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 Ti(OiPr)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 [Ti6O4(OAc)2(O3PPr)2] (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, [Ti5O(OiPr)11(OAc)(O3PCH2CH2CH2Br)3] and [Ti5O3(OiPr)6(OAc)4(O3P-

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] Compared 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 Ti(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 Ti(OiPr)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 Ti(OiPr)4 led to the centrosymmetric cluster [Ti6(μ2-O)2(μ2-O)2(μ2-O)2(OiPr)6(OAc)2(PEt3)2] (I; Figure 1, 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 Ti6O3 cluster core with two parallel Ti3O triangles connected by μ2-oxo and phosphonate bridges. The nearly cu...
bic Ti₆P₂O₁₀ core resembles that of polyhedral oligomeric silsesquioxanes (POSS) with a Si₆O₁₂ core. The titanium and phosphorus atoms form a distorted parallelepiped (Figure 2).

Figure 1. Molecular structure of [Ti₆(μ₃-O)₂(μ₂-O)₂(μ₂-OiPr)₄(OiPr)₆(OAc)₂(O₃PEt)₂] (1). Hydrogen atoms are omitted for clarity.

In contrast to the previously obtained clusters with symmetrical, phosphonate-substituted Ti₃(μ₃-O)(μ₂-O)iPr₂(OiPr)₃(OAc)₂(O₃SiFlMe)₂(PhNH₂)₂, although all titanium atoms in the titanasiloxane structure are five-coordinate.

In contrast to reactions of Ti(OiPr)₄ with bis(trimethylsilyl) phosphonates in the absence of acetic acid,[5] a series of isostructural clusters [Ti₆O₄(OiPr)₁₀(OAc)₂(O₃PR)₂] was obtained both with much bulkier groups at the phosphorus atom, such as R = CH₂-naphthyl (2), and with functional organic groups, such as R = vinyl (3), allyl (4), or CH₂CH₂CH₂Cl (5) [Equation (1)]. This cluster type therefore appears to be rather robust. With one exception (see below) we obtained this cluster type for the RPO₃H/HOAc/Ti(OiPr)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 (RPO₃H + HOAc) did not exceed that of Ti(OiPr)₄.

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 = CH₂Ph) and 7 (R = CH₂CH₂CH₂Br) 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 RPO₃H/HOAc/Ti(OiPr)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).

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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 $^1$H NMR spectroscopic data of 1–7 show five doublets for the CH$_3$ of the OPr ligands, although the signals of two bridging OPr 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 OPr 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 $^{1}$H NMR spectroscopic data, with corresponding signals 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 Ti(OPr)$_4$ in a 1:1:2 ratio, in one case another cluster type was obtained. Reaction of bis(trimethylsilyl) 3-bromopropylphosphonate with acetic acid and Ti(OPr)$_4$ at room temperature reproducibly resulted in the cluster [Ti$_5$(μ$_2$-O)(μ$_2$-OPr)$_2$(OPr)$_3$(OAc)(O$_3$PCH$_2$CH$_2$CH$_2$Br)$_3$] (8), the structure of which (Figure 3) is related to those of previously observed clusters [Ti$_4$(μ$_2$-O)(μ$_2$-OPr)$_3$(OPr)$_3$(O$_3$P-Pr)$_3$L] (L = neutral ligand).$^{14,5}$ The latter consist of a symmetrical Ti$_3$(μ$_2$-O)(μ$_2$-OPr)$_3$(OPr)$_3$ unit to which a Ti(OPr)$_2$L group is connected by means of three phosphonate ligands coordinating to two of the Ti atoms of the Ti$_3$O triangle and the capping Ti atom. In 8, the capping Ti(OPr)$_2$L group is replaced by a Ti$_3$(μ$_2$-OPr)(OPr)$_3$(μ$_2$-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 Ti$_3$(μ$_2$-OPr)(OPr)$_3$(μ$_2$-OAc) moiety in 8 is structurally related to Ti$_2$(OR)$_2$(μ$_2$-OOCR)$_2$.$^{11}$

The solution $^1$H 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 OPr as well as to the PCH$_2$ moiety. The CH signals of OPr appear at 4.6–5.4 ppm as five multiplets. The two well-separated triplets for the CH$_2$Br group at δ = 3.52 and 3.71 ppm have an intensity ratio of 1:2. The same is true for the two resonances at δ = 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 $^1$H NMR spectroscopic data, with corresponding signals at 23–25 ppm for CH$_3$ and 77–80 ppm for CH$_2$ groups. Two doublets were found for each CH$_3$ 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 Ti(OPr)$_4$ and acetic acid (1:2:2). [Ti$_5$(μ$_2$-O)(μ$_2$-OPr)$_3$(O$_3$P-Pr)$_3$(O$_3$P-xylyl)] (9; Figure 4) consists of five octahedrally coordinated titanium atoms that form two corner-sharing Ti$_3$O triangles (T1, T2, T3 and T4, T5), tilted by 52.2°. The cluster has a noncrystallographic $C_2$
axis passing through the \( \mu_2\)-oxygen O3 and Ti5, thus rendering the two Ti3O units chemically equivalent. The Ti3O units have the composition Ti3(\{\mu_1-O\}2{\mu}_2-O(Pr)\{O(Pr)\}_3{\mu}_2-OAc\})_2 and can be derived from the basic structural motif Ti3(\{\mu_1-O\}2{\mu}_2-O(Pr)\{O(Pr)\}_3) in the previously obtained acetate-free clusters\(^{[4,5]}\) and in 8, and the monosubstituted unit Ti3(\{\mu_1-O\}2{\mu}_2-O(Pr)\{O(Pr)\}_2{\mu}_2-OAc\}) in 1. The Ti3O triangles are connected with each other by one \( \mu_2\)-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 Ti3 cluster 8 or the Ti5 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 sterically hindered and the increased acidity of xyllyphosphonic acid (aromatic phosphonic acids are slightly more acidic) possibly play an additional role. In previous experiments, when only phosphonates were treated with Ti(O(Pr))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 \(^1\)H NMR spectrum show three singlets for the xyllyl 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 CH3 groups of the xyllyl 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 CH3 groups of the O(Pr) 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 O(Pr) 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 CH3 groups. The same can be assumed for one of the terminal CH3 groups (possibly interacting with each other) leading to two doublets at \( \delta = 1.46 \) and 1.51 ppm. The other two terminal O(Pr) 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 CH3 region is also attributed to sterically hindered rotation of the O(Pr) 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 esterification 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 alkoxo 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 \([\text{Ti}_6\text{O}_4\text{(O}(\text{Pr})_3\text{(OAc)}_2\text{(O}_2\text{Pr})_3]\) (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 phosphate and Ti(O(Pr))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 phosphate for 16 h in a Dean–Stark apparatus at 150 °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 CH2Cl2 followed by removing all volatiles in vacuo and characterization of the compounds by \(^{31}\)P and \(^1\)H 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 P2O5.

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

\([\text{Ti}_6\text{O}_4\text{(O}(\text{Pr})_3\text{(OAc)}_2\text{(O}_2\text{Pr})_3]\) (1): Bis(trimethylsilyl) ethylphosphonate (184 mg, 0.72 mmol) was added to Ti(O(Pr))4 (840 \( \mu \)L, 2.9 mmol) in isopropyl alcohol (3 mL). Acetic acid (83 \( \mu \)L) was added in one portion at 150 °C and purified by distillation.

The yield of compound 1 was 200 mg (43%). \(^1\)H NMR (250 MHz, C6D6): \( \delta = 1.30–1.48 \) (m, 4 H, CH2CH3), 1.37 (d, \( J = 5.98 \) Hz, 12 H, CHCH3), 1.40 (d, \( J = 6.05 \) Hz, 12 H, CHCH3), 1.52 (d, \( J = 6.08 \) Hz, 12 H, CHCH3), 1.63–1.79 (m, 4 H, CH2), 1.78 (d, \( J = 6.28 \) Hz, 12 H, CHCH3), 1.84 (d, \( J = 6.30 \) Hz, 12 H, CHCH3), 2.00 (s, 6 H, CH3), 2.18 ppm. Three observations were made in the \(^{13}\)C NMR spectrum. The increased number of signals in the CH3 region is also attributed to sterically hindered rotation of the O(Pr) groups.

Theoretical calculations were carried out at the DFT level of theory with the B3LYP functional and the 6-311G(d,p) basis set. The geometries of the clusters were optimized with the B3LYP density functional, and the quantum mechanical calculations were carried out using the Gaussian 09 program. The electronic structures of all compounds were determined at the B3LYP/6-311G(d,p) level of theory. The geometries were optimized until the gradient was less than 0.001 au/\( \text{Å} \). The vibrational frequencies were calculated to confirm that the optimized structures were true minima. The bond lengths, bond angles and dihedral angles of all compounds were calculated at the same level of theory. The Mulliken charges were calculated for all compounds.
the CH2Cl2 was removed, and after an additional two weeks, crystals of 3.2 mmol) in isopropyl alcohol (2 mL), then acetic acid (91 μL, 0.9 mmol) was added. Crystals of 3-chloropropyl)phosphonate (224 mg, 0.74 mmol) were obtained, yield 80 mg (21%).

1H NMR (250 MHz, CD2Cl2): δ = 1.38 (d, J = 6.20 Hz, 2 H, CH). COO) ppm.

13C NMR (62.9 MHz, CD2Cl2): δ = 23.36 (CH(C6H5)), 23.84 (CH(C6H5)), 24.20 (CH(C6H5)), 24.86 (CH(C6H5)), 35.49 (CH(C6H5)), 39.49 (CH(C6H5)), 76.58 (CH(C6H5)), 79.42 (CH(C6H5)), 128.95 (C(C6H5)), 130.51 (d, J = 203.96 Hz, CH(C6H5)), 177.88 (COO) ppm.

[TiO(OPr)i(μ-ac)2(OCH2CH2Cl)2] (7): Ti(OPr)i (29 mL, 100 mmol) and acetic acid (3.83 mL, 67 mmol) were added to a solution of bis(trimethylsilyl) (3-bromopropyl)phosphonate (11.68 g, 33.4 mmol) in iPrOH (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 twice with small portions of iPrOH and drying, a white powder of 7 was obtained. For single-crystal measurements, part of the powder was crystallized from CH2Cl2, yield 1 g (33%).

1H NMR (250 MHz, C6D6): δ = 1.37 (d, J = 6.15 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 = 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), 7.33 (t, J = 7.66 Hz, 4 H, CH)), 7.64 (d, J = 7.49 Hz, 4 H, CH) ppm.

13P NMR (101.2 MHz, CD2Cl2): δ = 23.66 ppm.

1H NMR (250 MHz, C6D6): δ = 1.39 (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), 1.94 (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 (dd, JPH = 49.52, Jtrans = 12.00, Jcis = 3.48 Hz, 4 H, CH=CH2), 6.21–6.56 (m, 4 H, CH=CH2) ppm.

13C NMR (101.2 MHz, CD2Cl2): δ = 15.80 ppm. 13C NMR (62.9 MHz, CD2Cl2): δ = 23.61 (CH(C6H5)), 23.97 (CH(C6H5)), 24.28 (CH(C6H5)), 24.72 (CH(C6H5)), 25.26 (CH(C6H5)), 25.32 (CCH(C6H5)), 77.78 (CH(C6H5)), 78.66 (CH(C6H5)), 79.49 (CH(C6H5)), 128.95 (C(C6H5)), 130.69 (d, J = 203.96 Hz, CH(C6H5)), 177.98 (COO) ppm.

[TiO(OPr)i(ac)2(μ-CH2Cl)2]H2] (5): Bis(trimethylsilyl) (3-chloropropyl)phosphonate (224 mg, 0.67 mmol) was added to Ti(OPr)i (290 μL, 1.2 mmol) in isopropyl alcohol (2 mL), then acetic acid (85 μL, 1.5 mmol) was quickly added. Crystals of 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, JHH = 7.30, JEH = 18.72 Hz, 4 H, PCH2), 1.92 (s, 6 H, CCH3), 2.15 (m, 4 H, CH3), 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.

13C NMR (62.9 MHz, CD2Cl2): δ = 15.44 ppm. 13C NMR (62.9 MHz, CD2Cl2): δ = 23.59 (s, CH3), 31.91 (s, CH3), 24.25 (s, CH3), 24.37 (m, 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, CH2), 77.82 (s, CH), 77.80 (s, CH), 79.54 (s, CH), 178.13 (s, COO) ppm.
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$_{50}$H$_{94}$Cl$_{4}$O$_{24}$P$_{2}$Ti$_{6}$ | C$_{24}$H$_{49}$O$_{24}$P$_{2}$Ti$_{6}$ |
|   | Formula weight            | 1276.22                   | 1500.65                   | 1272.38                   |
|   | Crystal system            | monoclinic                | monoclinic                | monoclinic                |
|   | Space group               | P $2_1/n$                 | C $2/c$                   | P $2_1/n$                 |
|   | a [Å]                     | 1226.23(6)                | 2259.5(2)                 | 1266.7(6)                 |
|   | b [Å]                     | 1649.58(9)                | 1682.61(13)               | 1664.31(8)                |
|   | c [Å]                     | 1464.69(7)                | 1830.97(15)               | 1460.95(8)                |
|   | $\alpha$ [°]              | 90                        | 90                        | 90                        |
|   | $\beta$ [°]               | 98.272(3)                 | 91.538(3)                 | 97.193(2)                 |
|   | $\gamma$ [°]              | 90                        | 90                        | 90                        |
|   | $\delta$ [°]              | 90                        | 90                        | 90                        |
|   | $V$ [Å$^3$]               | 2931.9(3)                 | 6958.10(10)               | 2911.4(3)                 |
|   | Z                          | 2                         | 4                         | 2                         |
|   | $D_1$, [Mg.m$^{-3}$]      | 1.446                     | 1.432                     | 1.451                     |
|   | $\mu$ [mm$^{-1}$]         | 0.904                     | 0.774                     | 0.91                      |
|   | Crystal size [mm]         | 0.5 $\times$ 0.5 $\times$ 0.5 | 0.5 $\times$ 0.5 $\times$ 0.4 | 0.5 $\times$ 0.5 $\times$ 0.3 |
|   | Measured reflections     | 121208                    | 93315                     | 43475                     |
|   | Observed reflections      | 16514                     | 10942                     | 5034                      |
|   | $I > 2\sigma(I)$          | 42.84                     | 33.22                     | 26.41                     |
|   | $\theta_{\text{max.}}$    | 79.57                     | 79.82                     | 79.57                     |
|   | $\theta_{\text{max.}}$    | 2038–2045 © 2014 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

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

|   | 4                          | 5                          | 6                          |
|---|---------------------------|---------------------------|---------------------------|
|   | Empirical formula         | C$_{38}$H$_{86}$O$_{24}$P$_{2}$Ti$_{6}$ | C$_{50}$H$_{94}$Cl$_{4}$O$_{24}$P$_{2}$Ti$_{6}$ | C$_{24}$H$_{49}$O$_{24}$P$_{2}$Ti$_{6}$ |
|   | Formula weight            | 1300.43                   | 1373.34                   | 1570.39                   |
|   | Crystal system            | triclinic                 | monoclinic                | monoclinic                |
|   | Space group               | P 1                       | P 2/$n$                   | P$_2$/c                    |
|   | a [Å]                     | 1146.80(9)                | 1376.54(5)                | 2643.8(3)                 |
|   | b [Å]                     | 1223.83(10)               | 1571.04(5)                | 1259.66(4)                |
|   | c [Å]                     | 1228.22(10)               | 1653.85(5)                | 2280.3(3)                 |
|   | $\alpha$ [°]              | 106.880(4)                | 90                        | 90                        |
|   | $\beta$ [°]               | 110.202(3)                | 112.1300(10)              | 108.761(4)                |
|   | $\gamma$ [°]              | 97.601(4)                 | 90                        | 90                        |
|   | $V$ [Å$^3$]               | 1495.2(2)                 | 3313.13(19)               | 7190.8(14)                |
|   | Z                          | 1                         | 2                         | 4                         |
|   | $D_1$, [Mg.m$^{-3}$]      | 1.444                     | 1.377                     | 1.451                     |
|   | $\mu$ [mm$^{-1}$]         | 0.888                     | 0.883                     | 0.896                     |
|   | Crystal size [mm]         | 0.3 $\times$ 0.3 $\times$ 0.3 | 0.5 $\times$ 0.4 $\times$ 0.4 | 0.32 $\times$ 0.27 $\times$ 0.23 |
|   | Measured reflections     | 62482                     | 88173                     | 287456                    |
|   | Observed reflections      | 12261                     | 5416                      | 16780                     |
|   | $I > 2\sigma(I)$          | 36.35                     | 28.95                     | 30.58                     |
|   | $\theta_{\text{max.}}$    | 90                        | 90                        | 90                        |
|   | $\theta_{\text{max.}}$    | 2038–2045 © 2014 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[31] P NMR (101.2 MHz, C$_6$D$_6$): $\delta = 6.40$ Hz, 4 H, CH$_2$Br), 4.69 (m, J = 6.44 Hz, 2 H, CH$_2$), 4.69 (m, J = 6.20 Hz, 2 H, CH)$_2$.

[32] $\delta_{\text{max.}}$, $\delta_{\text{min.}}$ [e$^{10^{-6}}$ pm$^{-3}$] 1.272, −0.362 for 4–6.
Table 3. Crystal data and structure refinement details for 7–9.

| 7       | 8       | 9       |
|---------|---------|---------|
| Empirical formula | C₄₀H₈₈Br₂O₂₄P₂Ti₆ | C₄₄H₉₈Br₃O₂₃P₃Ti₅ | C₄₂H₇₂O₂₃P₂Ti₅ |
| Formula weight | 1462.26 | 1567.36 | 1246.44 |
| Crystal system | orthorhombic | monoclinic | triclinic |
| Space group | P b c a | P 2₁/n | P 1 |
| a [Å] | 1632.40(3) | 1308.99(7) | 1210.96(6) |
| b [Å] | 1585.18(3) | 2291.37(13) | 1284.46(7) |
| c [Å] | 2401.10(4) | 2346.81(13) | 1908.81(11) |
| α [°] | 90 | 90 | 90 |
| β [°] | 90 | 102.29(2) | 101.46(3) |
| γ [°] | 90 | 96.627(3) | 96.627(3) |
| V (Å³) | 6213.2(2) | 6877.4(7) | 2860.8(3) |
| Z | 4 | 4 | 2 |
| D₁ [Mg m⁻³] | 1.563 | 1.514 | 1.447 |
| μ [mm⁻¹] | 2.142 | 2.434 | 0.797 |
| Crystal size [mm] | 0.6 x 0.5 x 0.5 | 0.6 x 0.4 x 0.35 | 0.7 x 0.6 x 0.4 |
| Measured reflections | 197274 | 137433 | |
| Observed reflections | 10744 | 13683 | |
| I > 2σ(I) | 34.37 | 28.32 | 19253 |
| R(F² > 2σ(F²)) | 0.0222, 0.0571, 1.049 | 0.0567, 0.1487, 1.031 | 36.37 |
| Refinements/parameters | 13047/345 | 16623/727 | 0.063, 0.1544, 1.084 |
| Weighting scheme[a] | w = 1/[σ²(Fo²) + (0.0552P)² + 2.6246P] | w = 1/[σ²(Fo²) + (0.0160P)² + 9.9669P] | 27635/789 |
| δmax/min. [e·Å⁻³] | 0.681,−0.423 | 5.461,−5.769 | 1.701,−1.112 |

[a] P = (Fo² + 2Fc²)/3.

CH₃COOH (35 µL, 0.61 mmol) was added. After 15 weeks, crystals of 9 were obtained, yield 200 mg (48%). ¹H NMR (250 MHz, CDCl₃, 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, CH₂(NH₂)), 5.07 (m, J = 6.23 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, CH₂), 8.03 (s, 2 H, CH₃), 8.08 (s, 2 H, CH₃) ppm. ¹³C NMR (62.9 MHz, CDCl₃, δ = 15.92 ppm. ¹³C NMR (62.9 MHz, CDCl₃, 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.

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