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Influence of the Phosphonate Ligand on the Structure of Phosphonate-Substituted Titanium Oxo Clusters

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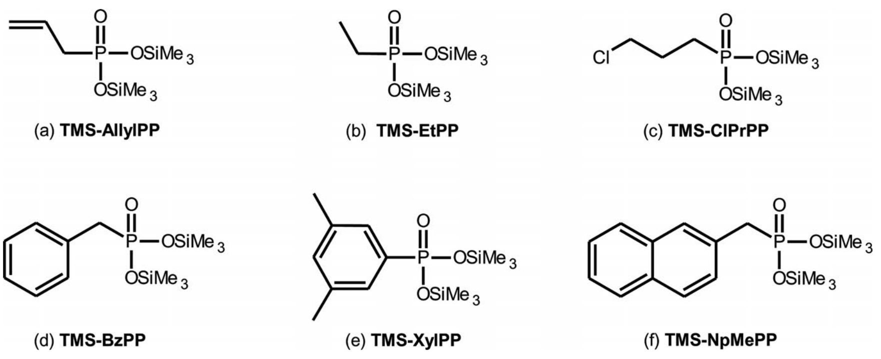
The reaction of titanium isopropoxide, Ti(O*i*Pr)$_4$, with bis(trimethylsilyl) phosphonates has led to structures containingTi$_3$O units [= Ti$_3$(μ^3-O)(μ^2-O*i*Pr)$_3$(O*i*Pr)$_3$(O$_3$PR)$_3$] as the basic structural motif. This unit can be capped by a single Ti(O*i*Pr)$_2$L group (L = neutral ligand) through phosphonate bridges (for R = xylyl), or sandwich-like structures can be formed with two Ti$_3$O units bonded to a central Ti atom (for R = CH$_2$CH$_2$CH$_2$Cl or benzyl). For R = allyl or ethyl, dimeric clusters were formed in which two Ti$_4$ cluster units are bridged by isopropyl phosphonate ligands. For comparison, Ti(O*i*Pr)$_4$ was also treated with allylphosphonic acid to yield a Ti$_4$ cluster. The reaction of Ti(O*i*Pr)$_4$ with the bulky bis(trimethylsilyl) 2-naphthylmethyphosphonate did not yield an oxo cluster but instead the phosphonate-substituted titanium alkoxide Ti$_4$(O*i*Pr)$_8$(O$_3$PCH$_2$naphthyl)$_4$.

Introduction

Metal oxo clusters are of great interest as nanosized inorganic building blocks for hybrid materials.[1] They can be easily processed, because they are molecular compounds. When incorporated into organic polymers, some of the properties of the polymers are improved in comparison with the parent polymers.[2] A common route to titanium oxo clusters is the addition of a carboxylic acid to titanium alkoxides, the water for hydrolysis being produced in situ through esterification of the acid.[3]

Phosphonates are often used as protecting ligands for titania nanoparticles[4] (leading to water-stable and functionalized nanoparticles with several applications) because of the stable Ti–O–P bonds. A few phosphonate- and phosphinate-substituted oxo clusters have been obtained by the reaction of titanium alkoxides with some phosphonic or phosphinic acids.[5–7] The formation of oxo groups in the clusters was attributed to residual moisture in the solvents or phosphonic acids[5–8] rather than to an esterification reaction. The compounds obtained by reaction with phosphinates had similar structures to comparable carboxylate-substituted derivatives.[5,7]



(a) **TMS-AllylPP** (b) **TMS-EtPP** (c) **TMS-ClPrPP**
(d) **TMS-BzPP** (e) **TMS-XylPP** (f) **TMS-NpMePP**

Scheme 1. Trimetylsilyl phosphonates used in this study.

In this article we first introduced polymerizable organic groups into metal oxo clusters by using functionalized phosphonate ligands for the preparation of class II hybrid materials. We then extended this study to other phosphonate ligands to elucidate the influence of organic sub-

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stituents on the structures of clusters. We mainly used the bis(trimethylsilyl) esters of phosphonic acids as the starting compounds, which have rarely been employed. For example, trimethylsilyl esters of phosphonic acids[9] have previously been used for reactions with $Ti(OiPr)_4$ instead of the parent acids. Use of the esters provides better reproducibility and easier handling compared with phosphonic acids themselves.

The bis(trimethylsilyl) phosphonates (Scheme 1a–f) employed include compounds with different functionalities as well as different steric demands. Allylphosphonic acid was also used to compare its behavior with that of the esters.

Results and Discussion

The phosphonate-substituted oxo clusters $[Ti_4(\mu_3\text{-}O)(\mu_2\text{-}OiPr)_3(OiPr)_5(O_3PR)_3(dmso)]$ (R = Ph, Me, *t*Bu, 4-NCC_6H_4) were obtained by Mehring et al.[6] by the reaction of $Ti(OiPr)_4$ with $RP(O)(OH)_2$. The structure of this cluster type consists of a symmetric $Ti_3(\mu_3\text{-}O)(\mu_2\text{-}OiPr)_3(OiPr)_3$ triangle in which three octahedrally coordinated Ti atoms are bridged by a μ_3-oxygen atom. The titanium atoms of the triangle are additionally bridged by three μ_2-O*i*Pr ligands, and each titanium atom is coordinated by a terminal O*i*Pr ligand. The fourth ("capping") Ti atom is connected to this triangular unit through the three phosphonate ligands. The vacant coordination sites at the fourth titanium atom are occupied by two terminal O*i*Pr groups and one dmso molecule; dmso was used as the solvent due to the low solubility of phosphonic acids in organic solvents.

We obtained cluster **1** with the same structure when allylphosphonic acid was used (Figure 1). The average Ti–O distance of the phosphonate groups is 197 pm, with the exception of the Ti–O bond at Ti1 *trans* to the terminal O*i*Pr ligands (204 pm). The average Ti–O bond length of the μ_2-O*i*Pr groups is 202 pm, and that of the terminal O*i*Pr ligands is 180 pm.

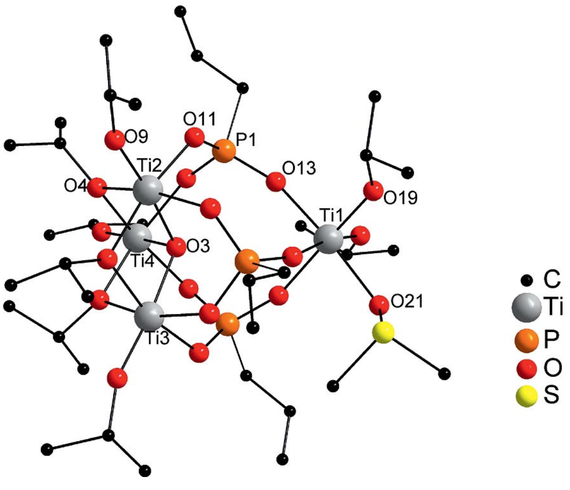

Figure 1. Molecular structure of $[Ti_4(\mu_3\text{-}O)(\mu_2\text{-}OiPr)_3(OiPr)_5(O_3P\text{-}allyl)_3(dmso)]$ (**1**). Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: Ti1–O21 208.7(3), Ti1–O13 195.5(4), Ti1–O19 181.7(4), Ti2–O3 193.3(4), Ti2–O11 197.1(4), Ti2–O9 176.4(4), Ti2–O4 203.8(4), O13–P1 151.6(4); P1–O13–Ti1 163.9(2), O13–P1–O11 112.5(2), Ti2–O3–Ti3 105.14(16), O19–Ti1–O13 90.62(15), O19–Ti1–O21 93.08(15), O3–Ti2–O11 88.34(14).

The ^{31}P NMR spectrum shows two signals, and hence the cluster has mirror symmetry in solution. Accordingly, the ^{1}H NMR spectrum shows four different O*i*Pr signals, and the ^{13}C NMR spectrum six doublets for the phosphorus-coupled carbon atoms of the allyl group.

The drawback of using phosphonic acids is their low solubility in organic solvents. Furthermore, reproducing the synthesis of crystalline **1** took several attempts. To overcome these problems, bis(trimethylsilyl) phosphonates were used in the remainder of this work.

When TMS-allylPP was treated with $Ti(OiPr)_4$ in a 1:2 ratio in isopropyl alcohol, the cluster $[Ti_8(\mu_3\text{-}O)_2(\mu_2\text{-}OiPr)_6(OiPr)_8(O_3P\text{-}allyl)_6\{O_2P(OiPr)allyl\}_2]$ (**2**) was formed (Figure 2). Cluster **2** consists of two Ti_4O units [= $Ti_4(\mu_3\text{-}O)_2(\mu_2\text{-}OiPr)_3(OiPr)_4(O_3P\text{-}allyl)_3$] as in **1**, which are connected by two mono(isopropyl esters) of allylphosphonate. The "capping" titanium atom of each Ti_4O unit is thus coordinated to only one terminal O*i*Pr ligand and the oxygen atoms of two allylphosphonate ester groups (instead of two terminal O*i*Pr ligands and a dmso molecule in **1**).

The bond lengths in **2** are similar to those in **1**, with an average Ti–O bond length of 197 pm for the phosphonate groups. An exception is again the Ti–O bond *trans* to the terminal O*i*Pr ligand on the "capping" titanium atom (204 pm). The bridging O*i*Pr groups have an average Ti–O bond length of 203 pm and the terminal O*i*Pr groups an average Ti–O bond length of 178 pm.

Cluster **2** was synthesized several times, and either triclinic (space group $P\bar{1}$, denoted as **2**) or monoclinic crystals (space group $P2_1/n$, denoted as **2b**) were obtained. The molecular structures are the same in both cases, and the bond lengths and angles are similar (only the values for **2** are given in Figure 2), but the packing of the clusters is different. The clusters are parallel to each other in **2** and aligned at an angle of 58.2° in **2b**.

The most remarkable feature of **2** is the isopropyl phosphonate groups. The formation of an isopropyl phosphonate indicates that, similarly to the reactions of carboxylic acids, esterification of the (noncoordinated or coordinated) phosphonic acid could also be the source of the oxo groups, especially because the ester/μ_3-O ratio in **2** is 1:1. The reactions of bis(trimethylsilyl) phosphonates with alcohols leads to the corresponding phosphonic acid and alkoxytrimethylsilane[10] in a fast reaction.[11] Use of the trimethylsilyl esters thus allows generation of the phosphonic acid in situ, which may substitute some of the O*i*Pr groups of $Ti(OiPr)_4$. The (coordinated or noncoordinated) phosphonic acid could then react with 2-propanol, possibly catalyzed by $Ti(OiPr)_x$ moieties,[12] to produce water for condensation and the observed isopropyl monoester.

Crystals of **2** (or **2b**) are soluble in common organic solvents. Its NMR spectroscopic data, however, are ambiguous. In the ^{31}P NMR spectrum, five peaks are observed. Interpretation of the ^{1}H NMR spectroscopic data was limited due to the high number of chemically similar groups.

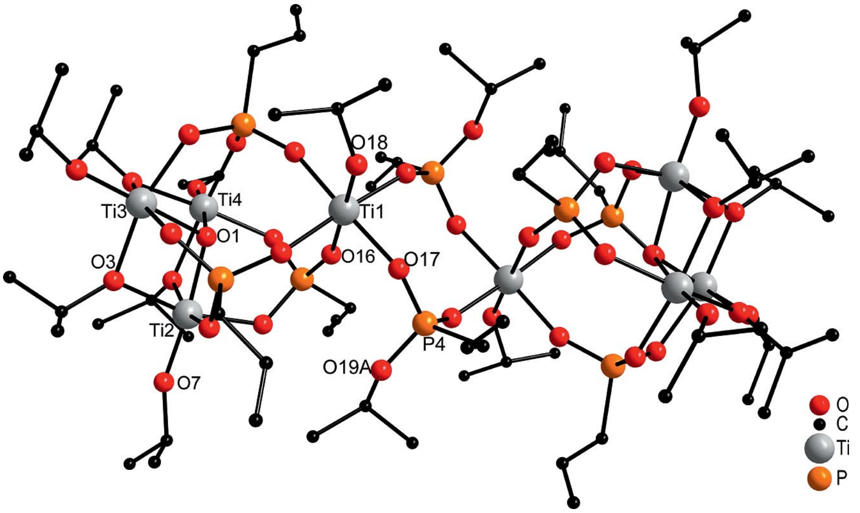

Figure 2. Molecular structure of $[Ti_8(\mu_3\text{-}O)_2(\mu_2\text{-}OiPr)_6(OiPr)_8(O_3P\text{-allyl})_6\{O_2P(OiPr)allyl\}_2]$ (**2**). Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: Ti1–O16 203.54(18), Ti1–O17 196.64(19), Ti1–O18 177.69(19), Ti2–O1 195.59(17), Ti2–O3 204.43(18), Ti2–O7 178.1(2), Ti3–O3 202.08(18), Ti3–O1 195.39(17), O17–P4 151.7(2), P4–O19A 150.2(4); O17–Ti1–O16 89.21(8), O18–Ti1–O17 92.61(8), O19A–P4–O17 107.63(17), O7–Ti2–O3 98.22(9), O1–Ti2–O3 76.48(7), Ti3–O1–Ti2 105.32(8).

The integrals fitted well, but the multiplicities and signal overlap led to very broad and indistinct signals. The ^{13}C NMR spectrum also shows five doublets for the allyl groups, but signal overlap again made it difficult to elucidate the symmetry of **2**.

The reaction of TMS-EtPP with $Ti(OiPr)_4$ in isopropyl alcohol resulted in $[Ti_8O_2(OiPr)_{14}(O_3PEt)_6\{O_2P(OiPr)Et\}_2]$ (**3**), which is isostructural with cluster **2**, and the bond lengths and angles are the same within error limits. The ^{31}P NMR spectroscopic data of **3** are in agreement with the solid-state structure, and the ^1H and ^{13}C NMR spectra generally confirmed the structural data, with the same limitations as already noted for **2**.

In the chemistry of silica-based hybrid materials, chloropropyl-substituted alkoxysilane precursors play an important role, because substitution of chlorine opens the door to derivatives with other more complex functional groups. With this in mind, TMS-ClPrPP was treated with $Ti(OiPr)_4$ in isopropyl alcohol to yield $[Ti_7O_2(OiPr)_{12}(O_3PCH_2CH_2CH_2Cl)_6]$ (**4**) (Figure 3). The structure of **4** is also based on Ti_3O units [= $Ti_3(\mu_3\text{-}O)(\mu_2\text{-}OiPr)_3(OiPr)_3(O_3P\text{-}R)_3$]. In contrast to **2** and **3**, the two Ti_3O units in **4** are connected by a single titanium atom, that is, a sandwich structure is formed with Ti3 as the central atom and the Ti_3O units as "ligands" (in this way of looking at the structures, **1** would be a half-sandwich structure). The bond lengths are similar to those in **1**; the Ti–O distances of the phosphonate groups are 198 pm for the titanium atoms of the Ti_3O units and 193 pm for the central Ti atom.

The ^{31}P NMR spectrum shows only one peak, which indicates the high symmetry and stability of this cluster in solution. This is also evidenced in the ^1H NMR spectrum, in which only two different signals for the OiPr groups are observed. The ^{13}C NMR spectrum confirms this observation, in which the coupling constant J_{PC} is seen. Other smaller signals indicate the presence of a side-product in which Cl is replaced by Br. This was also observed in the spectra of the precursors. Because 1-bromo-3-chloropropane was used for the preparation of ClPrPP, both halogens can react with dimethyl phosphite, and therefore a small amount of (3-bromopropyl)phosphonate was also formed. The presence of some bromine (replacing Cl) was also seen in the electron density map of the single-crystal measurements.

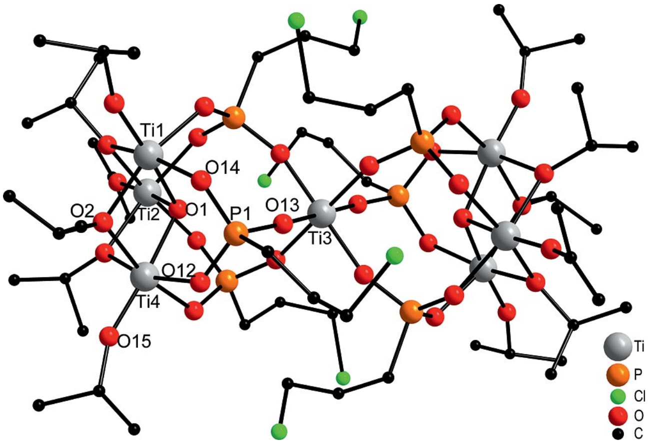

Figure 3. Molecular structure of $[Ti_7(\mu_3\text{-}O)_2(\mu_2\text{-}OiPr)_6(OiPr)_6(O_3PCH_2CH_2CH_2Cl)_6]$ (**4**). Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: Ti1–O1 195.9(2), Ti1–O14 198.1(2), Ti1–O2 202.3(2), Ti2–O1 196.3(2), Ti3–O13 192.6(2), Ti4–O1 195.8(2), Ti4–O12 198.7(2), Ti4–O15 177.4(3), P1–O12 153.3(3), P1–O13 152.2(3), P1–O14 153.4(3); O1–Ti1–O14 88.24(10), O1–Ti1–O2 76.59(9), O14–Ti1–O2 87.43(10), O13–P1–O12 112.00(14), O13–P1–O14 111.78(14), O12–P1–O14 111.55(14).

The reaction of TMS-BzlPP with $Ti(OiPr)_4$ yielded $Ti_7O_2(OiPr)_{12}(O_3PCH_2C_6H_5)_6$ (**5**), which is isostructural to **4**. Bond angles and distances of both compounds are very similar. The benzyl groups in the center of the structure adopt a paddle-wheel-like arrangement.

The previously described reactions indicate that the organic group of the phosphonate ligand has some (electronic or steric) influence on the structure of the formed clusters. To shed light on this issue, phosphonate ligands with sterically more demanding groups were included in this study. Furthermore, aromatic phosphonic acids are slightly more acidic.

The reaction of TMS-XylPP and Ti(O*i*Pr)$_4$ led to the formation of [Ti$_4$O(O*i*Pr)$_8$(O$_3$P-xyl)$_3$(*i*PrOH)] (**6**; Figure 4). The structure is analogous to that of **1**, the neutral ligand at the "capping" titanium atom being isopropyl alcohol (instead of dmso as in **1**).

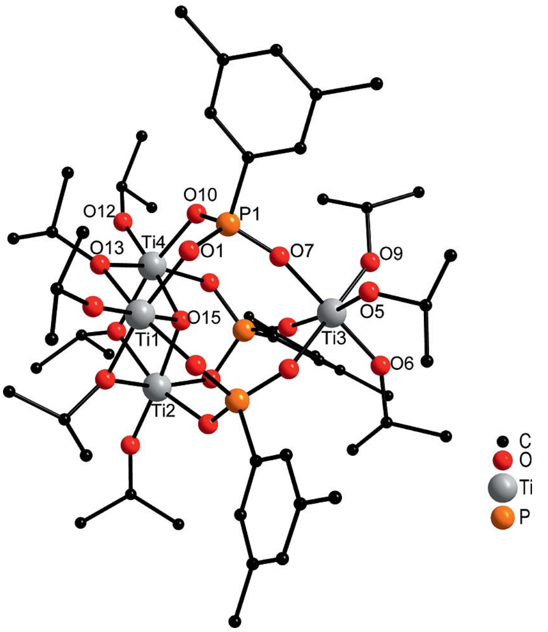

Figure 4. Molecular structure of [Ti$_4$(μ_3-O)(μ_2-O*i*Pr)$_3$(O*i*Pr)$_5$(O$_3$P-xyl)$_3$(*i*PrOH)] (**6**). Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: Ti1–O1 197.5(3), Ti1–O15 196.3(3), Ti4–O12 177.6(3), Ti4–O15 194.8(3), Ti4–O10 196.5(3), Ti4–O13 202.6(3), O7–P1 150.3(3), O1–P1 154.2(3), O10–P1 154.3(3), Ti3–O5 213.7(3), Ti3–O6 181.1(3), Ti3–O9 178.7(3), Ti3–O7 201.1(3); Ti4–O15–Ti1 105.36(13), O12–Ti4–O13 101.73(13), O15–Ti4–O13 76.85(12), O7–P1–O10 113.57(17), P1–O1–Ti1 124.52(17).

The appearance of only one signal in the ^{31}P NMR spectrum indicates that cluster **6** has C_3 symmetry in solution. This was confirmed by the ^{1}H NMR spectrum in which only three different signals for the CH$_3$ groups of O*i*Pr and only one singlet for the CH$_3$ of the xylyl group can be seen. The proton of the coordinated isopropyl alcohol exchanges easily on the NMR timescale, because only averaged signals of the isopropyl alcohol and the O*i*Pr groups were observed.

The reaction of a phosphonate with an even bulkier substituent, namely TMS-NpMePP, resulted in the complex [Ti$_4$(μ_2-O*i*Pr)(O*i*Pr)$_7$(O$_3$PMeNp)$_4$] (**7**; Figure 5). In **7**, two of the O*i*Pr ligands of Ti(O*i*Pr)$_4$ are substituted by one O$_3$P-MeNp ligand [formal composition Ti(O*i*Pr)$_2$(O$_3$PMeNp)], but no partial hydrolysis took place. This is in contrast to the reactions with the other bis(trimethylsilyl) phosphonates described in this article. The crystallization time of **7** was much shorter than for the other clusters reported in this article. Compound **7** could therefore represent the structure of an initially formed substitution product, which possibly crystallized more easily from the isopropyl alcohol solution due to the apolarity of the naphthyl group and thus escaped hydrolysis.

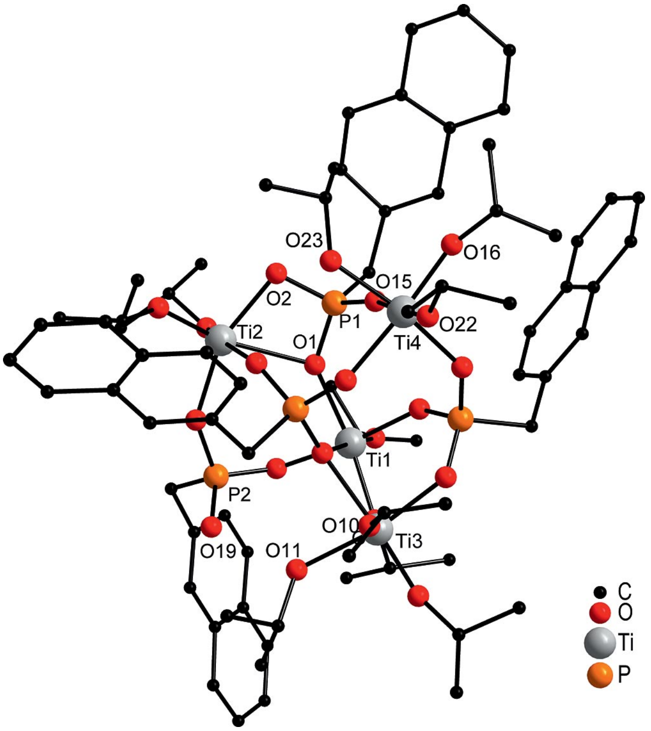

Figure 5. Molecular structure of [Ti$_4$(μ_2-O*i*Pr)(O*i*Pr)$_7$(O$_3$PMeNp)$_4$(*i*PrOH)$_2$·2*i*PrOH] (**7**). Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: Ti3–O11 206.5(3), Ti3–O10 177.4(3), Ti3–O13 209.9(3), Ti1–O1 201.7(3), Ti2–O1 232.1(3), Ti2–O2 201.8(3), Ti1–O13 194.4(3), P1–O1 156.2(3), P1–O2 153.0(3), P1–O15 149.4(3), P2–O19 150.0(4), Ti4–O15 205.5(3), Ti4–O16 189.9(4), Ti4–O23 201.2(4), Ti4–O22 176.5(3); P1–O1–Ti2 89.18(13), P1–O15–Ti4 156.8(2), P1–O2–Ti2 102.23(16), Ti1–O13–Ti3 110.58(13), O2–Ti2–O1 66.38(11), O11–Ti3–O13 83.98(13), O10–Ti3–O11 93.43(15), Ti1–O1–Ti2 128.60(14).

The structure of **7** consists of four octahedrally coordinated titanium atoms arranged in an irregular shape. In contrast to all the other structures, in which all the phosphonates bind in a 3.111 mode [*w.xyz* denotes 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*)[13]], just one phosphonate in **7** coordinates in the 3.111 mode. The other phosphonates coordinate in the 4.211, 3.211, and 2.110 modes. As a result of the high connectivity of the phosphonates, there is only one bridging O*i*Pr ligand.

The NMR measurements are in good agreement with the crystal structure. Four signals are detected in the ^{31}P NMR spectrum, with a shift difference of 8.80 ppm. The latter is attributed to the different binding modes of the phosphonate ligands. Three doublets for the CH$_2$ groups are detected in the ^{13}C NMR spectrum, although four were expected. One of these doublets has a higher intensity, which indicates signal overlap.

Conclusions

Trimethylsilyl esters of phosphonic acids are better precursors for the preparation of phosphonate-substituted titanium oxo clusters due their better solubility, as stated in earlier work.[7,9] This renders the reactions more reliable, and crystals of good quality were obtained easily.

It was previously proposed that metal alkoxides may react with $\mathrm{P\text{-}O\text{-}SiMe_3}$ in non-hydrolytic condensation processes.[9] The results presented in this article indicate that another possibility must also be considered. The reactions of bis(trimethylsilyl) phosphonates with isopropyl alcohol liberates phosphonic acid, which could substitute some of the O*i*Pr groups of $\mathrm{Ti(O}i\mathrm{Pr)_4}$. This latter reaction must be fast, because otherwise the (sparingly soluble) acids would precipitate. The formation of **7** indicates that the introduction of phosphonate ligands is not necessarily coupled to the formation of oxo groups. The latter might be due to the slow esterification of (coordinated or noncoordinated) phosphonic acid, as it is the case with carboxylic acids. This possibility is strongly supported by the presence of isopropyl phosphonate ligands in **2** and **3**.

The synthesis of **1** and **2** shows that titanium alkoxo derivatives with polymerizable organic groups can be prepared in which the organic groups are linked to Ti through robust phosphonate ligands. Owing to the presence of both organic double bonds and Ti-OR groups in **1**, this derivative appears to be suitable for the preparation of hybrid materials, similar to alkoxysilanes $\mathrm{(RO)_3Si\text{-}R'}$ with polymerizable groups R′.

From a structural point of view, it is interesting to note that the structures of the phosphonate-substituted oxo clusters are derived from a common motif, that is, $\mathrm{Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O}i\mathrm{Pr)_3(O}i\mathrm{Pr)_3(O_3P\text{-}R)_3}$. This $\mathrm{Ti_3O}$ motif can be varied in a variety of ways and thus appears to be a robust building block.

Experimental Section

General: Manipulations were carried out under an inert gas by using standard Schlenk and glove-box techniques. Diethyl ethylphosphonate, allyl bromide, 1-bromo-3-chloropropane, benzyl bromide, 1-bromo-3,5-dimethylbenzene, 2-(bromomethyl)naphthalene and triethyl phosphite were purchased from Sigma–Aldrich and used as received. Diethyl 3,5-dimethylphenylphosphonate was prepared by a procedure similar to that already reported.[14] The bis(trimethylsilyl) esters were prepared by adding bromotrimethylsilane (3 mol) to a solution of the corresponding diethyl phosphonate (1 mol) in $\mathrm{CH_2Cl_2}$. The bis(trimethylsilyl) esters were obtained after removing all volatiles in vacuo. All esters were characterized by ^{31}P and ^{1}H NMR measurements before use. Isopropyl alcohol was dried by heating at reflux in the presence of sodium and distillation; dmso was dried by heating in the presence at reflux of $\mathrm{CaSO_4}$ and distillation followed by heating at reflux in the presence of $\mathrm{CaH_2}$ and distillation. Samples for NMR measurements were obtained by washing the crystalline substances with *i*PrOH, drying and dissolving in the designated solvent.

$[\mathrm{Ti_4O(O}i\mathrm{Pr)_8\{O_3P(allyl)\}_3(dmso)}]$ (1): Allylphosphonic acid (315 mg, 2.6 mmol) was dissolved in water-free dmso (3 mL) under an inert gas, and $\mathrm{Ti(O}i\mathrm{Pr)_4}$ (1.5 mL, 5.2 mmol) was added slowly under vigorous stirring. The suspension formed was stirred until a clear solution was obtained. After 4 weeks, 0.6 g (62% yield) of crystalline **1** was obtained. ^{1}H NMR ($\mathrm{C_6D_6}$, 250 MHz): δ = 1.48 (d, J = 6.15 Hz, 12 H, $\mathrm{CHC}H_3$), 1.49 (d, J = 6.18 Hz, 12 H, $\mathrm{CHC}H_3$), 1.68 (d, J = 6.35 Hz, 12 H, $\mathrm{CHC}H_3$), 1.73 (d, J = 6.28 Hz, 12 H, $\mathrm{CHC}H_3$), 1.94 (s, 6 H, $\mathrm{SC}H_3$), 2.76 (dd, $J_{\mathrm{H,H}}$ = 7.30, $J_{\mathrm{P\text{-}H}}$ = 21.6 Hz, 4 H, $\mathrm{PC}H_2$), 2.87 (dd, $J_{\mathrm{H,H}}$ = 7.40, $J_{\mathrm{P\text{-}H}}$ = 22.0 Hz, 2 H, $\mathrm{PC}H_2$), 4.74 (m, 6 H, $\mathrm{CH{=}C}H_2$), 5.22 (m, 11 H, $C\mathrm{HCH_3}$), 6.31 (m, 3 H, $\mathrm{C}H\mathrm{{=}CH_2}$) ppm. ^{31}P NMR ($\mathrm{C_6D_6}$, 101.2 MHz): δ = 14.48, 16.01 ppm. ^{13}C NMR ($\mathrm{C_6D_6}$, 62.9 MHz): δ = 24.90 (s, $\mathrm{CH}C\mathrm{H_3}$), 24.97 (s, $\mathrm{CH}C\mathrm{H_3}$), 25.13 (s, $\mathrm{CH}C\mathrm{H_3}$), 25.19 (s, $\mathrm{CH}C\mathrm{H_3}$), 34.16 (d, J = 150.3 Hz, $\mathrm{P}C\mathrm{H_2}$), 34.85 (d, J = 151.4 Hz, $\mathrm{P}C\mathrm{H_2}$), 39.34 (s, $\mathrm{S}C\mathrm{H_3}$), 77.80 (s, $C\mathrm{HCH_3}$), 78.02 (s, $C\mathrm{HCH_3}$), 78.96 (s, $C\mathrm{HCH_3}$), 79.53 (s, $C\mathrm{HCH_3}$), 116.76 (d, J = 14.7 Hz, $\mathrm{CH{=}}C\mathrm{H_2}$), 117.49 (d, J = 15.1 Hz, $\mathrm{CH{=}}C\mathrm{H_2}$), 131.86 (d, J = 11.3 Hz, $\mathrm{CH_2{=}}C\mathrm{H}$), 132.65 (d, J = 10.9 Hz, $\mathrm{CH_2{=}}C\mathrm{H}$) ppm.

$[\mathrm{Ti_8O_2(O}i\mathrm{Pr)_{12}\{O_3P(allyl)\}_6\{O_2P(allyl)(O}i\mathrm{Pr)\}_2}]$ (2): Bis(trimethyl)silyl allylphosphonate (200 mg, 0.8 mmol) was added in a ratio of 1:2 to $\mathrm{Ti(O}i\mathrm{Pr)_4}$ (464 µL, 1.6 mmol) in isopropyl alcohol (1 mL). After 6 weeks, crystals of the cluster **2** or **2b** were obtained in 30% yield (70 mg). ^{1}H NMR ($\mathrm{C_6D_6}$, 250 MHz): δ = 1.36–1.50 (m, 48 H, $\mathrm{CHC}H_3$), 1.62–1.80 (m, 48 H, $\mathrm{CHC}H_3$), 2.65–2.94 (m, 8 H, $\mathrm{PC}H_2$), 3.05–3.34 (m, 6 H, $\mathrm{PC}H_2$), 3.62–3.88 (m, 2 H, $\mathrm{PC}H_2$), 4.61–4.79 (m, 6 H, $\mathrm{C}H\mathrm{CH_3}$), 5.11–538 (m, 24 H, $\mathrm{CH{=}C}H_2$, $\mathrm{C}H\mathrm{CH_3}$), 5.50–5.65 (d, 2 H, $\mathrm{CH{=}C}H_2$), 6.16–6.50 (m, 8 H, $\mathrm{C}H\mathrm{{=}CH_2}$) ppm. ^{31}P NMR ($\mathrm{C_6D_6}$, 101.2 MHz): δ = 13.77, 13.99, 15.50, 15.69, 16.57 ppm. ^{13}C NMR ($\mathrm{C_6D_6}$, 62.9 MHz): δ = 23.89 (s, $\mathrm{CH}C\mathrm{H_3}$), 24.06 (s, $\mathrm{CH}C\mathrm{H_3}$), 24.73 (s, $\mathrm{CH}C\mathrm{H_3}$), 24.84 (s, $\mathrm{CH}C\mathrm{H_3}$), 25.11 (s, $\mathrm{CH}C\mathrm{H_3}$), 25.28 (s, $\mathrm{CH}C\mathrm{H_3}$), 25.34 (s, $\mathrm{CH}C\mathrm{H_3}$), 32.84 (d, J = 145.5 Hz, $\mathrm{P}C\mathrm{H_2}$), 34.31 (d, J = 154.3 Hz, $\mathrm{P}C\mathrm{H_2}$), 34.86 (d, J = 149.9 Hz, $\mathrm{P}C\mathrm{H_2}$), 69.34 (s, $C\mathrm{HCH_3}$), 69.45 (s, $C\mathrm{HCH_3}$), 77.50 (s, $C\mathrm{HCH_3}$), 77.72 (s, $C\mathrm{HCH_3}$), 77.79 (s, $C\mathrm{HCH_3}$), 78.07 (s, $C\mathrm{HCH_3}$), 78.53 (s, $C\mathrm{HCH_3}$), 78.69 (s, $C\mathrm{HCH_3}$), 79.03 (s, $C\mathrm{HCH_3}$), 79.26, 82.34 (s, $C\mathrm{HCH_3}$), 82.67 (s, $C\mathrm{HCH_3}$), 116.35 (d, J = 14.6 Hz, $\mathrm{CH{=}}C\mathrm{H_2}$), 116.68 (d, J = 15.3 Hz, $\mathrm{CH{=}}C\mathrm{H_2}$), 116.88 (d, J = 15.3 Hz, $\mathrm{CH{=}}C\mathrm{H_2}$), 116.99 (d, J = 15.3 Hz, $\mathrm{CH{=}}C\mathrm{H_2}$), 117.34 (d, J = 14.2 Hz, $\mathrm{CH{=}}C\mathrm{H_2}$), 131.78 (d, J = 11.2 Hz, $C\mathrm{H{=}CH_2}$), 131.90 (d, J = 10.6 Hz, $C\mathrm{H{=}CH_2}$), 132.16 (d, J = 10.7 Hz, $C\mathrm{H{=}CH_2}$), 132.70 (d, J = 11.6 Hz, $C\mathrm{H{=}CH_2}$), 133.39 (d, J = 11.0 Hz, $C\mathrm{H{=}CH_2}$) ppm.

$[\mathrm{Ti_8(\mu_3\text{-}O)_2(\mu_2\text{-}O}i\mathrm{Pr)_6(O}i\mathrm{Pr)_8(O_3PCH_2CH_3)_6\{O_2(O}i\mathrm{Pr)PCH_2CH_3\}_2}]$ (3): $\mathrm{Ti(O}i\mathrm{Pr)_4}$ (420 µL, 1.45 mmol) was diluted with *i*PrOH (3 mL), and then bis(trimethylsilyl) ethylphosphonate (200 µL, 0.72 mmol) was added quickly. The mixture was stirred for 5 min. Crystals of **3** were obtained after 4 weeks. Yield: 40 mg (45%). ^{1}H NMR ($\mathrm{CDCl_3}$, 250 MHz): δ = 1.02–1.48 (m, 120 H, $\mathrm{C}H_3$), 1.48–2.18 (m, 16 H, $\mathrm{C}H_2$), 4.42–4.70 (m, 6 H, $\mathrm{C}H$), 4.74–5.02 (m, 10 H, $\mathrm{C}H$) ppm. ^{31}P NMR ($\mathrm{CDCl_3}$, 101.2 MHz): δ = 18.91, 19.01, 19.22, 19.58, 20.11, 20.37, 20.61, 24.12 ppm. ^{13}C NMR ($\mathrm{CD_2Cl_2}$, 62.90 MHz): δ = 7.23 (d, J = 51.3 Hz, $\mathrm{CH_2}C\mathrm{H_3}$), 19.98 (d, J = 155.2 Hz, $\mathrm{CH_2}$), 23.97 (s, $\mathrm{CH_2}C\mathrm{H_3}$), 24.26 (s, $\mathrm{CH}C\mathrm{H_3}$), 24.52 (s, $\mathrm{CH}C\mathrm{H_3}$), 24.69 (s, $\mathrm{CH}C\mathrm{H_3}$), 25.10 (s, $\mathrm{CH}C\mathrm{H_3}$), 64.16 (s, $C\mathrm{HCH_3}$), 68.45 (s, $C\mathrm{HCH_3}$), 77.91 (s, $C\mathrm{HCH_3}$), 79.02 (s, $C\mathrm{HCH_3}$), 79.54 (s, $C\mathrm{HCH_3}$) ppm.

$[\mathrm{Ti_7(\mu_3\text{-}O)_2(\mu_2\text{-}O}i\mathrm{Pr)_6(O}i\mathrm{Pr)_6(O_3PCH_2CH_2CH_2Cl)_6}]$ (4): Bis(trimethylsilyl) (3-chloropropyl)phosphonate (300 µL, 1.11 mmol) was diluted with *i*PrOH (2 mL), and then Ti(O*i*Pr)$_4$ (576 µL, 2 mmol) was added quickly under an inert gas. After 14 weeks, small crystals were obtained; for further growth, 0.5 mL of volatiles was distilled off to yield crystals suitable for single-crystal XRD after a further 2 weeks. Yield: 100 mg (17%). ^{1}H NMR (CD$_3$Cl, 250 MHz): δ = 1.45 (d, 36 H, CHC*H*$_3$), 1.63 [d, 36 H, CHC*H*$_3$ (µ$_2$-O*i*Pr)], 1.91 (dt, 12 H, PC*H*$_2$), 2.38 (m, 12 H, CH$_2$C*H*$_2$CH$_2$), 3.84 (t, 12 H, C*H*$_2$Cl), 4.68 (m, 6 H, C*H*CH$_3$), 5.16 [m, 6 H, C*H*CH$_3$ (µ$_2$-O*i*Pr)] ppm. ^{31}P NMR (CD$_3$Cl, 101.2 MHz): δ = 18.76 ppm. ^{13}C NMR (C$_6$D$_6$, 62.90 MHz): δ = 24.33 (*J* = 148 Hz, PCH$_2$), 24.47 (CH*C*H$_3$), 24.74 (*C*HCH$_3$), 26.74 (*J* = 5 Hz, CH$_2$), 46.33 (*J* = 13 Hz, CH$_2$Cl), 78.46 (*C*HCH$_3$), 79.78 (CHCH$_3$) ppm. The ^{1}H NMR spectrum shows a small triplet at δ = 3.72 ppm, and the ^{31}P NMR spectrum a small signal at δ = 18.50 ppm for the bromo species.

[Ti$_7$(µ$_3$-O)$_2$(µ$_2$-O*i*Pr)$_6$(O*i*Pr)$_6$(O$_3$PCH$_2$C$_6$H$_5$)$_6$] (5): Bis(trimethylsilyl) benzylphosphonate (200 µL, 0.64 mmol) was diluted with *i*PrOH (1 mL), and then Ti(O*i*Pr)$_4$ (370 µL, 1.28 mmol) was added quickly. Crystals suitable for single-crystal XRD were obtained after 9 weeks. Yield: 150 mg (66%). ^{1}H NMR (C$_6$D$_6$, 250 MHz): δ = 1.12–1.49 (m, 72 H, CHC*H*$_3$), 3.13–3.96 (m, 12 H, PC*H*$_2$), 4.45–5.41 (m, 12 H, C*H*CH$_3$), 7.21–8.08 [m, 30 H, C*H* (Ph)] ppm. ^{31}P NMR (CD$_2$Cl$_2$, 101.2 MHz): δ = 13.13, 13.573, 15.39, 15.73, 23.63, 24.28 ppm.

[Ti$_4$O(O*i*Pr)$_8$(O$_3$P-xyl)$_3$(*i*PrOH)] (6): Bis(trimethylsilyl) (3,5-dimethylphenyl)phosphonate (100 mg, 0.3 mmol) was diluted with *i*PrOH (1 mL), and then Ti(O*i*Pr)$_4$ (176 µL, 0.6 mmol) was added quickly. Crystals suitable for single-crystal XRD were obtained after 3 weeks. Yield: 100 mg (72%). ^{1}H NMR (CD$_3$Cl, 250 MHz): δ = 1.17 (d, *J* = 6.1 Hz, 18 H, CHC*H*$_3$), 1.40 (d, *J* = 6.2 Hz, 18 H, CHC*H*$_3$), 1.46 (d, *J* = 6.3 Hz, 18 H, CHC*H*$_3$), 2.34 (s, 18 H, CC*H*$_3$), 4.71 (m, 5 H, C*H*CH$_3$), 5.06 (m, 4 H, C*H*CH$_3$), 7.11 (s, 3 H, CC*H*), 7.53 (d, *J* = 13.9 Hz, CC*H*) ppm. ^{31}P NMR (CD$_3$Cl, 101.2 MHz): δ = 10.18 ppm. ^{13}C NMR (C$_6$D$_6$, 62.90 MHz): δ = 21.10 (C*C*H$_3$), 24.79 (CH*C*H$_3$), 24.93 (CH*C*H$_3$), 78.12 (*C*HCH$_3$), 78.83 (d), 129.47 (*J* = 10.7 Hz, CCH), 131.38 (*J* = 197 Hz, PC), 131.77 (C*C*H), 136.76 [*J* = 16 Hz, C(xyl)] ppm.

[Ti$_4$(µ$_2$-O*i*Pr)(O*i*Pr)$_7$(O$_3$PMeNp)$_4$(*i*PrOH)$_2$·2*i*PrOH] (7): Bis(trimethylsilyl) (2-naphthylmethyl)phosphonate (420 mg, 1.15 mmol) was dissolved in *i*PrOH (2 mL), and Ti(O*i*Pr)$_4$ (665 µL, 2.3 mmol) was added quickly. Crystals suitable for single-crystal XRD were obtained after 1 d. Yield: 200 mg (40%). ^{1}H NMR (C$_6$D$_6$, 250 MHz): δ = 1.00–1.65 (m, 60 H, C*H*$_3$), 3.20–3.90 (m, 8 H, C*H*$_2$), 4.00–4.60 (m, 6 H, C*H*), 5.00–5.60 (m, 6 H, C*H*), 7.20–8.20 (m, 28 H, CC*H*) ppm. ^{31}P NMR (C$_6$D$_6$, 101.2 MHz): δ = 12.82, 13.24, 17.43, 21.62 ppm. ^{13}C NMR (C$_6$D$_6$, 62.90 MHz): δ = 22.87, 23.60, 23.90, 24.05, 24.29, 24.56, 24.79, 24.93, 25.47, 25.81, 26.17, 26.34 (all *C*H$_3$), 35.77 (*J* = 143 Hz, CH$_2$), 36.61 (*J* = 140 Hz, CH$_2$), 37.01 (*J* = 143 Hz, CH$_2$), 71.77 (*C*HCH$_3$), 78.38 (*C*HCH$_3$), 78.74 (*C*HCH$_3$), 81.09 (*C*HCH$_3$), 81.84 (*C*HCH$_3$), 82.68 (*C*HCH$_3$), 84.57 (*C*HCH$_3$), 124.77, 124.91, 125.15, 125.61, 125.71, 127.59, 128.78, 129.09, 129.25, 129.59, 130.51, 132.49, 132.83, 132.98, 133.92, 134.33, 134.50 (arom. C-H or C from naphthyl) ppm.

X-ray Structure Analyses: All measurements were performed at 100 K by 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. Data were collected with ϕ- and ω-scans and a 0.5° frame width. The data were corrected for polarization and Lorentzian effects, and an empirical absorption correction (SADABS) was employed. The cell dimensions were refined by using all unique reflections. SAINT PLUS software (Bruker Analytical X-ray Instruments, 2007) was used to integrate the frames. The symmetry was then checked by using the PLATON program. The X-ray crystal data are presented in Tables 1 and 2. The structures were solved by the Patterson method (SHELXS97),[15] and 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 on the corresponding atom, those bonded to oxygen atoms were identified in the electron density map. The carbon atoms of the different O*i*Pr ligands of **1**, **2**, **2b**, **3**, **4**, and **7** were disordered as well as the carbon atoms of the different phosphonates of **1**, **2b**, and **3**. In **2** and **2b**, the isopropyl ester

Table 1. Crystal data and structure refinement details for **1**–**3**.

Compound	**1**	**2**	**2b**	**3**
Empirical formula	$C_{70}H_{155}O_{38}P_6S_2Ti_8$	$C_{72}H_{152}O_{40}P_8Ti_8$	$C_{72}H_{152}O_{40}P_8Ti_8$	$C_{32}H_{76}O_{20}P_4Ti_4$
M_r	2238.08	2288.90	2288.90	1096.41
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a [pm]	3366.33(17)	1192.63(4)	1260.81(4)	1173.14(3)
b [pm]	1270.76(7)	1315.97(4)	1873.03(6)	1266.27(4)
c [pm]	2763.86(14)	1888.04(8)	2282.43(8)	1870.42(5)
α [°]	90	95.737(2)	90	90.5310(10)
β [°]	114.257(2)	93.920(2)	93.6370(10)	95.6330(10)
γ [°]	90	114.5600(10)	90	114.4040(10)
V [10^6 pm^3]	10779.4(10)	2661.77(17)	5379.18	2514.25(12)
Z	4	1	2	2
D_X [Mg m^{-3}]	1.379	1.428	1.413	1.448
μ [mm^{-1}]	0.762	0.766	0.758	0.807
Crystal size [mm]	0.3 × 0.2 × 0.2	0.4 × 0.3 × 0.2	0.4 × 0.4 × 0.3	0.6 × 0.5 × 0.4
No. measured refl.	116818	52732	121493	99598
Independent refl.	32005	19103	18194	16665
Observed refl. [$I > 2\sigma(I)$]	16463	12969	13342	13216
θ_{max} [°]	30.56	32.64	31.75	31.55
R [$F^2 > 2\sigma(F)$], $wR(F^2)$, S	0.0633, 0.1665, 0.939	0.0548, 0.1685, 1.019	0.0682, 0.1966, 1.098	0.0601, 0.1840, 1.074
Refl./param.	32005/1205	19103/719	18194/663	16665/820
Weighting scheme[a]	$w = 1/[\sigma^2(F_o^2) + (0.0761P)^2]$	$w = 1/[\sigma^2(F_o^2) + (0.0861P)^2 + 2.4222P]$	$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2 + 17.5872P]$	$w = 1/[\sigma^2(F_o^2) + (0.0863P)^2 + 6.1747P]$
$\delta\rho_{max,min}$ [10^{-6} e pm^{-3}]	1.551, –1.760	1.619, –1.634	2.329, –1.886	2.944, –1.597

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

Table 2. Crystal data and structure refinement details for **4**–**7**.

Compound	**4**	**5**	**6**	**7**
Empirical formula	$C_{27}H_{60}Cl_3O_{16}P_3Ti_{3.50}$	$C_{78}H_{126}O_{32}P_6Ti_7$	$C_{111}H_{204}O_{41}P_6Ti_8$	$C_{77}H_{113}O_{23}P_4Ti_4$
M_r	1007.66	2096.91	2763.76	1722.15
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a [pm]	1474.51(4)	1348.84(17)	1416.99(12)	1327.97(14)
b [pm]	1506.18(4)	1496.1(2)	2272.53(18)	1421.57(15)
c [pm]	2021.22(6)	2399.1(3)	2227.81(17)	2497.7(3)
α [°]	90	90	90	83.599(4)
β [°]	104.184(2)	98.141(4)	101.300(4)	74.598(4)
γ [°]	90	90	90	83.251(4)
V [10^6 pm^3]	4352.0(2)	4792.4(11)	7034.8(10)	4498.5(9)
Z	4	2	2	2
D_X [Mg m^{-3}]	1.538	1.453	1.305	1.270
μ [mm^{-1}]	0.978	0.730	0.571	0.479
Crystal size [mm]	0.3 × 0.2 × 0.2	0.2 × 0.2 × 0.1	0.5 × 0.3 × 0.2	0.6 × 0.5 × 0.4
No. measured refl.	113501	62552	105744	116779
Independent refl.	8719	8294	12938	18623
Observed refl. [$I > 2\sigma(I)$]	6723	5573	7468	12241
θ_{max} [°]	26.24	24.87	25.41	26.63
R [$F^2 > 2\sigma(F)$], $wR(F^2)$, S	0.0465, 0.1306, 1.049	0.0704, 0.2205, 1.035	0.0528, 0.1229, 1.000	0.0715, 0.2450, 1.041
Refl./parameters	8719/517	8294/556	12938/799	18623/1124
Weighting scheme[a]	$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 11.9306P]$	$w = 1/[\sigma^2(F_o^2) + (0.1079P)^2 + 27.4456P]$	$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 10.814P]$	$w = 1/[\sigma^2(F_o^2) + (0.1379P)^2 + 7.4926P]$
$\delta\rho_{max,min}$ [10^{-6} e pm^{-3}]	1.477, –0.690	1.767, –1.104	0.662, –0.533	1.539, –0.705

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

and the allyl group were interchangeably disordered. The positions of the disordered groups were refined with about 50% occupancy each. CCDC-948341 (for **1**), -948342 (for **2**), -948343 (for **2b**), -948344 (for **3**), -948345 (for **4**), -948346 (for **5**), -948347 (for **6**) and -948348 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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