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Acetic Acid Mediated Synthesis of Phosphonate-Substituted Titanium Oxo Clusters

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New phosphonate/acetate-substituted titanium oxo/alkoxo clusters were prepared from $\text{Ti}(\text{O}i\text{Pr})_4$ and bis(trimethylsilyl) phosphonates in the presence of acetic acid, which served to generate water in situ through ester formation. The process led to clusters with a higher degree of condensation than in previously known phosphonate-substituted titanium oxo clusters. The clusters $[\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_{10}(\text{OAc})_2(\text{O}_3\text{PR})_2]$ ($\text{OAc} =$

acetate) were obtained for a large variety of functional and non-functional groups R under a range of reaction conditions. This cluster type, which is also retained in solution, therefore appears to be very robust. Two other clusters, $[\text{Ti}_5\text{O}(\text{O}i\text{Pr})_{11}(\text{OAc})(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{Br})_3]$ and $[\text{Ti}_5\text{O}_3(\text{O}i\text{Pr})_6(\text{OAc})_4(\text{O}_3\text{P-xylyl})_2]$, were only isolated in special cases.

Introduction

Metal alkoxides are often substituted by less easily hydrolyzable organic groups to moderate their reactivity in sol-gel processes and to introduce functional or non-functional organic groups for inorganic–organic hybrid materials.^[1] Such substituted metal alkoxide derivatives are obtained by reacting metal alkoxides with a protic compound, such as β -diketonates, amino alcohols, or oximes. Reaction with carboxylic acids is a special case because this normally does not result in carboxylate-substituted metal alkoxides but, instead, in carboxylate-substituted metal oxo clusters. This is due to the fact that carboxylic acids not only provide carboxylate ligands but also act as an in situ water source through esterification with the eliminated alcohol. Such oxo clusters have been used as nanosized building blocks for the construction of inorganic–organic hybrid polymers or as linker units in metal–organic frameworks (MOF).^[2]

Whereas carboxylate-substituted oxo/alkoxo clusters of titanium have been particularly well investigated,^[3] only a few phosphonate-substituted derivatives are known.^[4,5] The latter are interesting for hybrid materials because of the strong Ti–O–P bonds, especially when phosphonate ligands with functional organic groups are employed.^[6]

We have recently shown that titanium oxo clusters can be easily prepared by using bis(trimethylsilyl) esters.^[5] Com-

pared with the corresponding phosphonic acids, the esters have the advantage that they are soluble in organic solvents. Their reaction with alcohol liberates phosphonic acid, which substitutes part of the OR groups of $\text{Ti}(\text{OR})_4$ in a relatively fast reaction. Oxo groups are generated in situ by esterification of either coordinated or non-coordinated phosphonic acid, as in the case of carboxylic acids. However, because esterification of phosphonic acids appears to be slow, oxo clusters with a low degree of condensation (defined O/Ti ratio of the Ti/O core^[7]) (0.25 or 0.29) were obtained, although higher degrees of condensation can be achieved under solvothermal conditions.^[8]

In this article we report the results of experiments in which $\text{Ti}(\text{O}i\text{Pr})_4$ was treated with mixtures of various bis(trimethylsilyl) esters of phosphonic acids and acetic acid. The fundamental idea was to increase the proportion of in situ generated water by taking advantage of the easier ester formation of acetic acid. We will show that this approach leads to the formation of titanium oxo clusters substituted by both phosphonate and acetate ligands with an increased degree of condensation.

Results and Discussion

Reaction of one molar equivalent of bis(trimethylsilyl) ethylphosphonate with two equivalents of acetic acid and four equivalents of $\text{Ti}(\text{O}i\text{Pr})_4$ led to the centrosymmetric cluster $[\text{Ti}_6(\mu_3\text{-O})_2(\mu_2\text{-O})_2(\mu_2\text{-O}i\text{Pr})_4(\text{O}i\text{Pr})_6(\text{OAc})_2(\text{O}_3\text{PET})_2]$ (**1**; Figure 1, $\text{OAc} =$ acetate), with a high degree of condensation (0.67). The cluster was, to the best of our knowledge, also the first mixed carboxylate-phosphonate titanium oxo cluster to be characterized. This new cluster type consists of a Ti_6O_4 cluster core with two parallel Ti_3O triangles connected by μ_2 -oxo and phosphonate bridges. The nearly cu-

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bic $\text{Ti}_6\text{P}_2\text{O}_{10}$ core resembles that of polyhedral oligomeric silsesquioxanes (POSS) with a Si_8O_{12} core. The titanium and phosphorus atoms form a distorted parallelepiped (Figure 2).

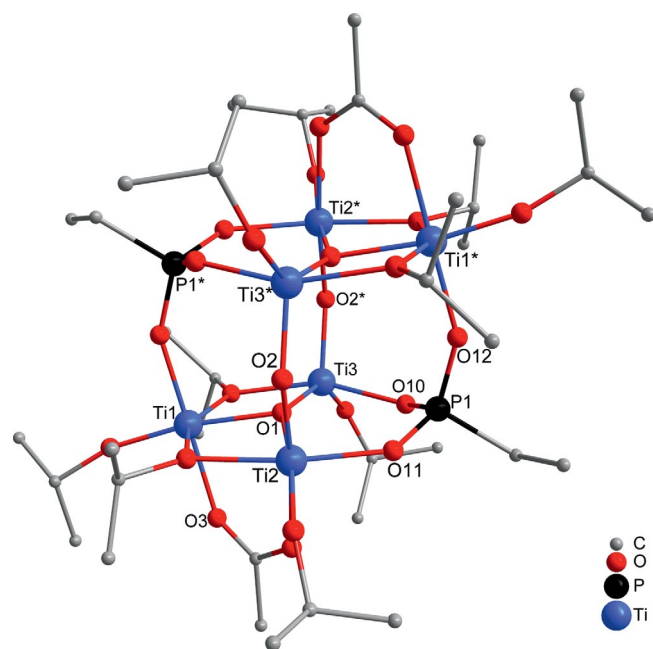


Figure 1. Molecular structure of $[\text{Ti}_6(\mu_3\text{-O})_2(\mu_2\text{-O})_2(\mu_2\text{-O}i\text{Pr})_4(\text{O}i\text{Pr})_6(\text{OAc})_2(\text{O}_3\text{PEt})_2]$ (**1**). Hydrogen atoms are omitted for clarity.

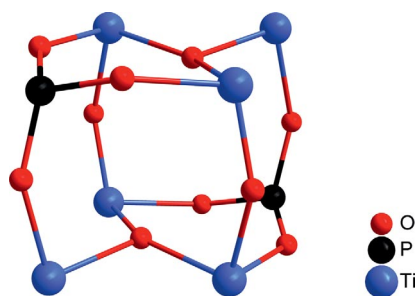


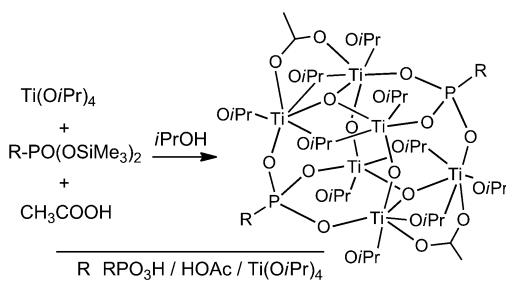
Figure 2. Core structure of the carboxylate-phosphonate-substituted titanium oxo clusters **1–7**. Isopropoxo and acetate ligands as well as the substituents at the phosphorus atoms are omitted for clarity.

In contrast to the previously obtained clusters with symmetrical, phosphonate-substituted $\text{Ti}_3(\mu_3\text{-O})(\mu_2\text{-O}i\text{Pr})_3(\text{O}i\text{Pr})_3$ units as the basic structural motif,^[4,5] the structure of **1** is based on unsymmetrically substituted $\text{Ti}_3(\mu_3\text{-O})(\mu_2\text{-O}i\text{Pr})_2(\text{O}i\text{Pr})_3(\mu_2\text{-OAc})$ units. Two Ti atoms (Ti1 and Ti2) of this unit are bridged by both an *OiPr* and an acetate ligand, whereas Ti1 and Ti3 are singly bridged by a $\mu_2\text{-O}i\text{Pr}$ group. A terminal *OiPr* ligand is coordinated to each Ti atom. The two Ti_3O triangles are connected through a $\mu_2\text{-O}$ unit between Ti2 and Ti3* (* denotes the symmetry-related atom in the second Ti_3O unit) as well as two phosphonate ligands connecting Ti2, Ti3 and Ti1* (and Ti2*, Ti3*, Ti1, respectively). The acetate-bridged atoms Ti1 and Ti2 are thus octahedrally coordinated, whereas Ti3 has a

distorted trigonal bipyramidal coordination sphere. Because of the asymmetric substitution of the Ti_3O triangle, the $\mu_3\text{-O}$ (O1) is not in the center of the triangle but has instead a significantly shorter distance to Ti3 [190.61(6) pm] than to the octahedrally coordinated atoms Ti1 and Ti2 [198.04(6) and 199.58(5) pm]. Otherwise, the Ti–O bond lengths at the five-coordinate Ti3 are longer than the corresponding distances of Ti1 and Ti2.

The core of the structure of **1** is comparable to that of $[\text{Ti}_6(\mu_3\text{-O})_2(\mu_2\text{-O})_2(\mu_2\text{-O}i\text{Pr})_4(\text{O}i\text{Pr})_6(\text{O}_3\text{SiFIMe})_2(\text{PhNH}_2)_2]$ (F1 = 9-methylfluorenyl),^[9] although all titanium atoms in the titanasiloxane structure are five-coordinate.

In contrast to reactions of $\text{Ti}(\text{O}i\text{Pr})_4$ with bis(trimethylsilyl) phosphonates in the absence of acetic acid,^[5] a series of isostructural clusters $[\text{Ti}_6\text{O}_4(\text{O}i\text{Pr})_{10}(\text{OAc})_2(\text{O}_3\text{PR})_2]$ was obtained both with much bulkier groups at the phosphorus atom, such as R = $\text{CH}_2\text{-naphthyl}$ (**2**), and with functional organic groups, such as R = vinyl (**3**), allyl (**4**), or $\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ (**5**) [Equation (1)]. This cluster type therefore appears to be rather robust. With one exception (see below) we obtained this cluster type for the $\text{RPO}_3\text{H}/\text{HOAc}/\text{Ti}(\text{O}i\text{Pr})_4$ ratio of 1:1:2. In some cases this ratio was varied slightly for the preparation of **1–5**, from 1:1:2 to 1:2:3 and 1:2:4, but the same cluster was always obtained. Note that, in each case, the molar ratio of $(\text{RPO}_3\text{H} + \text{HOAc})$ did not exceed that of $\text{Ti}(\text{O}i\text{Pr})_4$.



R $\text{RPO}_3\text{H} / \text{HOAc} / \text{Ti}(\text{O}i\text{Pr})_4$

- | | | |
|---|--|--------------|
| 1 | Et | 1:1:2, 1:2:4 |
| 2 | $\text{CH}_2\text{-naphthyl}$ | 1:1:2 |
| 3 | vinyl | 1:1:2 |
| 4 | allyl | 1:1:2, 1:2:3 |
| 5 | $\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ | 1:1:2, 1:2:4 |
| 6 | benzyl | 1:2:3 |
| 7 | $\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ | 1:2:4, 1:2:3 |

(1)

Clusters **1–5** crystallized from the reaction mixture at room temperature within several weeks. To obtain the cluster faster and in higher yield, the synthesis of **1**, as an example, was repeated by heating the reaction mixture (1:2:3) to reflux overnight. The NMR spectra of the resulting powder were the same as those of the sample prepared at room temperature. With this faster preparation process, the isostructural clusters **6** (R = CH_2Ph) and **7** (R = $\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$) were additionally obtained. It can be assumed that clusters **2–5** can also be more rapidly obtained by this modification of the synthesis. Cluster **7** was only obtained for $\text{RPO}_3\text{H}/\text{HOAc}/\text{Ti}(\text{O}i\text{Pr})_4$ ratios of 1:2:4 or 1:2:3; surprisingly, for a 1:1:2 ratio another cluster was obtained (see below for cluster **8**).

Clusters **1–7** were well-soluble in organic solvents. Their NMR spectra were very similar, and were consistent with the solid-state structures (see the Supporting Information), which shows that the clusters are stable in solution and are not in equilibrium with other structures. The ^1H NMR spectroscopic data of **1–7** show five doublets for the CH_3 of the *OiPr* ligands, although the signals of two bridging *OiPr* ligands overlap at about 1.7 ppm; the other three doublets partly overlap at 1.3–1.5 ppm. For the CH group of the *OiPr* ligands, three different multiplets were found, in a few cases two of them partly overlap. The singlet for the CH_3 group of the acetate ligands was observed at about 2.0 ppm. Only one signal between 10 and 30 ppm was observed in the ^{31}P NMR spectra, indicating that the clusters are centrosymmetric in solution. ^{13}C NMR spectra were in good agreement with the ^1H NMR spectroscopic data, with six signals for the CH_3 groups at 23–26 ppm, three signals for the CH groups at 76–79 ppm, and one signal at around 180 ppm for the carboxylate ligand.

Upon reaction of the aforementioned bis(trimethylsilyl) phosphonates with acetic acid and $\text{Ti}(\text{O}i\text{Pr})_4$ in a 1:1:2 ratio, in one case another cluster type was obtained. Reaction of bis(trimethylsilyl) 3-bromopropylphosphonate at room temperature reproducibly resulted in the cluster $[\text{Ti}_5(\mu_3\text{-O})(\mu_2\text{-O}i\text{Pr})_4(\text{O}i\text{Pr})_7(\text{OAc})(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{Br})_3]$ (**8**), the structure of which (Figure 3) is related to those of previously observed clusters $[\text{Ti}_4(\mu_3\text{-O})(\mu_2\text{-O}i\text{Pr})_3(\text{O}i\text{Pr})_5(\text{O}_3\text{PR})_3\text{L}]$ (L = neutral ligand).^[4,5] The latter consist of a symmetrical $\text{Ti}_3(\mu_3\text{-O})(\mu_2\text{-O}i\text{Pr})_3(\text{O}i\text{Pr})_3$ unit to which a $\text{Ti}(\text{O}i\text{Pr})_2\text{L}$ group is connected by means of three phosphonate ligands coordinating to two of the Ti atoms of the Ti_3O triangle and the capping Ti atom. In **8**, the capping $\text{Ti}(\text{O}i\text{Pr})_2\text{L}$

group is replaced by a $\text{Ti}_2(\mu_2\text{-O}i\text{Pr})(\text{O}i\text{Pr})_4(\mu_2\text{-OAc})$ moiety. Two of the phosphonate ligands are coordinated to only one Ti atom of the Ti_2 unit, whereas the third bridges both of them. This phosphonate ligand has a binding mode of 4.211 (*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*]^[10]), whereas the other two phosphonate ligands, as well as those in the cluster **1–7**, have a 3.111 binding mode. The $\text{Ti}_2(\mu_2\text{-O}i\text{Pr})(\text{O}i\text{Pr})_4(\mu_2\text{-OAc})$ moiety in **8** is structurally related to $\text{Ti}_2(\text{OR})_6(\mu_2\text{-OOCR}')_2$.^[11]

The solution ^1H NMR spectrum showed several overlapping signals in the region of 1.2–2.0 ppm that can be assigned to the CH_3 groups of *OiPr* as well as to the PCH_2 group. The CH signals of *OiPr* appear at 4.6–5.4 ppm as five multiplets. The two well-separated triplets for the CH_2Br group at $\delta = 3.52$ and 3.71 ppm have an intensity ratio of 1:2. The same is true for the two resonances at $\delta = 27.44$ and 30.34 ppm in the ^{31}P NMR spectrum. This is in good agreement with the structure in the crystalline state. Solution ^{13}C NMR spectroscopic data confirm the ^1H NMR spectroscopic data, with corresponding signals at 23–25 ppm for CH_3 and 77–80 ppm for CH groups. Two doublets were found for each CH_2 group of the bromopropyl moiety; the signals of the P- CH_2 groups could not be unequivocally assigned.

Another Ti_5 cluster was obtained from the reaction of bis(trimethylsilyl) 3,5-dimethylphenylphosphonate with $\text{Ti}(\text{O}i\text{Pr})_4$ and acetic acid (1:2:2). $[\text{Ti}_5(\mu_3\text{-O})_2(\mu_2\text{-O})(\mu_2\text{-O}i\text{Pr})_2(\text{O}i\text{Pr})_4(\text{OAc})_4(\text{O}_3\text{P-xylyl})_2]$ (**9**; Figure 4) consists of five octahedrally coordinated titanium atoms that form two corner-sharing Ti_3O triangles (Ti1, Ti2, Ti3 and Ti3, Ti4, Ti5), tilted by 52.2° . The cluster has a noncrystallographic C_2

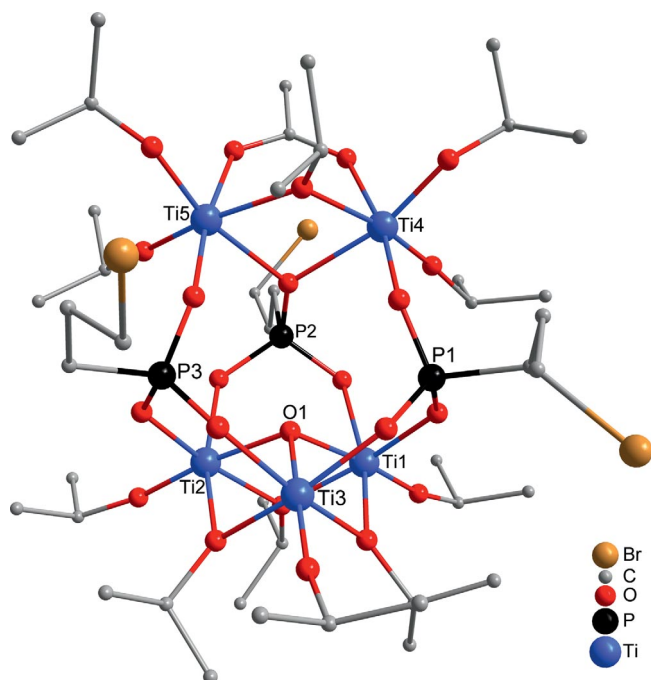


Figure 3. Molecular structure of $[\text{Ti}_5(\mu_3\text{-O})(\mu_2\text{-O}i\text{Pr})_4(\text{O}i\text{Pr})_7(\text{OAc})(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{Br})_3]$ (**8**). Hydrogen atoms are omitted for clarity.

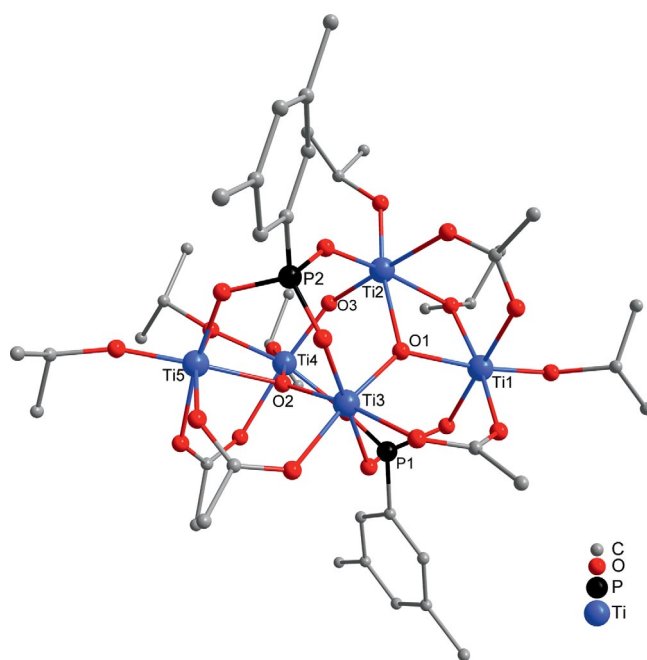


Figure 4. Molecular structure of $[\text{Ti}_5(\mu_3\text{-O})_2(\mu_2\text{-O})(\mu_2\text{-O}i\text{Pr})_2(\text{O}i\text{Pr})_4(\text{OAc})_4(\text{O}_3\text{P-xylyl})_2]$ (**9**). Hydrogen atoms are omitted for clarity.

axis passing through the μ_2 -oxygen O3 and Ti5, thus rendering the two Ti_3O units chemically equivalent. The Ti_3O units have the composition $Ti_3(\mu_3-O)(\mu_2-OiPr)(OiPr)_2(\mu_2-OAc)_2$ and can be derived from the basic structural motif $Ti_3(\mu_3-O)(\mu_2-OiPr)_3(OiPr)_3$ in the previously obtained acetate-free clusters^[4,5] and in **8**, and the monosubstituted unit $Ti_3(\mu_3-O)(\mu_2-OiPr)_2(OiPr)_3(\mu_2-OAc)$ in **1**. The Ti_3O triangles are connected with each other by one μ_2 -O and two phosphonate ligands in a 3.111 binding mode. The central Ti3 atom is coordinated by an oxygen atom of both phosphonate ligands and the other four Ti atoms are coordinated by the oxygen atoms of just one phosphonate ligand.

Cluster **9** has another degree of condensation (0.6) and a higher proportion of acetate ligands than the Ti_5 cluster **8** or the Ti_6 clusters **1–7**. This is attributed to the higher amount of acetic acid used for the preparation, which apparently led to the higher proportion of acetate ligands in the product. The steric hindrance and the increased acidity of xylylphosphonic acid (aromatic phosphonic acids are slightly more acidic) possibly play an additional role. In previous experiments, when only phosphonates were treated with $Ti(OiPr)_4$, the steric bulk of the phosphonate substituents had a significant influence on the cluster structure.^[5]

The approximate C_2 symmetry is retained in solution because only one signal was observed in the ^{31}P NMR spectrum. The solution 1H NMR spectrum shows three singlets for the xylyl CH groups at $\delta = 6.91, 8.03$ and 8.08 ppm and three multiplets for the isopropoxy CH groups at $\delta = 5.07, 5.22$ and 5.66 ppm. One singlet at $\delta = 2.18$ ppm was assigned to the CH_3 groups of the xylyl moieties and two singlets at $\delta = 1.95$ and 1.98 ppm to the two acetate ligands. These signals are consistent with respect to shift, number and intensity with the solid-state structure.

Five doublets were found for the CH_3 groups of the OiPr ligands. Their total intensity corresponded to the calculated value, but only three were expected because of the C_2 symmetry. Two doublets at $\delta = 1.90$ and 1.91 ppm overlap with a shift difference of only 0.01 ppm and can be assigned to the two bridging OiPr ligands, which should be symmetry-equivalent. It is therefore assumed that rotation around the O–CH bond is hindered, resulting in different chemical shifts for the two CH_3 groups. The same can be assumed for one of the terminal CH_3 groups (possibly interacting with each other) leading to two doublets at $\delta = 1.46$ and 1.51 ppm. The other two terminal OiPr ligands show a doublet at $\delta = 1.54$ ppm. The same observations were made in the ^{13}C NMR spectrum. The increased number of signals in the CH_3 region is also attributed to sterically hindered rotation of the OiPr groups.

Conclusions

We have shown that addition of acetic acid to an appropriate mixture of reactants does indeed result in a higher degree of condensation of the obtained oxo clusters compared with the clusters prepared from only bis(trimethylsilyl)phosphonates. This is attributed to the easier esterifica-

tion of acetic acid compared with phosphonic acids. The higher condensation ratio goes hand in hand with incorporation of acetate ligands in the coordination sphere of the clusters; the new titanium oxo clusters are the first examples of a mixed ligand sphere containing carboxylate, phosphonate and alkoxy ligands.

Whereas reactions of $Ti(OR)_4$ with carboxylic acids lead to a great variety of cluster types, depending on the OR group, the acid, and the $Ti(OR)_4$ /acid ratio,^[3] the reaction with various phosphonates and acetic acid led to the same cluster type $[Ti_6O_4(OiPr)_{10}(OAc)_2(O_3PR)_2]$ (**1–7**), which therefore appears to be a rather robust structural entity. The cluster core has an inversion center, and therefore the phosphonate ligands are opposite to each other. Because phosphonate ligands with functional organic groups are easily introduced, reactions of these groups should be possible, e.g., polymerization, thiol-en or addition reactions, by which chains of clusters and hybrid materials with anisotropic structures could be generated.

Experimental Section

General Methods: Manipulations were carried out under an argon atmosphere using standard Schlenk and glove box techniques. Diethyl ethylphosphonate, diethyl (3-bromopropyl)phosphonate, diethyl vinylphosphonate, allyl bromide, 1-bromo-3-chloropropane, benzyl bromide, 1-bromo-3,5-dimethylbenzene, 2-(bromomethyl)naphthalene, triethyl phosphite and $Ti(OiPr)_4$ were purchased from Sigma–Aldrich and used as received. Diethyl (3,5-dimethylphenyl)phosphonate was prepared as reported.^[12] Other diethyl phosphonates were prepared by reaction of the corresponding bromide with triethyl phosphite for 16 h in a Dean–Stark apparatus at $150^\circ C$ and purified by distillation.

The bis(trimethylsilyl) esters were prepared by adding bromotrimethylsilane (3 equiv.) to a solution of the corresponding diethyl phosphonate (1 equiv.) in CH_2Cl_2 followed by removing all volatiles in vacuo and characterization of the compounds by ^{31}P and 1H NMR spectroscopy.

Isopropyl alcohol was dried by heating to reflux over sodium and distillation. Samples for NMR measurements were obtained by washing the crystalline compounds with isopropyl alcohol and drying. Acetic acid was purified by distillation from P_4O_{10} .

The given yields refer to crystallized compounds. No attempts were made to increase the crystal crop; i.e., the actual yields were higher.

[$Ti_6O_4(OiPr)_{10}(OAc)_2(O_3PEt)_2$] (1**):** Bis(trimethylsilyl) ethylphosphonate (184 mg, 0.72 mmol) was added to $Ti(OiPr)_4$ (840 μL , 2.9 mmol) in isopropyl alcohol (3 mL). Acetic acid (83 μL , 1.4 mmol) was then quickly added. Cluster **1** crystallized after eight weeks, yield 200 mg (43%). 1H NMR (250 MHz, C_6D_6): $\delta = 1.30$ – 1.48 (m, 4 H, CH_2CH_3), 1.37 (d, $J = 5.98$ Hz, 12 H, $CHCH_3$), 1.40 (d, $J = 6.05$ Hz, 12 H, $CHCH_3$), 1.52 (d, $J = 6.08$ Hz, 12 H, $CHCH_3$), 1.63– 1.79 (m, 4 H, CH_2), 1.78 (d, $J = 6.28$ Hz, 12 H, $CHCH_3$), 1.84 (d, $J = 6.30$ Hz, 12 H, $CHCH_3$), 2.00 (s, 6 H, CCH_3), 4.84 (m, $J = 6.20$ Hz, 2 H, CH), 5.03 (m, $J = 6.12$ Hz, 4 H, CH), 5.36 (m, $J = 6.28$ Hz, 4 H, CH) ppm. ^{31}P NMR (101.2 MHz, C_6D_6): $\delta = 18.0$ ppm. ^{13}C NMR (62.9 MHz, C_6D_6): $\delta = 7.45$ (d, $J = 6.73$ Hz, CH_3), 20.00 (d, $J = 158.1$ Hz, CH_2), 23.62 (s, CH_3), 23.97 (s, CH_3), 24.25 (s, CH_3), 24.70 (s, CH_3), 25.22 (s, CH_3), 25.31 (s, CH_3), 77.48 (s, CH), 78.45 (s, CH), 79.21 (s, CH), 177.87 (s, COO) ppm.

[Ti₆O₄(OiPr)₁₀(OAc)₂(O₃PCH₂C₁₀H₇)₂] (2): Ti(OiPr)₄ (627 μL, 2.16 mmol) was added to a solution of CH₃COOH (62 μL, 1.08 mmol) and bis(trimethylsilyl) (naphthylmethyl)phosphonate (396 mg, 1.08 mmol) in isopropyl alcohol (2 mL). After 5 min stirring, the flask allowed to stand for crystallization at room temperature. Crystals of **2** were obtained after three months, yield 200 mg (25%). ¹H NMR (400 MHz, C₆D₆): δ = 1.30 (d, *J* = 5.68 Hz, 12 H, CHCH₃), 1.41 (d, *J* = 6.16 Hz, 12 H, CHCH₃), 1.44 (d, *J* = 5.32 Hz, 12 H, CHCH₃), 1.61 (d, *J* = 6.04 Hz, 12 H, CHCH₃), 1.67 (d, *J* = 5.32 Hz, 12 H, CHCH₃), 1.89 (s, 6 H, CCH₃), 3.32 (d, *J*_{P,H} = 22.65 Hz, 4 H, PCH₂), 4.85 (m, *J* = 6.16 Hz, 2 H, CH), 4.95 (m, 4 H, CH), 5.23 (m, *J* = 6.06 Hz, 4 H, CH), 7.33 (t, *J* = 7.43 Hz, 2 H, CH_{Ar}), 7.39 (t, *J* = 7.63 Hz, 2 H, CH_{Ar}), 7.76 (d, *J* = 8.00 Hz, 2 H, CH_{Ar}), 7.84 (d, *J* = 9.04 Hz, 2 H, CH_{Ar}), 7.85 (d, *J* = 6.61 Hz, 2 H, CH_{Ar}), 7.89 (d, *J* = 7.72 Hz, 4 H, CH_{Ar}) ppm. ³¹P NMR (162 MHz, C₆D₆): δ = 11.58 ppm. ¹³C NMR (100.6 MHz, C₆D₆): δ = 23.49 (CHCH₃), 23.81 (CHCH₃), 24.16 (CHCH₃), 24.87 (CHCH₃), 25.31 (CCH₃), 35.23 (d, *J* = 151.8 Hz, PCH₂), 77.75 (CHCH₃), 78.71 (CHCH₃), 79.27 (CHCH₃), 125.10 (CH_{Ar}), 125.54 (CH_{Ar}), 127.25 (CH_{Ar}), 128.74 (d, *J* = 8.78 Hz, CH_{Ar}), 129.32 (d, *J* = 4.61 Hz, CCH₂Ar), 132.48 (CH_{Ar}), 132.56 (CH_{Ar}), 132.64 (d, *J* = 9.67 Hz, CH_{Ar}), 133.87 (C_{Ar}), 133.92 (C_{Ar}), 177.95 (COO) ppm.

[Ti₆O₄(OiPr)₁₀(OAc)₂(O₃P-vinyl)₂] (3): Bis(trimethylsilyl) vinylphosphonate (0.45 M in CH₂Cl₂, 2 mL, 0.9 mmol) was added to Ti(OiPr)₄ (522 μL, 1.8 mmol) in isopropyl alcohol (1 mL). Acetic acid (51.5 μL, 0.9 mmol) was then quickly added. After five months the CH₂Cl₂ was removed, and after an additional two weeks, crystals of **3** were obtained, yield 80 mg (21%). ¹H NMR (250 MHz, CDCl₃): δ = 1.38 (d, *J* = 6.16 Hz, 12 H, CHCH₃), 1.39 (d, *J* = 6.16 Hz, 12 H, CHCH₃), 1.52 (d, *J* = 6.10 Hz, 12 H, CHCH₃), 1.80 (d, *J* = 6.32 Hz, 12 H, CHCH₃), 1.84 (d, *J* = 6.32 Hz, 12 H, CHCH₃), 1.99 (s, 6 H, CCH₃), 4.85 (m, *J* = 6.20 Hz, 2 H, CH), 5.05 (m, *J* = 6.12 Hz, 4 H, CH), 5.38 (m, *J* = 6.28 Hz, 4 H, CH), 5.72 (ddd, *J*_{P,H} = 49.52, *J*_{trans} = 12.00, *J*_{cis} = 3.48 Hz, 4 H, CH=CH₂), 6.21–6.56 (m, 4 H, CH=CH₂) ppm. ³¹P NMR (101.2 MHz, C₆D₆): δ = 15.80 ppm. ¹³C NMR (62.9 MHz, C₆D₆): δ = 23.61 (CHCH₃), 23.97 (CHCH₃), 24.28 (CHCH₃), 24.72 (CHCH₃), 25.26 (CHCH₃), 25.32 (CCH₃), 77.78 (CHCH₃), 78.66 (CHCH₃), 79.49 (CHCH₃), 128.95 (s, CH₂), 130.69 (d, *J* = 203.96 Hz, CH=CH₂), 177.98 (COO) ppm.

[Ti₆O₄(OiPr)₁₀(OAc)₂(O₃P-allyl)₂] (4): Bis(trimethylsilyl) allylphosphonate (400 mg, 1.6 mmol) was added to Ti(OiPr)₄ (930 μL, 3.2 mmol) in isopropyl alcohol (2 mL), then acetic acid (91 μL, 1.6 mmol) was quickly added. Crystals of **4** were obtained after three weeks, yield 500 mg (48%). ¹H NMR (250 MHz, CD₂Cl₂): δ = 1.11 (d, *J* = 6.13 Hz, 12 H, CHCH₃), 1.20 (d, *J* = 6.10 Hz, 12 H, CHCH₃), 1.34 (d, *J* = 6.23 Hz, 12 H, CHCH₃), 1.43 (d, *J* = 6.33 Hz, 12 H, CHCH₃), 1.47 (d, *J* = 6.48 Hz, 12 H, CHCH₃), 1.90 (s, 6 H, CCH₃), 2.43 (dd, *J*_{H,H} = 7.4, *J*_{P,H} = 23.0 Hz, 4 H, CH=CH₂), 4.73 (m, 6 H, CH), 4.97 (m, 4 H, CH), 5.09 (m, 4 H, CH=CH₂), 5.90 (m, 2 H, CH=CH₂) ppm. ³¹P NMR (101.2 MHz, CD₂Cl₂): δ = 11.9 ppm. ¹³C NMR (62.9 MHz, CD₂Cl₂): δ = 23.38 (s, CH₃), 23.61 (s, CH₃), 23.76 (s, CH₃), 24.38 (s, CH₃), 24.77 (s, CH₃), 24.89 (s, CH₃), 32.85 (d, *J* = 154.13 Hz, PCH₂), 77.21 (s, CH), 78.52 (s, CH), 80.05 (s, CH), 117.12 (d, *J* = 14.96 Hz, CH₂), 130.66 (d, *J* = 11.47 Hz, CH), 177.70 (s, COO) ppm.

[Ti₆O₄(OiPr)₁₀(OAc)₂(O₃PCH₂CH₂CH₂Cl)₂] (5): Bis(trimethylsilyl) (3-chloropropyl)phosphonate (224 mg, 0.74 mmol) was added to Ti(OiPr)₄ (860 μL, 3.0 mmol) in isopropyl alcohol (3 mL), then acetic acid (85 μL, 1.5 mmol) was quickly added. Cluster **5** crystallized after three weeks, yield 100 mg (20%). ¹H NMR (250 MHz,

CD₂Cl₂): δ = 1.13 (d, *J* = 6.00 Hz, 12 H, CHCH₃), 1.21 (d, *J* = 5.95 Hz, 12 H, CHCH₃), 1.35 (d, *J* = 6.05 Hz, 12 H, CHCH₃), 1.45 (d, *J* = 5.80 Hz, 12 H, CHCH₃), 1.47 (d, *J* = 5.33 Hz, 12 H, CHCH₃), 1.71 (m, *J*_{H,H} = 7.30, *J*_{P,H} = 18.72 Hz, 4 H, PCH₂), 1.92 (s, 6 H, CCH₃), 2.15 (m, 4 H, CH₂), 3.75 (t, *J* = 6.71 Hz, 4 H, CH₂Cl), 4.76 (m, *J* = 6.58 Hz, 6 H, CH), 4.98 (m, *J* = 6.16 Hz, 4 H, CH) ppm. ³¹P NMR (101.2 MHz, CD₂Cl₂): δ = 15.44 ppm. ¹³C NMR (62.9 MHz, CD₂Cl₂): δ = 23.59 (s, CH₃), 23.91 (s, CH₃), 24.25 (s, CH₃), 24.37 (d, *J* = 157.3 Hz, PCH₂), 24.71 (s, CH₃), 25.28 (s, CH₃), 27.57 (d, *J* = 4.94 Hz, CH₂), 44.94 (d, *J* = 12.97 Hz, CH₂Cl), 77.82 (s, CH), 78.70 (s, CH), 79.54 (s, CH), 178.13 (s, COO) ppm.

[Ti₆O₄(OiPr)₁₀(OAc)₂(O₃PCH₂Ph)₂] (6): Ti(OiPr)₄ (2.8 mL, 9.5 mmol) and acetic acid (365 μL, 6.4 mmol) were added to a solution of bis(trimethylsilyl) benzylphosphonate (1 g, 3.2 mmol) in isopropyl alcohol (20 mL). After heating to reflux overnight and cooling to room temperature, a cloudy mixture was obtained. The suspension was concentrated under vacuum and filtered. After washing two times with small portions of *i*PrOH and drying, a white powder of **6** was obtained. Part of the powder was crystallized from CH₂Cl₂, yield 1 g (45%). ¹H NMR (250 MHz, CDCl₃): δ = 1.34 (d, *J* = 6.13 Hz, 12 H, CHCH₃), 1.42 (d, *J* = 6.20 Hz, 12 H, CHCH₃), 1.47 (d, *J* = 6.10 Hz, 12 H, CHCH₃), 1.67 (d, *J* = 6.25 Hz, 12 H, CHCH₃), 1.73 (d, *J* = 6.23 Hz, 12 H, CHCH₃), 1.98 (s, 6 H, CCH₃), 3.19 (d, *J*_{P,H} = 22.54 Hz, 4 H, PCH₂), 4.87 (m, *J* = 6.21 Hz, 2 H, CH), 4.97 (m, *J* = 6.04 Hz, 4 H, CH), 5.25 (m, *J* = 6.24 Hz, 4 H, CH), 7.2 (m, 2 H, CH_{Ph}), 7.33 (t, *J* = 7.66 Hz, 4 H, CH_{Ph}), 7.64 (d, *J* = 7.49 Hz, 4 H, CH_{Ph}) ppm. ³¹P NMR (101.2 MHz, CDCl₃): δ = 23.6 ppm. ¹³C NMR (62.9 MHz, C₆D₆): δ = 23.62 (CHCH₃), 23.84 (CHCH₃), 24.20 (CHCH₃), 24.86 (CHCH₃), 25.35 (CCH₃), 34.94 (d, *J* = 152.2 Hz, PCH₂), 77.73 (CHCH₃), 78.69 (CHCH₃), 79.16 (CHCH₃), 125.83 (d, *J* = 2.96 Hz, CH_{Ph}), 130.51 (d, *J* = 6.82 Hz, CH_{Ph}), 134.91 (d, *J* = 9.07 Hz, C_{Ar}CH₂), 177.88 (COO) ppm.

[Ti₆O₄(OiPr)₁₀(OAc)₂(O₃PCH₂CH₂CH₂Br)₂] (7): Ti(OiPr)₄ (29 mL, 100 mmol) and acetic acid (3.83 mL, 67 mmol) were added to a solution of bis(trimethylsilyl) (3-bromopropyl)phosphonate (11.63 g, 33.4 mmol) in *i*PrOH (50 mL). After heating to reflux overnight and cooling to room temperature, a cloudy mixture was obtained. The suspension was concentrated under vacuum and filtered. After washing two times with *n*-hexane and drying, a white powder of **7** was obtained. For single-crystal measurements, part of the powder was crystallized from CH₂Cl₂, yield 8 g (33%). ¹H NMR (250 MHz, C₆D₆): δ = 1.37 (d, *J* = 6.15 Hz, 12 H, CHCH₃), 1.41 (d, *J* = 6.40 Hz, 12 H, CHCH₃), 1.51 (d, *J* = 6.08 Hz, 12 H, CHCH₃), 1.71 (m, 4 H, PCH₂), 1.76 (d, *J* = 6.16 Hz, 12 H, CHCH₃), 1.82 (d, *J* = 5.90 Hz, 12 H, CHCH₃), 2.04 (s, 6 H, CCH₃), 2.35 (m, *J*_{H,H} = 7.23, *J*_{P,H} = 17.30 Hz, 4 H, CH₂), 3.52 (t, *J* = 7.35 Hz, 4 H, CH₂Br), 4.85 (m, *J* = 6.20 Hz, 2 H, CH), 5.00 (m, *J* = 6.00 Hz, 4 H, CH), 5.33 (m, *J* = 6.28 Hz, 4 H, CH) ppm. ³¹P NMR (101.2 MHz, C₆D₆): δ = 15.5 ppm. ¹³C NMR (62.9 MHz, C₆D₆): δ = 23.64 (s, CH₃), 23.91 (s, CH₃), 24.25 (s, CH₃), 24.74 (s, CH₃), 25.29 (s, CH₃), 25.33 (s, CH₃), 25.71 (d, *J* = 157.2 Hz, PCH₂), 27.85 (d, *J* = 4.49 Hz, CH₂), 33.71 (d, *J* = 12.98 Hz, CH₂Br), 77.83 (s, CH), 78.70 (s, CH), 79.54 (s, CH), 178.14 (s, COO) ppm.

[Ti₅O(OiPr)₁₁(OAc)(O₃PCH₂CH₂CH₂Br)₃] (8): Bis(trimethylsilyl) (3-bromopropyl)phosphonate (233 mg, 0.67 mmol) was added to Ti(OiPr)₄ (388 μL, 1.34 mmol) in isopropyl alcohol (2 mL), then acetic acid (38.3 μL, 0.67 mmol) was quickly added. Cluster **8** crystallized after 12 weeks, yield 100 mg (26%). ¹H NMR (250 MHz, C₆D₆): δ = 1.38 (d, *J* = 7.90 Hz, 6 H, CHCH₃), 1.41 (d, *J* = 6.40 Hz,

6 H, CHCH₃), 1.45 (d, *J* = 6.15 Hz, 18 H, CHCH₃), 1.51 (d, *J* = 6.05 Hz, 6 H, CHCH₃), 1.63 (d, *J* = 6.30 Hz, 12 H, CHCH₃), 1.79 (m, 18 H, CHCH₃), 1.85–2.01 (m, 6 H, PCH₂), 2.04 (s, 3 H, CCH₃), 2.29–2.54 (m, 6 H, CH₂), 3.52 (t, *J* = 7.23 Hz, 2 H, CH₂Br), 3.71 (t, *J* = 6.40 Hz, 4 H, CH₂Br), 4.69 (m, *J* = 6.20 Hz, 2 H, CH), 4.84 (m, *J* = 6.28 Hz, 1 H, CH), 5.00 (m, *J* = 6.16 Hz, 2 H, CH), 5.16 (m, *J* = 6.44 Hz, 3 H, CH), 5.33 (m, *J* = 6.24 Hz, 3 H, CH) ppm. ³¹P NMR (101.2 MHz, C₆D₆): δ = 27.44 (1 P), 30.34 (2 P) ppm. ¹³C NMR (62.9 MHz, C₆D₆): δ = 23.65 (s, CH₃), 23.96 (s, CH₃),

24.26 (s, CH₃), 24.49 (s, CH₃), 24.74 (s, CH₃), 24.81 (s, CH₃), 25.22 (s, CH₃), 25.31 (s, CH₃), 26.95 (d, *J* = 4.52 Hz, CH₂), 27.86 (d, *J* = 4.99 Hz, CH₂), 33.73 (d, *J* = 12.59 Hz, CH₂Br), 35.82 (d, *J* = 15.06 Hz, CH₂Br), 77.84 (s, CH), 78.49 (s, CH), 78.73 (s, CH), 79.57 (s, CH), 79.82 (s, CH), 178.17 (s, COO) ppm.

[Ti₅O₃(OiPr)₆(OAc)₄(O₃P-xylyl)₂] (9): Bis(trimethylsilyl) xylylphosphonate (100 mg, 0.30 mmol) was added to a solution of Ti(OiPr)₄ (176 μL, 0.61 mmol) in isopropyl alcohol (1 mL), then

Table 1. Crystal data and structure refinement details for 1–9.

	1	2	3
Empirical formula	C ₃₈ H ₈₆ O ₂₄ P ₂ Ti ₆	C ₅₆ H ₉₄ O ₂₄ P ₂ Ti ₆	C ₃₈ H ₈₂ O ₂₄ P ₂ Ti ₆
Formula weight	1276.22	1500.65	1272.38
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [pm]	1226.23(6)	2259.5(2)	1206.87(6)
<i>b</i> [pm]	1649.58(9)	1682.61(13)	1664.31(8)
<i>c</i> [pm]	1464.69(7)	1830.97(15)	1460.95(8)
<i>α</i> [°]	90	90	90
<i>β</i> [°]	98.272(3)	91.538(3)	97.193(2)
<i>γ</i> [°]	90	90	90
<i>V</i> (pm ³ ·10 ⁶)	2931.9(3)	6958.5(10)	2911.4(3)
<i>Z</i>	2	4	2
<i>D_x</i> [Mg m ⁻³]	1.446	1.432	1.451
<i>μ</i> [mm ⁻¹]	0.904	0.774	0.91
Crystal size [mm]	0.5 × 0.5 × 0.5	0.5 × 0.5 × 0.4	0.5 × 0.4 × 0.3
Measured reflections	121208	93315	43475
Observed reflections	16514	10942	5034
[<i>I</i> > 2σ(<i>I</i>)]			
<i>θ</i> _{max.} [°]	42.84	33.22	26.41
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i>)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.0323, 0.0862, 1.037	0.0356, 0.1004, 1.043	0.0424, 0.1002, 1.106
Reflections/parameters	21197/418	13284/408	5971/448
Weighting scheme ^[a]	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0344 <i>P</i>) ² + 1.21 <i>P</i>]	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0417 <i>P</i>) ² + 14.8148 <i>P</i>]	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0344 <i>P</i>) ² + 9.7385 <i>P</i>]
δρ _{max.,min.} [e·10 ⁻⁶ pm ⁻³]	0.885, -1.307	1.246, -0.424	1.641, -0.957

[a] *P* = (*F*_o² + 2*F*_c²)/3.

Table 2. Crystal data and structure refinement details for 4–6.

	4	5	6
Empirical formula	C ₄₀ H ₈₆ O ₂₄ P ₂ Ti ₆	C ₄₀ H ₈₈ Cl ₂ O ₂₄ P ₂ Ti ₆	C ₅₀ H ₉₄ Cl ₄ O ₂₄ P ₂ Ti ₆
Formula weight	1300.43	1373.34	1570.39
Crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [pm]	1146.80(9)	1376.54(5)	2643.8(3)
<i>b</i> [pm]	1223.83(10)	1571.04(5)	1259.66(14)
<i>c</i> [pm]	1228.22(10)	1653.85(5)	2280.3(3)
<i>α</i> [°]	106.880(4)	90	90
<i>β</i> [°]	110.202(3)	112.1300(10)	108.761(4)
<i>γ</i> [°]	97.601(4)	90	90
<i>V</i> (pm ³ ·10 ⁶)	1495.2(2)	3313.13(19)	7190.8(14)
<i>Z</i>	1	2	4
<i>D_x</i> [Mg m ⁻³]	1.444	1.377	1.451
<i>μ</i> [mm ⁻¹]	0.888	0.883	0.896
Crystal size [mm]	0.3 × 0.3 × 0.3	0.5 × 0.4 × 0.4	0.32 × 0.27 × 0.23
Measured reflections	62482	88173	287456
Observed reflections	12261	5416	16780
[<i>I</i> > 2σ(<i>I</i>)]			
<i>θ</i> _{max.} [°]	36.35	28.95	30.58
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i>)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.0263, 0.0726, 1.036	0.0647, 0.2177, 1.094	0.044, 0.1256, 1.068
Reflections/parameters	14474/336	8720/443	21997/894
Weighting scheme ^[a]	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0313 <i>P</i>) ² + 0.6556 <i>P</i>]	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0889 <i>P</i>) ² + 3.5722 <i>P</i>]	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0517 <i>P</i>) ² + 11.3637 <i>P</i>]
δρ _{max.,min.} [e·10 ⁻⁶ pm ⁻³]	1.272, -0.362	0.741, -0.477	1.5, -1.368

[a] *P* = (*F*_o² + 2*F*_c²)/3.

Table 3. Crystal data and structure refinement details for 7–9.

	7	8	9
Empirical formula	C ₄₀ H ₈₈ Br ₂ O ₂₄ P ₂ Ti ₆	C ₄₄ H ₉₈ Br ₃ O ₂₃ P ₃ Ti ₅	C ₄₂ H ₇₂ O ₂₃ P ₂ Ti ₅
Formula weight	1462.26	1567.36	1246.44
Crystal system	orthorhombic	monoclinic	triclinic
Space group	<i>Pbc</i>	<i>P2₁/n</i>	<i>P1</i>
<i>a</i> [pm]	1632.40(3)	1308.99(7)	1210.96(6)
<i>b</i> [pm]	1585.18(3)	2291.37(13)	1284.46(7)
<i>c</i> [pm]	2401.10(4)	2346.81(13)	1908.81(11)
α [°]	90	90	101.464(3)
β [°]	90	102.299(2)	96.661(3)
γ [°]	90	90	96.627(3)
<i>V</i> (pm ³ ·10 ⁶)	6213.2(2)	6877.4(7)	2860.8(3)
<i>Z</i>	4	4	2
<i>D_x</i> [Mg m ⁻³]	1.563	1.514	1.447
μ [mm ⁻¹]	2.142	2.434	0.797
Crystal size [mm]	0.6 × 0.5 × 0.5	0.6 × 0.4 × 0.35	0.7 × 0.6 × 0.4
Measured reflections	196724	127718	137433
Observed reflections	10744	13683	
[<i>I</i> > 2σ(<i>I</i>)]			19253
θ_{\max} [°]	34.37	28.32	36.37
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i>)], <i>wR</i> [<i>F</i> ²], <i>S</i>	0.0222, 0.0571, 1.049	0.0567, 0.1487, 1.031	0.063, 0.1544, 1.084
Reflections/parameters	13047/345	16623/727	27635/789
Weighting scheme ^[a]	$w = 1/[\sigma^2(F_o^2) + (0.0251P)^2 + 2.6246P]$	$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 46.4092P]$	$w = 1/[\sigma^2(F_o^2) + (0.0160P)^2 + 9.9669P]$
$\delta\rho_{\max,\min}$ [e·10 ⁻⁶ pm ⁻³]	0.681, -0.423	5.461, -5.769	1.701, -1.112

[a] $P = (F_o^2 + 2F_c^2)/3$.

CH₃COOH (35 μ L, 0.61 mmol) was added. After 15 weeks, crystals of **9** were obtained, yield 200 mg (48%). ¹H NMR (250 MHz, C₆D₆): δ = 1.46 (d, *J* = 6.15 Hz, 6 H, CHCH₃), 1.51 (d, *J* = 6.78 Hz, 6 H, CHCH₃), 1.54 (d, *J* = 6.33 Hz, 12 H, CHCH₃), 1.90 (d, *J* = 6.20 Hz, 6 H, CHCH₃), 1.91 (d, *J* = 6.32 Hz, 6 H, CHCH₃), 1.95 (s, 6 H, CCH₃), 1.98 (s, 6 H, CCH₃), 2.18 (s, 12 H, CH₃(X_{yl})), 5.07 (m, *J* = 6.20 Hz, 2 H, CH), 5.22 (m, *J* = 6.12 Hz, 2 H, CH), 5.66 (m, *J* = 6.32 Hz, 2 H, CH), 6.91 (s, 2 H, CH_{Xyl}), 8.03 (s, 2 H, CH_{Xyl}), 8.08 (s, 2 H, CH_{Xyl}) ppm. ³¹P NMR (101.2 MHz, C₆D₆): δ = 15.92 ppm. ¹³C NMR (62.9 MHz, C₆D₆): δ = 20.92 (CH₃), 22.90 (CH₃), 23.30 (CH₃), 23.93 (CH₃), 24.05 (CH₃), 24.11 (CH₃), 24.16 (CH₃), 24.60 (CH₃), 24.77 (CH₃), 25.19 (CH₃), 80.57 (CHCH₃), 81.41 (CHCH₃), 82.27 (CHCH₃), 129.80 (d, *J* = 10.0 Hz, CH), 131.44 (d, *J* = 201.0 Hz, PC), 132.53 (d, *J* = 2.8 Hz, CH), 137.24 (d, *J* = 16.3 Hz, C), 177.87 (COO), 180.11 (COO) ppm.

X-ray Structure Analyses: All measurements were performed at 100 K using Mo-*K*_α (λ = 71.073 pm) radiation. Data were collected with a Bruker AXS SMART APEX II four-circle diffractometer with κ -geometry. Crystals of **5** cracked when cooled to 100 K; apparently a phase transition took place at about 180 K. The measurements of **5** were therefore carried out at 213 K. Data were collected with ϕ and ω -scans and different frame widths. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was employed. The cell dimensions were refined with all unique reflections. SAINT PLUS software (Bruker Analytical X-ray Instruments, 2007) was used to integrate the frames. Details of the X-ray investigations are given in Table 1 (for **1–3**), Table 2 (for **4–6**), and Table 3 (for **7–9**). The structures were solved by the Patterson method (SHELXS97^[13]). 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 by riding with the corresponding atom. Positions of disordered carbon and halogen atoms were refined with two sites, with about 50% occupancy each. Disordered groups: three OiPr ligands of **1**; one vinyl group of **3**; three OiPr

ligands and one chloropropyl group of **5**; four OiPr ligands and one dichloromethane of **6**; four OiPr ligands of **9**.

CCDC-981140 (for **1**), -981141 (for **2**), -981142 (for **3**), -981143 (for **4**), -981144 (for **5**), -981145 (for **6**), -981146 (for **7**), -981147 (for **8**), and -981148 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Copies of ¹H and ¹³C NMR spectra.

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