.38 (OCH), 123.16 (=CH₂ (OMc)), 128.66 (=CH₂ (vinyl)), 130.81 (d (¹J_{P,C} = 204.2 Hz), CH (vinyl)), 140.22 (=CMe), 173.41 (COO) ppm.

7: yield 160 mg (34 %); ¹H NMR (C₆D₆, 250 MHz): δ = 1.30 (d, ³J_{H,H} = 6.09 Hz, 12H, OCHMe), 1.41–1.49 (m, 24H, OCHMe), 1.65 (d, ³J_{H,H} = 6.24 Hz, 12H, OCHMe), 1.72 (d, ³J_{H,H} = 6.24 Hz, 12H, OCHMe), 2.07 (s, 6H, =CMe), 3.20 (d, ²J_{P,H} = 22.69 Hz, 4H, PCH₂), 4.83–5.02 (m, ³J_{H,H} = 6.07 Hz, 6H, OCH), 5.18–5.33 (m, ³J_{H,H} = 6.24 Hz, 6H, OCH), 5.40 (br, 2H, =CH₂), 6.32 (br, 2H, =CH₂), 7.18–7.28 (m, 2H, Ph), 7.31–7.39 (m, 4H, Ph), 7.63–7.68 (m, 4H, Ph) ppm; ³¹P NMR (C₆D₆, 101.2 MHz): δ = 23.34 ppm; ¹³C NMR (C₆D₆, 62.9 MHz): δ = 18.64 (=CMe), 23.81 (OCHMe), 24.15 (OCHMe), 24.95 (OCHMe), 25.26 (OCHMe), 35.18 (d,

$^1J_{P,C} = 152.25$ Hz, PCH₂), 77.74 (OCH), 78.69 (OCH), 79.05 (OCH), 123.12 (CH₂ (OMc)), 125.83 (d, $J_{P,C} = 3.00$ Hz, Ph), 130.44 (d, $J_{P,C} = 6.98$ Hz, Ph), 134.88 (d, $J_{P,C} = 8.98$ Hz, Ph), 140.19 (=CMe-), 173.34 (COO) ppm.

8: yield 180 mg (33 %); 1H NMR (C₆D₆, 250 MHz): $\delta = 1.31$ (d, $^3J_{H,H} = 6.10$ Hz, 12H, OCHMe), 1.41 (d, $^3J_{H,H} = 6.10$ Hz, 12H, OCHMe), 1.50 (d, $^3J_{H,H} = 6.03$ Hz, 12H, OCHMe), 1.77 (d, $^3J_{H,H} = 6.24$ Hz, 12H, OCHMe), 1.84 (d, $^3J_{H,H} = 6.21$ Hz, 12H, OCHMe), 2.09 (s, 6H, =CMe), 2.68 (dd, $^2J_{P,H} = 22.69$ Hz, $^3J_{H,H} = 7.08$ Hz, 4H, PCH₂), 4.85 (m, $^3J_{H,H} = 6.09$ Hz, 2H, OCH), 5.00 (m, $^3J_{H,H} = 6.05$ Hz, 4H, OCH), 5.22–5.45 (m, 10H, OCH + CH₂ (OMc) + CH₂ (allyl)), 6.16–6.35 (m, 2H, CH (allyl)), 6.38 (br, 2H, =CH₂ (OMc)) ppm; ^{31}P NMR (C₆D₆, 101.2 MHz): $\delta = 24.16$ ppm; ^{13}C NMR (C₆D₆, 62.9 MHz): $\delta = 18.59$ (=CMe), 23.95 (OCHMe), 24.21 (OCHMe), 24.75 (OCHMe), 25.17 (OCHMe), 33.31 (d, $^1J_{P,C} = 154.33$ Hz, PCH₂), 77.70 (OCH), 78.59 (OCH), 79.31 (OCH), 117.29 (d, $^3J_{P,C} = 14.96$ Hz, =CH₂), 123.14 (CH₂ (OMc)), 130.96 (d, $^2J_{P,C} = 10.97$ Hz, =CH), 140.20 (C (OMc)), 173.28 (COO) ppm.

9: yield 100 mg (22 %); 1H NMR (C₆D₆, 250 MHz): $\delta = 1.31$ (d, $^3J_{H,H} = 6.10$ Hz, 12H, OCHMe), 1.42 (d, $^3J_{H,H} = 6.15$ Hz, 12H, OCHMe), 1.50 (d, $^3J_{H,H} = 6.08$ Hz, 12H, OCHMe), 1.76 (d, $^3J_{H,H} = 6.24$ Hz, 12H, OCHMe), 1.82 (d, $^3J_{H,H} = 6.20$ Hz, 12H, OCHMe), 1.89 (s, 6H, CH₃ (OMc ester)), 2.10 (s, 6H, =CMe), 2.33–2.50 (m, 4H, PCH₂), 4.79–5.06 (m, 10H, OCH + CH₂O), 5.26 (br, 2H, CH₂ (OMc ester)), 5.36 (m, $^3J_{H,H} = 6.24$ Hz, 4H, OCH), 5.43 (br, 2H, =CH₂), 6.20 (br, 2H, CH₂ (OMc ester)), 6.38 (br, 2H, =CH₂) ppm; ^{31}P NMR (C₆D₆, 101.2 MHz): $\delta = 23.59$ ppm; ^{13}C NMR (C₆D₆, 62.9 MHz): $\delta = 18.03$ (CH₃ (OMc ester)), 18.60 (=CMe), 23.90 (OCHMe), 24.19 (OCHMe), 24.71 (OCHMe), 25.16 (OCHMe), 27.88 (d, $^1J_{P,C} = 152.46$ Hz, PCH₂), 60.92 (d, $^2J_{P,C} = 3.98$ Hz, OCH₂), 78.03 (OCH), 78.80 (OCH), 79.71 (OCH), 123.67 (CH₂ (OMc)), 124.64 (CH₂ (OMc ester)), 136.68 (C (OMc ester)), 139.94 (=CMe-), 166.56 (COO (OMc ester)), 173.50 (COO) ppm.

10: yield 120 mg (24 %); 1H NMR (C₆D₆, 250 MHz): $\delta = 1.26$ (d, $^3J_{H,H} = 6.09$ Hz, 12H, OCHMe), 1.38 (d, $^3J_{H,H} = 6.24$ Hz, 12H, OCHMe), 1.41 (d, $^3J_{H,H} = 6.09$ Hz, 12H, OCHMe), 1.67 (d, $^3J_{H,H} = 6.24$ Hz, 12H, OCHMe), 1.77 (d, $^3J_{H,H} = 6.24$ Hz, 12H, OCHMe), 1.80–1.89 (m, 4H, CH₂CN), 2.02 (s, 6H, =CMe), 2.54–2.66 (m, 4H, PCH₂), 4.79 (m, 2H, OCH), 4.89 (m, 4H, OCH), 5.29 (m, 4H, OCH), 5.36 (br, 2H, =CH₂), 6.29 (br, 2H, =CH₂) ppm; ^{31}P NMR (C₆D₆, 101.2 MHz): $\delta = 24.16$ ppm; ^{13}C NMR (C₆D₆, 62.9 MHz): $\delta = 11.67$ (d, $^2J_{P,C} = 2.50$ Hz, CH₂CN), 18.46 (=CMe), 22.04 (PCH₂), 23.80 (OCHMe), 24.16 (OCHMe), 24.63 (OCHMe), 25.05 (OCHMe), 25.11 (OCHMe), 78.13 (OCH), 78.94 (OCH), 79.96 (OCH),

118.86 (d, $^3J_{P,C} = 18.95$ Hz, CN), 123.61 (=CH₂), 139.83 (=CMe-), 173.48 (COO) ppm.

11: yield 230 mg (48 %); 1H NMR (C₆D₆, 250 MHz): $\delta = 1.23$ –1.47 (m, 6H, CH₃CH₂P), 1.32 (d, $^3J_{H,H} = 6.09$ Hz, 12H, OCHMe), 1.41 (d, $^3J_{H,H} = 6.24$ Hz, 12H, OCHMe), 1.50 (d, $^3J_{H,H} = 6.09$ Hz, 12H, OCHMe), 1.65–1.93 (m, 4H, PCH₂), 1.77 (d, $^3J_{H,H} = 6.24$ Hz, 12H, OCHMe), 1.84 (d, $^3J_{H,H} = 6.24$ Hz, 12H, OCHMe), 2.09 (s, 6H, =CMe), 4.86 (m, $^3J_{H,H} = 6.09$ Hz, 2H, OCH), 5.00 (m, $^3J_{H,H} = 6.09$ Hz, 4H, OCH), 5.27–5.37 (m, 4H, OCH), 5.39 (br, 2H, CH₂ (OMc)), 6.36 (br, 2H, CH₂ (OMc)) ppm; ^{31}P NMR (C₆D₆, 101.2 MHz): $\delta = 29.82$ ppm; ^{13}C NMR (C₆D₆, 62.9 MHz): $\delta = 7.42$ (d, $^2J_{P,C} = 6.28$ Hz, CH₃CH₂P), 18.58 (=CMe), 20.00 (d, $^1J_{P,C} = 158.57$ Hz, PCH₂), 23.93 (OCHMe), 24.20 (OCHMe), 24.75 (OCHMe), 25.13 (OCHMe), 25.21 (OCHMe), 77.51 (OCH), 78.44 (OCH), 79.09 (OCH), 122.99 (=CH₂), 140.28 (=CMe-), 173.23 (COO) ppm.

12: yield 260 mg (53 %); 1H NMR (C₆D₆, 250 MHz): $\delta = 1.32$ (d, $^3J_{H,H} = 6.09$ Hz, 12H, OCHMe), 1.39 (d, $^3J_{H,H} = 6.24$ Hz, 12H, OCHMe), 1.48 (d, $^3J_{H,H} = 6.09$ Hz, 12H, OCHMe), 1.71 (d, $^3J_{H,H} = 6.24$ Hz, 12H, OCHMe), 1.80 (d, $^3J_{H,H} = 6.24$ Hz, 12H, OCHMe), 2.05 (s, 6H, =CMe), 2.46 (m, 4H, MeCO), 3.00 (d, $^2J_{P,H} = 23.91$ Hz, 4H, PCH₂), 4.81 (m, $^3J_{H,H} = 6.17$ Hz, 2H, OCH), 4.98 (m, $^3J_{H,H} = 6.13$ Hz, 4H, OCH), 5.31 (m, $^3J_{H,H} = 6.32$ Hz, 4H, OCH), 5.38 (br, 2H, CH₂ (OMc)), 6.32 (br, 2H, =CH₂) ppm; ^{31}P NMR (C₆D₆, 101.2 MHz): $\delta = 18.69$ ppm; ^{13}C NMR (C₆D₆, 62.9 MHz): $\delta = 18.51$ (=CMe), 23.80 (OCHMe), 24.19 (OCHMe), 24.72 (OCHMe), 25.20 (OCHMe), 30.50 (CH₃-CO), 45.25 (d, $^1J_{P,C} = 139.17$ Hz, PCH₂), 78.29 (OCH), 78.94 (OCH), 79.90 (OCH), 123.59 (CH₂ (OMc)), 139.89 (C (OMc)), 173.48 (COO), 199.11 (d, $^2J_{P,C} = 5.58$ Hz, C=O) ppm.

X-ray structure analyses

All measurements were performed using MoK α radiation ($\lambda = 71.073$ pm). Data were collected on a Bruker AXS SMART APEX II four-circle diffractometer with κ -geometry at 100 K with φ and ω -scans and 0.5° frame width (Table 1) and corrected for polarization and Lorentz effects. An empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections. SAINT Plus (Bruker Analytical X-ray Instruments, 2007) was used to integrate the frames. Symmetry was checked with the program PLATON.

The structures were solved by the Patterson method (SHELXS97). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL97) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. In **1**, **3**, **4**, **6**–**9**,

Table 1 Crystal data and structure refinement details

Compound	1	2	3	4
Emp. formula	C ₄₃ H ₉₇ O ₂₃ P ₃ Ti ₅	C ₄₆ H ₁₀₀ Br ₃ O ₂₃ P ₃ Ti ₅	C ₉₄ H ₁₈₂ O ₅₄ P ₁₀ Ti ₁₀	C ₄₄ H ₉₂ Br ₂ O ₂₄ P ₂ Ti ₆
<i>M_r</i>	1314.62	1593.4	2965.1	1514.35
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pc</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /pm	2756.6 (1)	1291.63 (5)	1366.83 (13)	1346.04 (2)
<i>b</i> /pm	1861.8 (1)	2301.65 (9)	1403.15 (13)	1532.03 (3)
<i>c</i> /pm	2600.8 (1)	2441.36 (9)	2110.25 (17)	1689.82 (3)
α /°	90	90	73.525 (4)	90
β /°	105.268 (2)	101.4782 (14)	75.199 (4)	108.9870 (10)
γ /°	90	90	64.922 (5)	90
<i>V</i> /pm ³ × 10 ⁶	12877 (1)	7112.7 (5)	3472.3 (5)	3295.11 (10)
<i>Z</i>	8	4	1	2
<i>D_x</i> /g cm ⁻³	1.36	1.488	1.418	1.526
μ /mm ⁻¹	0.735	2.355	0.739	2.023
Crystal size/mm	0.25 × 0.2 × 0.15	0.52 × 0.15 × 0.1	0.25 × 0.15 × 0.1	0.48 × 0.44 × 0.4
No. measured refl.	230,762	101,719	76,823	43500
Obs. refl. [<i>I</i> > 2σ(<i>I</i>)]	17,441	23,566	8533	8180
θ_{\max} /°	25.07	26.37	25.15	30.55
R [<i>F</i> ² > 2σ(<i>F</i>)], wR (<i>F</i> ²), <i>S</i>	0.0355, 0.0965, 1.074	0.0433, 0.1134, 1.076	0.0429, 0.1083, 1.035	0.0386, 0.1101, 1.089
Refl./param.	22815/1413	27296/1497	12361/828	10086/393
Weighting scheme ^a	<i>a</i> = 0.0409 <i>P</i> , <i>b</i> = 14.5476	<i>a</i> = 0.0588, <i>b</i> = 8.0538	<i>a</i> = 0.0457, <i>b</i> = 3.3285	<i>a</i> = 0.0621, <i>b</i> = 0.1815
$\delta\rho_{\max, \min}$ /e × 10 ⁻⁶ pm ⁻³	1.00, -0.92	1.418, -1.716	0.78, -0.49	1.329, -1.132
Compound	5	6	7	8
Emp. formula	C ₅₀ H ₉₀ O ₂₄ P ₂ Ti ₆	C ₄₂ H ₈₄ O ₂₄ P ₂ Ti ₆	C ₅₂ H ₉₄ O ₂₄ P ₂ Ti ₆	C ₄₄ H ₉₀ O ₂₄ P ₂ Ti ₆
<i>M_r</i>	1424.56	1322.43	1452.61	1352.5
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> /pm	1388.4 (1)	1162.8 (1)	1376.21 (9)	1270.28 (9)
<i>b</i> /pm	1742.4 (2)	1264.4 (2)	1326.97 (8)	1443.4 (1)
<i>c</i> /pm	1411.0 (1)	1265.7 (2)	1936.70 (11)	1838.2 (1)
α /°	90	107.721 (3)	90	92.141 (3)
β /°	91.423 (3)	95.875 (3)	101.120 (2)	90.567 (3)
γ /°	90	113.308 (3)	90	94.006 (3)
<i>V</i> /pm ³ × 10 ⁶	3412.4 (5)	1574.4 (3)	3470.4 (4)	3359.7 (4)
<i>Z</i>	2	1	2	2
<i>D_x</i> /g cm ⁻³	1.386	1.395	1.39	1.337
μ /mm ⁻¹	0.785	0.844	0.773	0.793
Crystal size/mm	0.45 × 0.42 × 0.38	0.42 × 0.38 × 0.37	0.38 × 0.37 × 0.3	0.42 × 0.37 × 0.34
No. measured refl.	86,933	37,906	42,971	81,110
Obs. refl. [<i>I</i> > 2σ(<i>I</i>)]	5075	3906	9040	12,077
θ_{\max} /°	26.4	25.14	30.51	28.6
R [<i>F</i> ² > 2σ(<i>F</i>)], wR (<i>F</i> ²), <i>S</i>	0.0869, 0.2767, 1.171	0.0928, 0.2097, 1.059	0.0322, 0.1005, 1.088	0.0588, 0.1819, 1.075
Refl./param.	6991/382	5595/413	10,593/495	16,783/799
Weighting scheme ^a	<i>a</i> = 0.1198, <i>b</i> = 22.3579	<i>a</i> = 0.0146, <i>b</i> = 20.0056	<i>a</i> = 0.0503, <i>b</i> = 2.2610	<i>a</i> = 0.0765, <i>b</i> = 4.8222
$\delta\rho_{\max, \min}$ /e × 10 ⁻⁶ pm ⁻³	1.945, -0.978	1.541, -0.836	1.131, -0.82	1.317, -0.753

Table 1 continued

Compound	9	10	11	12
Emp. formula	C ₅₀ H ₉₈ O ₂₈ P ₂ Ti ₆	C ₄₄ H ₈₇ N ₂ O ₂₄ P ₂ Ti ₆	C ₄₂ H ₉₀ O ₂₄ P ₂ Ti ₆	C ₄₄ H ₉₀ O ₂₆ P ₂ Ti ₆
<i>M_r</i>	1496.62	1377.5	1328.48	1384.5
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> /pm	1316.93 (9)	1993.57 (3)	1191.1 (1)	2114.2 (6)
<i>b</i> /pm	1318.99 (9)	1909.15 (3)	1254.1 (1)	1306.8 (3)
<i>c</i> /pm	2275.93 (16)	1830.71 (3)	1321.9 (1)	2454.2 (7)
α /°	93.586 (2)	90	67.017 (3)	90
β /°	98.919 (2)	99.4200 (10)	89.871 (3)	104.112 (8)
γ /°	113.5566 (19)	90	65.009 (3)	90
<i>V</i> /pm ³ × 10 ⁶	3546.1 (4)	6873.77 (19)	1616.0 (3)	6576 (3)
<i>Z</i>	2	4	1	4
<i>D_x</i> /g cm ⁻³	1.402	1.331	1.365	1.399
μ /mm ⁻¹	0.763	0.777	0.823	0.814
Crystal size/mm	0.45 × 0.43 × 0.4	0.48 × 0.42 × 0.38	0.55 × 0.5 × 0.45	0.51 × 0.41 × 0.32
No. measured refl.	136,754	52,967	15,444	130,844
Obs. refl. [<i>I</i> > 2σ(<i>I</i>)]	17,747	8622	3838	7964
θ_{\max} /°	30.56	25.11	25.03	30.58
R [<i>F</i> ² > 2σ(<i>F</i>)], wR (<i>F</i> ²), <i>S</i>	0.0567, 0.1295, 1.079	0.063, 0.1999, 1.074	0.0922, 0.2265, 1.045	0.067, 0.1946, 1.165
Refl./param.	21,716/894	12,226/724	5543/492	10,080/407
Weighting scheme ^a	<i>a</i> = 0.0178, <i>b</i> = 11.8092	<i>a</i> = 0.0994, <i>b</i> = 8.5071	<i>a</i> = 0.0483, <i>b</i> = 17.8591	<i>a</i> = 0.0659, <i>b</i> = 45.3501
$\delta\rho_{\max, \min}$ /e × 10 ⁻⁶ pm ⁻³	1.49, -1.873	0.732, -0.342	1.435, -0.834	1.147, -0.653

$$^a w = \frac{1}{\sigma^2(F_0)^2 + (aP)^2 + bP} \text{ where } P = \frac{F_0^2 + 2F_c^2}{3}$$

11, and **12** OiPr ligands were disordered. In **6** and **12** one OiPr ligand was additionally refined for three different positions. In **6**, **9**, and **11** the methacrylate ligand was bridging either between Ti(1) and Ti(2) or between Ti(1) and Ti(3). Two allyl groups in **3** and one Br atom in **2** were also disordered.

CCDC-1027711 (for **1**), -1027712 (for **2**), -1027713 (for **3**), -1027714 (for **4**), -1027715 (for **5**), -1027716 (for **6**), -1027717 (for **7**), -1027718 (for **8**), -1027719 (for **9**), -1027720 (for **10**), -1027721 (for **11**), and -1027722 (for **12**) contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments This work was supported by the Fonds zur Förderung der wissenschaftlichen Forschung (FWF), Austria (Project P22915). The X-ray measurements were carried out at the X-ray Center of Vienna University of Technology.

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