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DISSERTATION

Carboxylate- and Phosphonate-Substituted Titanium and Zirconium Oxo Clusters

ausgeführt zum Zwecke der Erlangung des akademischen Grades
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unter der Leitung von

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"Fast alles ist leichter begonnen als beendet."

J.W. von Goethe

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Kurzfassung

In dieser Arbeit wurden neue Titan- und Zirkonium-Oxo-Cluster hergestellt. Durch funktionalisierte Endgruppen können diese in sogenannte Klasse-II-Hybridmaterialen eingebaut werden. Einige dieser Cluster wurden hergestellt indem ein Metallalkoxid mit einer funktionalisierten oder nicht-funktionalisierten Carbonsäure zur Reaktion gebracht wurde. Der bei dieser Reaktion entstandene Cluster wurde direkt aus dieser Reaktionslösung kristallisiert. Die Kristalle wurden anschließend mittels Einkristallröntgenbeugung und in Lösung mittels NMR charakterisiert. Neue Cluster konnten durch Variation der Carbonsäure hergestellt werden. Dabei zeigte sich, dass Carbonsäuren mit koordinationsfähigen Gruppen nur begrenzt verwendet werden können. Beim Einsatz der Imidazolylbuttersäure kam es nicht zur Clusterbildung, stattdessen bildete sich ein Koordinationspolymer. Um einen Zusammenhang zwischen Eduktverhältnis und erhaltenen Cluster zu erkennen wurde exemplarisch Methacrylsäure und Titanisopropoxid in verschiedenen Verhältnissen miteinander umgesetzt.

Für den Einsatz der Cluster in Klasse-II-Hybridmaterialen ist es oft notwendig die Anzahl der funktionellen Liganden zu begrenzen und diese in einer spezifischen räumlichen Anordnung an der Oberfläche des Clusters zu arrangieren. Dazu wurde die sterisch anspruchsvolle Carbonsäure Triphenylessigsäure mit Essigsäure und Titanisopropoxid umgesetzt. Selbst mit dieser sterisch stark gehinderten Säure wurde jedoch keine Änderung der Ligandenanordnung beobachtet. Außer Carbonsäuren wurden auch Calixarene eingesetzt. Diese Verbindungen können mit vier Sauerstoffatomen an die Oberfläche des Clusters binden, wodurch vier Koordinationsstellen an einem Metallzentrum besetzt werden und damit eine andere Anordnung der Metallatome erzielt wird. Dabei bildeten sich jedoch generell kleinere Strukturen.

Ein weiterer Teil der Arbeit beschäftigt sich mit der Verwendung von zyklischen Anhydriden. Bei der äquimolaren Reaktion von Titanisopropoxid mit Phthalsäureanhydrid wurde ein dimerer Metallkomplex mit zwei koordinierenden Monoisopropylestern der Phthalsäure erhalten. Wenn dieselbe Reaktion in der Gegenwart von Essigsäure durchgeführt wurde, wurde ein Ti_6O_6-Cluster mit koordinierenden Monoisopropylestern der Phthalsäure erhalten. Die Oxo-Brücken dieses Titan-Oxo-Clusters wurden durch die Veresterung der zugegebenen Essigsäure erhalten, die daher Wasser *in situ* erzeugt. Bei der Reaktion von Maleinsäureanhydrid mit Titanisopropoxid wurde im Gegensatz zur Reaktion mit Phthalsäureanhydrid ein Cluster mit Dicarboxylatliganden erhalten.

In der Nanochemie werden Phosphonsäuren eingesetzt um Titandioxid- und Zirkoniumdioxid-Nanopartikel zu stabilisieren. Daher ist ein Teil der Arbeit der Herstellung von Zirkonium- und Titanclustern mit Phosphonatliganden gewidmet. Dabei zeigte sich, dass die Bis(trimethylsilyl)ester der Phosphonsäuren sehr gut zur Funktionalisierung von Titan-Oxo-Clustern geeignet sind. Einige neue Strukturen von Titan-Oxo-Clustern mit Phosphonatliganden wurden dabei aufgeklärt und so die Anzahl der bekannten Titan-Oxo-Cluster wesentlich erhöht und besser zugänglich gemacht. Im Zuge dieser Arbeit wurde der erste Zirkonium-Oxo-Cluster mit Phosphonatliganden hergestellt und charakterisiert. Aufgrund der zuvor gewonnenen Erkenntnisse

wurde auch eine Mischung aus einem Phosphonsäurederivat und Essigsäure verwendet und so die gleiche Struktur mit verschiedenen Phosphonatliganden erhalten, wobei auch Acetatliganden in die Clusterstruktur eingebaut wurden. Die Stabilität dieser ersten Titan-Oxo-Cluster mit gemischter Ligandensphäre aus Alkoxo-, Phosphonat- und Carboxylatliganden in Lösung wurde mit Hilfe von NMR-Experimenten nachgewiesen.

Abstract

This work deals with the synthesis of new titanium and zirconium oxo clusters. By using functionalized ligands, these clusters can be incorporated in class II hybrid materials. Some of the clusters described in this work were obtained by the reaction of a metal alkoxide with a functional or non-functional carboxylic acid. Crystals of the clusters were obtained directly from the reaction solution. These crystals were characterized by single crystal XRD and solution NMR spectroscopy. New clusters were obtained by variation of the carboxylic acid. It was found that carboxylic acids with non-coordinating functional groups can be used to obtain new clusters regardless of the steric demand of the acid. When reacting imidazolylbutyric acid with titanium isopropoxide the outcome was a coordination polymer rather than a cluster. Using methacrylic acid, a carboxylic acid which is frequently used in cluster chemistry, several different clusters were synthesized to show the correlation between precursor ratio and obtained cluster.

For the use in hybrid materials it is desired to control the reactivity of the clusters, and thus the number of functional groups. Therefore some control for the arrangement of the ligands on the surface of the cluster is needed. The sterically demanding triphenylacetic acid was reacted in a mixture with acetic acid and titanium isopropoxide. The outcome, however, showed no significant difference in the ligand sphere. Therefore calixarenes were used, since they occupy four coordination sites on the cluster surface. This led to a different arrangement of the central metal atoms but also smaller structures.

In another part of this work, the reactivity of cyclic anhydrides with titanium isopropoxide was investigated. Reacting equimolar amounts of phthalic anhydride with titanium isopropoxide, a dimeric complex with two monoisopropyl phthalate ligands was formed. The same reaction in presence of acetic acid led to the formation of a cluster with a Ti_6O_6 core and monoisopropyl phthalate ligands. The oxo-bridges of the cluster were obtained through esterification of the acetic acid, which acted as *in situ* source of water. In contrast, reaction of maleic anhydride with titanium isopropoxide led to the formation of a cluster with dicarboxylate ligands.

Phosphonic acids are frequently used to stabilize and functionalize titania and zirconia nanoparticles. Therefore, part of this work deals with the synthesis of phosphonate-substituted titanium and zirconium oxo clusters. It was shown that bis(trimethylsilyl) phosphonates are viable precursors for the preparation of phosphonate-substituted titanium oxo clusters, of which several new structures were synthesized and characterized. The first phosphonate substituted zirconium oxo cluster was subsequently synthesized during this work. Based on the results of previous experiments of this work, a mixture of a bis(trimethylsilyl) phosphonate and acetic acid was used and reacted with titanium isopropoxide. The same cluster core was found with various phosphonates, all containing acetate ligands. These titanium oxo cluster thus have a mixed-ligand sphere of acetate, phosphonate and alkoxo ligands. The stability of these titanium oxo clusters in solution was proven by NMR-experiments.

Part of this work has been published

1. Czakler, M.; Artner, C.; Schubert, U. *Preparation of Carboxylato-Coordinated Titanium Alkoxides from Carboxylic Anhydrides: Alkoxido Group Transfer from Metal Atom to Carbonyl Group.* European Journal of Inorganic Chemistry **2012**, 3485-3489.
2. Czakler, M.; Artner, C.; Schubert, U. *Influence of the Phosphonate Ligand on the Structure of Phosphonate-Substituted Titanium Oxo Clusters.* European Journal of Inorganic Chemistry **2013**, 5790-5796.
3. Artner, C.; Czakler, M.; Schubert, U. *Crown-Ether-Like Structures Derived from a* Ti_8O_8*(carboxylate)*$_{16}$ *Metallacycle.* Chemistry - A European Journal **2014**, *20*, 493-498.
4. Czakler, M.; Artner, C.; Schubert, U. *Acetic Acid Mediated Synthesis of Phosphonate-Substituted Titanium Oxo Clusters.* Eur. J. Inorg. Chem. **2014**, 2038-2045.
5. Czakler, M.; Puchberger, M.; Artner, C.; Schubert, U. *A Coordination Polymer with Unusual Structural Features from Imidazolylbutyric Acid and Titanium Isopropoxide.* Monatshefte für Chemie - Chemical Monthly **2014**, *8*, 1259-1262.

Part of this work has been submitted for publication

1. Czakler, M.; Artner, C.; Maurer, C; Schubert, U. *Calix[4]arene derivatives of titanium and zirconium alkoxides.* Z. Naturforsch. **2014**.

Glossary

XRD	X-ray diffraction
NMR	Nuclear magnetic resonance
IR	Infrared

E	Element
En	Atom position of E
En*	Symmetry equivalent atom position of En
μ_n	Ligand bridging n atoms
η_1	Hapticity

Chemicals

Et	Ethyl	CH_3CH_2-
Allyl	Allyl	$CH_2{=}CH{-}CH_2$-
Vinyl	Vinyl	$CH_2{=}CH$-
Bz	Benzyl	$C_6H_5CH_2$-
McOH	Methacrylic acid	$CH_2{=}(CH_3)CCOOH$
AdaOH	Adamantanecarboxylic acid	$C_{10}H_{15}COOH$
EtOH	Ethanol	CH_3CH_2OH
^{i}PrOH	2-Propanol	$(CH_3)_2CHOH$
^{n}BuOH	1-Butanol	$CH_3(CH_2)_3OH$
Calix^{tBu}(OH)$_4$	^{t}Butyl-calix[4]arene	5,11,17,23-Tetra-^{t}butyl- -25,26,27,28-tetrahydroxycalix[4]arene

Crystallography

a, b, c	Unit cell lenghts
α, β, γ	Unit cell angles
V	Unit cell volume
λ	Wavelengths
M_r	Molecular mass
Z	Formula units
D_x	Calculated density
μ	Absorption coefficient
Θ	Diffraction angle

NMR

δ	Chemical shift
s	singlet
d	doublet
dd	doublet of doublet
dt	doublet of triplet
ddd	doublet of doublet of doublet
t	triplet
m	multiplet

IR

s	strong
m	middle
w	weak
b	broad

Clusters of this work

Table 1: *Oxo clusters and complexes presented in this work.*

Abbreviation	**Formula**	**Descripted in**
Carboxylate substituted oxo clusters and complexes		
TiCycloBu	$Ti_6O_6(O^iPr)_2(OOCC_4H_7)_{10}$	Section 3.1
TiBenzCl	$Ti_4O_2(O^iPr)_6(OOC-C_6H_4-Cl)_6)$	Section 3.1
TiTPA	$Ti_3O_2(O^iPr)_3(OOCCPh_3)_5$	Section 3.1.1
TiAda	$Ti_3O(O^iPr)_6(OOC-\text{adamantyl})_4$	Section 3.1.1
ZrAda	$Zr_6O_4(OH)_4(OOC-\text{adamantyl})_{12}$	Section 3.1.1
TiBenzMeCl	$Ti_2(O^iPr)_6(OOC-C_6H_4-CH_2Cl)_2(^iPrOH)$	Section 3.1.2
ZrBenzMeCl	$Zr_{10}O_8(O^nBu)_{16}(OOC-C_6H_4-CH_2Cl)_8$	Section 3.1.2
ZrPentin	$Zr_9O_6(O^nBu)_{18}(OOC-C \equiv C-CH_2CH_3)_6$	Section 3.1.2
TiBuImid	$[Ti(O^iPr)_3(OOCCH_2CH_2CH_2C_3N_2H_3)]_n$	Section 3.2
TiOMc1	$Ti_2(O^iPr)_6(OMc)_2{}^iPrOH$	Section 3.3
TiOMc2	$Ti_6O_4(O^iPr)_8(OMc)_8$	Section 3.3
TiOMc6	$Ti_9O_8(O^iPr)_4(OMc)_{16}$	Section 3.3
TiOMc8	$Ti_8O_8(OMc)_{16}$	Section 3.3
Carboxylate substituted oxo clusters and complexes from anhydrides		
TiPhthal1	$Ti_2(O^iPr)_6(OOC-C_6H_4-COO^iPr)_2(^iPrOH)$	Section 4.1.1
TiPhthal2	$Ti_6O_6(O^iPr)_6(OOC-C_6H_4-COO^iPr)_6$	Section 4.1.1
TiMal	$Ti_6O_3(O^iPr)_{14}(OOC-CH{=}CH-COO)_2$	Section 4.1.2
Oxo clusters and complexes with other ligands		
Zr3Calix	$Zr_3(O^nBu)_8(Calix^{tBu}O_4)$	Section 5.1
TiCalix	$Ti_2(O^nBu)_2(Calix^{tBu}O_3(OH))_2$	Section 5.1
Zr4Calix2	$Zr_4O(O^nBu)_6(Calix^{tBu}O_4)_2(^nBuOH)_2$	Section 5.1
ZrHexOx	$Zr_{10}O_4(O^nBu)_{18}((ON)_2\text{cyclohexan})_4(OAc)_6$	Section 5.2
Phosphonate substituted oxo clusters and complexes		
TiDMSOAllylPA	$Ti_4O(O^iPr)_8(O_3P-\text{allyl})_3(DMSO)$	Section 6.1.1
TiAllylPP	$Ti_8O_2(O^iPr)_{14}(O_3P-\text{allyl})_6(O_2P(O^iPr)\text{allyl})_2$	Section 6.1.1
TiAllylPP2	$Ti_8O_2(O^iPr)_{14}(O_3P-\text{allyl})_6(O_2P(O^iPr)\text{allyl})_2$	Section 6.1.1
TiEtPP	$Ti_8O_2(O^iPr)_{14}(O_3P-\text{ethyl})_6(O_2P(O^iPr)\text{ethyl})_2$	Section 6.1.1

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Abbreviation	**Formula**	**Descripted in**
TiClPrPP	$\mathrm{Ti_7O_2(O^iPr)_{12}(O_3PCH_2CH_2CH_2Cl)_6}$	Section 6.1.1
TiBzlPP	$\mathrm{Ti_7O_2(O^iPr)_{12}(O_3P{-}CH_2{-}C_6H_5)_6}$	Section 6.1.1
TiBrPrPP	$\mathrm{Ti_7O_2(O^iPr)_{12}(O_3PCH_2CH_2CH_2Br)_6}$	Section 6.1.1
TiXylPP	$\mathrm{Ti_4O(O^iPr)_8(O_3P{-}xyl)_3(^iPrOH)}$	Section 6.1.1
TiNpMePP	$\mathrm{Ti_4(O^iPr)_8(O_3PMeNp)_4(^iPrOH)_2}$	Section 6.1.1
TiCl3MePP	$\mathrm{Ti_4O(O^iPr)_8(O_3PCCl_3)_3(DMF)}$	Section 6.1.1
TiVinylPP	$\mathrm{Ti_8O_2(O^iPr)_{14}(PO_4)_2(O_3P(vinyl))_4(^iPrOH)_2}$	Section 6.1.1
ZrPhPP	$\mathrm{Zr_6O_2(O^nBu)_{12}(O_3P{-}Ph)_4}$	Section 6.1.2
TiOAcEtPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PEt)_2}$	Section 6.1.3
TiOAcNpMePP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2naphthyl)_2}$	Section 6.1.3
TiOAcVinylPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3P{-}vinyl)_2}$	Section 6.1.3
TiOAcAllylPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3P{-}allyl)_2}$	Section 6.1.3
TiOAcClPrPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2CH_2CH_2Cl)_2}$	Section 6.1.3
TiOAcBzlPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2C_6H_5)_2}$	Section 6.1.3
TiOAcBrPrPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2CH_2CH_2Br)_2}$	Section 6.1.3
TiOAcPhPA	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3P{-}C_6H_5)_2}$	Section 6.1.3
TiOAcBrPrPP2	$\mathrm{Ti_5O(O^iPr)_{11}(OAc)(O_3PCH_2CH_2CH_2Br)_3}$	Section 6.1.3
TiOAcXylPP	$\mathrm{Ti_5O_3(O^iPr)_6(OAc)_4(O_3P{-}xylyl)_2}$	Section 6.1.3
TiOPhPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(O_3P{-}C_6H_5)_2(O_2P(O^iPr)C_6H_5)_2}$	Section 6.1.4
TiOMcEtPP	$\mathrm{Ti_5O(O^iPr)_{11}(OMc)(O_3PEt)_3}$	Section 6.1.5
TiOMcAllylPP	$\mathrm{Ti_{10}(O^iPr)_{16}(O_3PCH_2CH{=}CH_2)_{10}(OMc)_4}$	Section 6.1.5

Contents

Part I

Introduction

Chapter 1

Introduction

Advancement in technology requires the development of new materials. Present-day materials must meet the highest criteria to enable specialized applications. In many cases it is desired to control the properties of these materials which then need to be readily available.

The chemistry of materials is divided into two major subgenres. As in synthetic chemistry it is generally distinguished between an organic (generally including a C-H bond) and an inorganic part. While organic materials, such as common polymers, have a low density and are generally cheap, inorganic materials have enhanced thermal properties and generally show increased hardness. One class of materials taking advantage of both organic and inorganic parts are hybrid materials, where both are ideally combined on the nanoscale to obtain the best of both components, providing low cost and low density with good thermal and mechanical properties. Depending on the chemical bond, hybrid materials are divided into class I and class II.[1] Class II hybrid materials, in contrast to class I hybrid materials, have covalent bonds between the organic and inorganic part of the nanocomposite, where in most cases the inorganic part is embedded in an organic matrix.

For further improvement of these hybrid materials, very defined precursors have to be provided. The so called ”nanobuilding blocks” (NBB) enable combination on the nanoscale in a Lego$^{\text{TM}}$-brick like fashion. By controlled functionalization of these NBB they can be combined on the molecular level to design new materials with predefined properties. Nanoparticles are well established precursors for class I and class II hybrid materials, but they are often obtained as a mixture of different sizes and shapes and can therefore not be used for well-defined nano structures. Clusters, in contrast, are structures with uniform size and shape. They can be seen as large complexes or small nanoparticles, with the advantage that clusters are often soluble in organic solvents (instead of suspended nanoparticles) and can be analyzed using standard analytical techniques for molecular compounds such as NMR spectroscopy or single crystal X-ray diffraction. These advantages make oxo clusters interesting for the use in hybrid materials.[2–5] Many functional oxo clusters are known, but control of the ligand arrangement on the cluster surface is yet to be gained to enable the use of clusters in a straightforward fashion.

1.1 Sol-gel process

Oxo clusters can be described as small nanoparticles or large complexes, but also as intermediates of the sol-gel process, since they are partly hydrolyzed products of metal alkoxides.

The precursors used in this work are titanium and zirconium alkoxides. These can be hydrolyzed in a controlled manner in the sol-gel process to obtain TiO_2 and ZrO_2 with different properties (*e.g.* high surface area, functionalities). The sol-gel process itself is very well established for silicon alkoxides. In a first step the hydrolysis and condensation reactions are taking place to form the sol from the molecular precursors (scheme 1.1).[6–8]

$$\begin{array}{rcll} \mathrm{Si(OR)_4 + H_2O} & \longrightarrow & \mathrm{Si(OH)(OR)_3 + ROH} & \text{Hydrolysis} \\ \\ \mathrm{2\ Si(OH)(OR)_3} & \longrightarrow & \mathrm{(OR)_3Si{-}O{-}Si(OR)_3 + H_2O} & \text{Condensation} \\ \mathrm{Si(OH)(OR)_3 + Si(OR)_4} & \longrightarrow & \mathrm{(OR)_3Si{-}O{-}Si(OR)_3 + ROH} & \text{Condensation} \end{array}$$

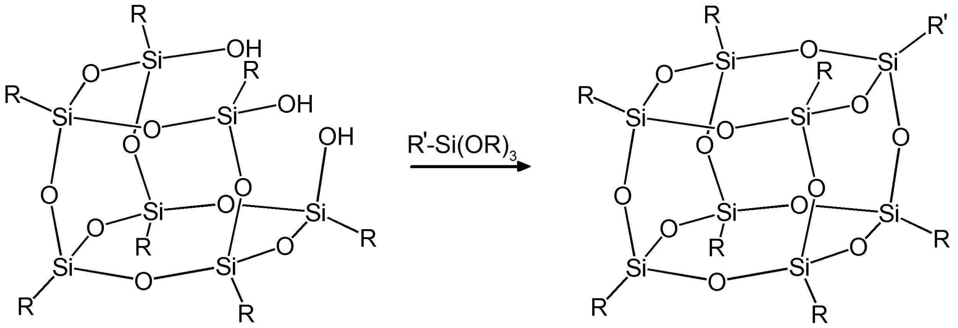
Scheme 1.1: *Reactions occurring during sol-gel processing of silicon alkoxides.*

With progression of these reactions, the so-called sol is formed, which is a colloidal suspension of particles in the reaction solution. During gelation connections between the sol particles are formed, creating a continuous 3D network, the gel. After gelation, the solvent and unreacted small oligomers or monomers are trapped within the gel and are strongly interacting with the gel (hydrogel). After aging, these gels are often dried, which commonly leads to a collapse of the 3D-network due to shrinking, yielding so-called xerogels. Aerogels, which are solvent-free gels still containing the initially formed 3-dimensional network, can be obtained by supercritical extraction.

Depending on the process parameters (pH, T, ...) it is possible to influence the materials chemical properties, and especially their morphology. For example it is possible to get coatings which is one of the many applications of the sol-gel process.[9–13]

Another example is the Stöber-process which yields silica nanoparticles in a base-catalyzed sol-gel reaction.[14] There is a variety of properties and applications of these nanoparticles which are readily available, stable and can be functionalized.[15–26] Interesting compounds related to the sol-gel process are polyhedral oligomeric silsesquioxanes (POSS)[27–35] of which the cubane cage structure is special due to the possibility to functionalize it on one side.[36–44] To this end an open cage structure is formed first, which has seven organic substituents of the same kind on the silicon atoms. This open cage structure is then reacted with $R'\text{-}Si(OR)_3$ introducing different functionalities (see scheme 1.2).[45–48]

The sol-gel processing of titanium and zirconium alkoxides has some differences, although the underlying reactions are in principle the same. Due to their lower electronegativity and the



Scheme 1.2: *Silsesquioxane cage structure and its anisotropic functionalization.*

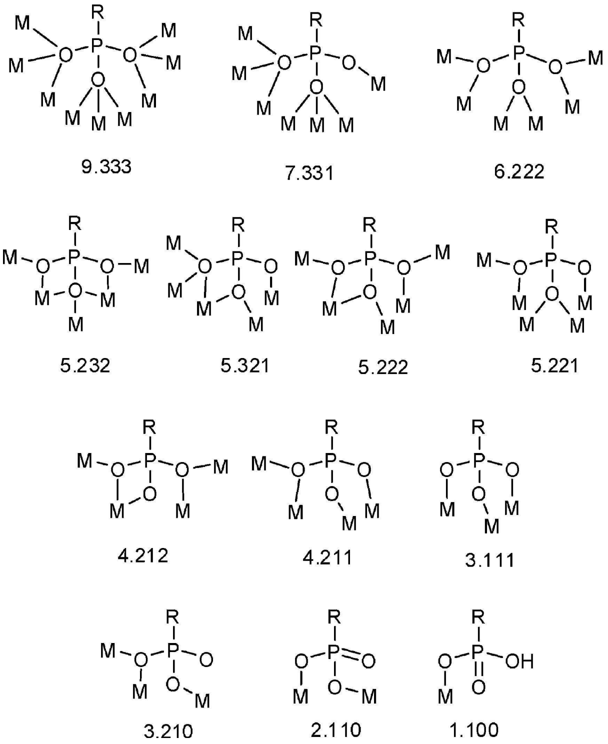
tendency to higher coordination numbers these alkoxides are more reactive towards hydrolysis and generally to nucleophilic attack. The alkoxo ligands are therefore often modified for sol-gel processing.[49] As for silicon alkoxides, increasing chain lengths and branching of the OR groups lower the reactivity of titanium and zirconium alkoxides, but here another effect has to be considered. Due to their size and increased coordination number with the same charge, titanium and zirconium alkoxides tend to form dimers or oligomers. The larger the degree of oligomerization, the lower the reaction rate, thus titanium methoxide is reacting slower than titanium isopropoxide.[8]

One main advantage of silicon precursors is that they can be directly functionalized since the Si-C bond is stable towards hydrolysis. This is not the case for the Ti-C or Zr-C bonds. Thus zirconia[50,51] and titania[52,53] nanoparticles cannot be functionalized like silica nanoparticles, which are stabilized and functionalized using R-Si$(OR)_3$[54–56].

1.2 Phosphonic acid and its derivatives

Organophosphonic acids - similar to organoalkoxysilanes - are well known in metal oxide nanoparticle chemistry, since the phosphonate ligands form almost covalent bonding to different metal oxide surfaces. The thus formed M-O-P (M = Ti, Zr) bond was proven to be stable even towards hydrolysis.[59–65] Several different binding modes of the phosphonates have to be considered, some exhibiting hydrogen bonding.[66–73] Those binding modes are best labeled as has been done by Chandrasekhar *et al.*[74] (see scheme 1.3).

Due to the nature of the formation reactions, many organophosphonic acids are obtained as their esters in the first step. These esters are then hydrolyzed to obtain the acids. In general, this is done by refluxing in concentrated hydrochloric acid.[75,76] For double bond containing phosphonates this is not possible since an addition reaction occurs. Therefore another route to obtain phosphonic acids from their alkyl esters has been established.[75,77–81] In this route the alkyl ester is transesterified with trimethylbromosilane to the bis(trimethylsilyl)ester which is then hydrolyzed using water or methanol.

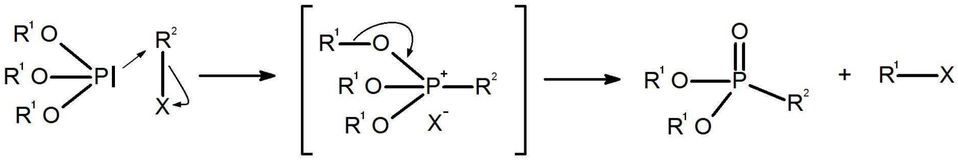


Scheme 1.3: *Phosphonate binding modes with the proposed labeling (w.xyz refers to the number of metal atoms to which the phosphonate ligand is coordinated [w], and the number of metal atoms to which each oxygen is coordinated [x,y,z]). Picture taken from Chandrasekhar et al.*[74].

1.2.1 Michaelis-Arbuzov rearrangement

A facile route to alkylphosphonic acids is the Michaelis-Arbuzov rearrangement. This synthesis was well studied and was first described in 1898 with iodomethane and triphenyl phosphite.[82] The reaction has been studied in detail by Abramov *et al.*[83–85] and summarized by Bhattacharya *et al.*[86]. In this reaction, a trivalent phosphorous atom (phosphite) is converted into a pentavalent phosphorous atom (phosphonate) by the addition of an alkyl halide. The reaction is shown in scheme 1.4. In the first step, the lone pair of the phosphorous atom attacks the α-carbon atom with a positive partial charge of the alkyl halide $\mathrm{R{-}CH_2^{\delta+}{-}X}$. The transition state consists of a tetravalent positively charged phosphorous atom with the corresponding halide anion. Through dissociation of one alkyl group of the phosphite, the P=O double bond and an alkyl halide is formed.

The reaction itself is convenient although the alkyl halide which is formed as a byproduct can react the same way as the alkyl halide used as starting compound and therefore unwanted alkyl phosphonates can be obtained in considerable amount. For example, reactions involving triethylphosphite lead to diethyl ethylphosphonate as byproduct, which has to be removed by distillation. The reactivity of alkyl halides towards Michaelis-Arbuzov rearrangement is: iodoalkanes > bromoalkanes > chloroalkanes. The Michaelis-Arbuzov rearrangement is the

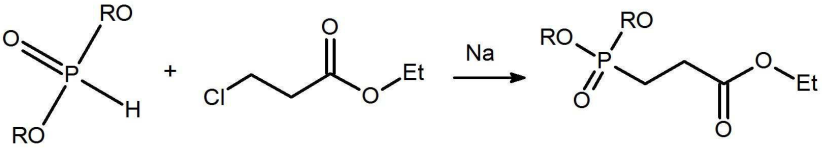


Scheme 1.4: Reaction pathway of the Michaelis-Arbuzov rearrangement.

preferential reaction to obtain alkyl substituted phosphonates; for arylphosphonates or various other functionalities, the Michaelis-Arbuzov rearrangement is not feasible.

1.2.2 Other possibilities to obtain phosphonic acids

Like the Michaelis-Arbuzov reaction, the Michaelis-Becker reaction leads to alkyl-substituted phosphonates (see scheme 1.5). It has been used to obtain phosphonoacetic esters from the corresponding α-chloroacetate.[87,88]



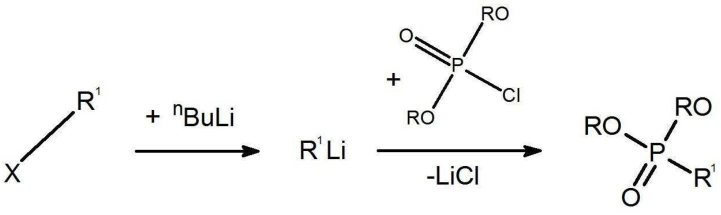
Scheme 1.5: Michaelis-Becker reaction yielding the ethyl ester of 3-(diethoxyphosphinyl) propanoic acid.

The reaction results in lower yields than the Michaelis-Arbuzov rearrangement, thus phase transfer catalysis can be used to increase the yield.[89]

The Abramov and Pudovik reactions generate organophosphonates from a P-H bond or trialkyl phosphites.[90–96] In the case of P-H bonds, the reaction proceeds *via* addition of unsaturated bonds, while the trialkyl phosphites are reacted with carbonyls. Another possibility to obtain phosphonic acids is the Horner-Wadsworth-Emmons reaction, which paves the way to functional phosphonic acids using ketones and aldehydes.[88,97–99]

Another versatile route to phosphonates is the S_N P(V) reaction.[100] This reaction is possible with either Grignard or organolithium reagents.[101] Due to side reactions, the Grignard reagent[102–104] is less suitable than the organolithium reagent.[105,106] The reaction is shown in scheme 1.6 with organolithium compounds using Li^{n}Bu and dialkylchlorophosphate.

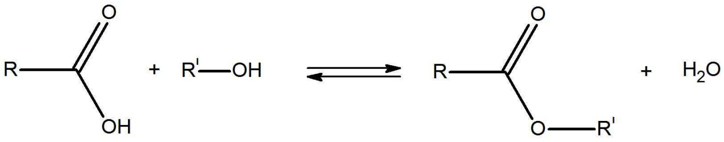
The S_N P(V) reaction offers the possibility to obtain different functional phosphonates[105,107,108] as well as arylphosphonates[109–111].



Scheme 1.6: *Reaction sequence of a* S_N *P(V) using Li*^{n}*Bu and dialkylchlorophosphate.*

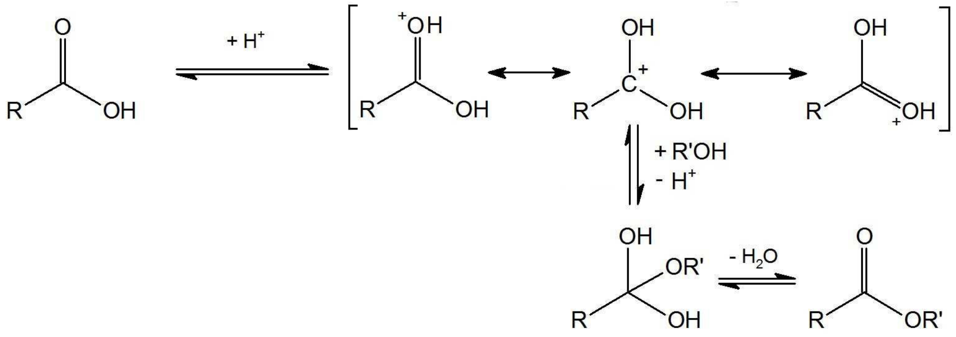
1.3 Esterification of carboxylic acids

Zirconium and titanium oxo clusters are often obtained from the reaction of carboxylic acids with the corresponding metal alkoxide. 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.[112,113] The esterification thus is an important process in the generation of titanium and zirconium oxo clusters. In general esterification is a slow reaction and without catalyst the equilibrium of the reaction of acetic acid and ethanol in molar ratio of 1:1 is not reached after one year at room temperature.[114] Esterification of carboxylic acids (see equation 1.1) was studied in detail by Berthelot *et al.*,[114] the data obtained were used later to formulate the law of mass action.[115–117]



(1.1)

Under acidic conditions the rate of esterification is greatly increased, either by the addition of an inorganic acid or when using the carboxylic acid in excess. Most frequently sulfuric acid is used to catalyze the reaction, which enables Fischer esterification.[118] It is interesting that this reaction is called Fischer esterification, since sulfuric acid was used more than fifty years earlier to accelerate the esterification of butyric acid by Pelouze and Gélis.[119] The reaction pathway of the acid-catalyzed esterification reaction (see equation 1.2) was elucidated by Roberts *et al.* through isotopic labeling.[120]



(1.2)

Acidity and steric hindrance determine the reaction rate of the esterification of a carboxylic acid with an alcohol. Higher acidity of the carboxylic acid means a stronger positive partial charge on the carbonyl carbon atom, which increases the reaction rate of esterification. The larger the organic moiety bound to the carboxylic group or to the alcohol the lower the esterification rate.[121,122] Therefore, α-substituted aliphatic and *ortho*-substituted aromatic carboxylic acids are esterified very slowly in low yield.[123] Furthermore, the rate of esterification is: primary alcohols > secondary alcohols > tertiary alcohols. Tertiary alcohols also show a different reaction pathway, involving a carbenium-ion.[124]

The reaction rate generally decreases when switching from methanol to ethanol and even further to 2-propanol. In addition, the extent of the reaction rate decrease is dependent on the carboxylic acid as the following example will demonstrate: The rate of esterification for butyric acid with methanol is half of that of acetic acid with methanol, for butyric acid with ethanol it is one third compared to the reaction rate of acetic acid with ethanol.[249]

The reverse reaction of esterification is the hydrolysis of the ester. In this work, the hydrolysis of the ester is competing with the irreversible and fast hydrolysis and condensation reactions of metal alkoxides, therefore it can be assumed that no hydrolysis of the ester is taking place in these reactions.

A large number of esterification reactions was developed to protect the carboxylic group in organic synthesis.[125–129] Because many of those reactions result in unwanted byproducts, there is interest in catalysis of the esterification reaction. It was shown that group 4 metal compounds are catalytically active in the esterification reaction.[129–137]

1.4 Titanium and zirconium oxo clusters

The first definition of clusters was given by F.A. Cotton. Clusters were described as compounds containing a finite number of metal atoms and metal-metal bonds.[138] However, nowadays the term "cluster" is also used for polynuclear compounds without M-M bonds. Oxo clusters (in this thesis also sometimes referred to simply as cluster) are defined as metal oxo complexes with a nuclearity higher than 2. These molecules exhibit at least one metal-oxygen-metal bond and are uncharged in difference to polyoxometallates (POM).

Titanium and zirconium oxo clusters can also be seen as small, very defined nanoparticles with only surface atoms. Proper ligands are needed during the synthesis to stabilize the formed core. Therefore the kind of provided ligand has a high impact on cluster formation. The synthesis of titanium and zirconium oxo clusters is mainly done by partial hydrolysis of titanium and zirconium alkoxides, although chlorides and other precursors have also been used. Since oxo clusters are obtained by partial hydrolysis, water is needed for condensation. This can be provided either directly or *in situ* through esterification of carboxylic acids. If water is directly added to the reaction system it is diluted in some cases and in other cases it is provided through diffusion of atmospheric moisture into the flask, allowing a slow condensation.

1.4.1 Titanium oxo alkoxo clusters

Direct addition of water to titanium alkoxides leads to the formation of titanium oxo alkoxo clusters.[139–143] While the primary hydrolysis products of titanium isopropoxide were illuminated by Day *et al.* other alkoxides have not been studied as intensively.[141] There are only few cluster cores obtained from different titanium alkoxides. For example, $Ti_{12}O_{16}$ has been found for $Ti(O^iPr)_4$ and for $Ti(ONp)_4$ (Np = neopentyl). The $Ti_{12}O_{16}$ core has also been found for a different reaction where $Ti(O^iPr)_4$ was reacted with acetic acid (or myristic acid) in a ratio of 1:1.2 and reflux for 48 hours. This is notable since carboxylic acids can substitute part of the alkoxo ligands, but in this case and in the case of the $Ti_{17}O_{24}$ cluster core, a titanium oxo alkoxo cluster has been obtained using a low amount of carboxylic acid.[144] The $Ti_{17}O_{24}$ core was obtained in a solvothermal reaction.

Other titanium oxo alkoxo clusters have been obtained using ketones as oxolation source, such as $Ti_3O(O^iPr)_7(O_3C_9H_{15})$ and $Ti_{11}O_{13}(O^iPr)_{18}$. An acetone condensation product ($O_3C_9H_{18}$ = 2,6-dimethylhept-3-en-2,4,6-triol) was obtained as ligand in the Ti_3O structure. Oxo aryloxo clusters have been obtained using steric demanding diphenol compounds. These clusters were obtained from (S)-binol derivatives[145,146] ($Ti_4(\mu_3\text{-}O)_4(\text{Onaphthyl}{-}\text{naphthyl}{-}O)_6$) or 2,2'-biphenol[147] ($Ti_5(\mu_3\text{-}O)_2(O^iPr)_8(O{-}Ph{-}Ph{-}O)_4$). In both cases the reactions were done in air, and therefore atmospheric moisture is the oxolation source.

1.4.2 Zirconium oxo alkoxo clusters

Zirconium oxo alkoxo clusters were also prepared through addition of water or through atmospheric moisture. Only two cores of this class of oxo clusters are known. The smaller one is the Zr_3O cluster core, in which the zirconium atoms form a equilateral triangle with a μ_3-oxo bridge.[143,148–150] Crystal structures of these clusters have been reported with ^{t}butoxo and/or neopentoxo ligands, rather steric demanding groups. One of these clusters includes a μ_2-hydroxo group replacing one edge-bridging alkoxo ligand.[148] But the preparation of Zr_3O clusters has also been reported with propoxo and ethoxo ligands.[151]

The larger zirconium oxo alkoxo cluster core $Zr_{13}O_8$ is also the largest zirconium oxo cluster. This cluster core was obtained twice, both times with methoxo ligands.[151,152]

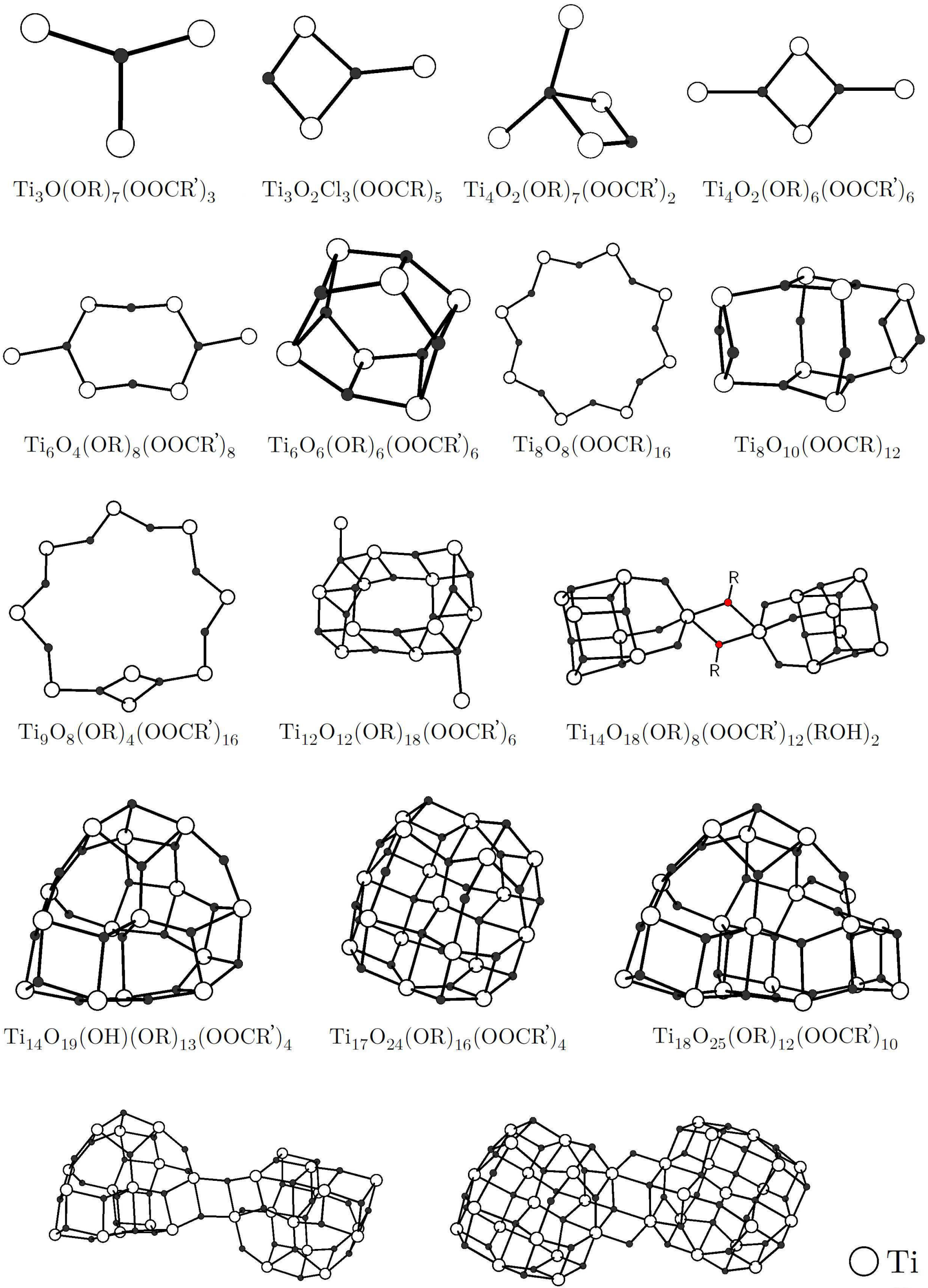
A $Zr_{10}O_{10}$ cluster core has been obtained with a mixed ligand sphere of chloro and 2-methoxyethoxo groups.[153] Zirconium oxo aryloxo clusters include BINOL derivatives[154], catecholato ligands[155] or other aryloxo ligands[156]. In the latter two cases the ligand sphere also includes pyridine ligands.

1.4.3 Carboxylate substituted titanium oxo (alkoxo) clusters

While few titanium oxo alkoxo clusters without carboxylate ligands have been obtained using esterification of carboxylic acids as water source, the majority of the reactions of carboxylic acids with titanium alkoxides leads to the formation of carboxylate substituted titanium oxo alkoxo clusters. The first step in the reaction of titanium alkoxides with an excess of carboxylic acid is the substitution of an alkoxo group with a carboxylic group. The liberated alcohol can then react with further carboxylic acid, forming an ester. The side product of ester formation, water, reacts with the (partly substituted) titanium alkoxide, which leads to condensation and therefore to oxo cluster formation. (*e.g.* equation 1.3)

$$
\begin{array}{rcll}
6\,\mathrm{Ti(OR)_4} + 6\,\mathrm{R^{'}{-}COOH} & \longrightarrow & 6\,\mathrm{Ti(OOC{-}R^{'})(OR)_3} + 6\,\mathrm{ROH} & \text{Substitution} \\
6\,\mathrm{ROH} + 6\,\mathrm{R^{'}{-}COOH} & \longrightarrow & 6\,\mathrm{R^{'}{-}COOR} + 6\,\mathrm{H_2O} & \text{Esterification} \\
6\,\mathrm{Ti(OOC{-}R^{'})(OR)_3} + 6\,\mathrm{H_2O} & \longrightarrow & \mathrm{Ti_6O_6(OOC{-}R^{'})_6(OR)_6} + 6\,\mathrm{ROH} & \text{Condensation} \\
\hline
6\,\mathrm{Ti(OR)_4} + 12\,\mathrm{R^{'}COOH} & \longrightarrow & \mathrm{Ti_6O_6(OOCR^{'})_6(OR)_6} + 6\,\mathrm{R^{'}COOR} + 6\,\mathrm{ROH} &
\end{array}
\tag{1.3}
$$

More than 60 carboxylate titanium oxo (alkoxo) clusters are known which exhibit nuclearities in the range from 3 to 34. Among these, nuclearities higher than 10 have only been obtained with low amounts of carboxylic acids (molar ratio $\mathrm{Ti(OR)_4}$:RCOOH not exceeding 1:1.5). Other carboxylate substituted titanium oxo clusters with a high nuclearity have been obtained by partial substitution of the alkoxo groups of large oxo alkoxo clusters. Of all carboxylate titanium oxo clusters[157–159] several have been obtained with the same cluster core, these cores are shown in figure 1.1.



$Ti_3O(OR)_7(OOCR')_3$ $Ti_3O_2Cl_3(OOCR)_5$ $Ti_4O_2(OR)_7(OOCR')_2$ $Ti_4O_2(OR)_6(OOCR')_6$

$Ti_6O_4(OR)_8(OOCR')_8$ $Ti_6O_6(OR)_6(OOCR')_6$ $Ti_8O_8(OOCR)_{16}$ $Ti_8O_{10}(OOCR)_{12}$

$Ti_9O_8(OR)_4(OOCR')_{16}$ $Ti_{12}O_{12}(OR)_{18}(OOCR')_6$ $Ti_{14}O_{18}(OR)_8(OOCR')_{12}(ROH)_2$

$Ti_{14}O_{19}(OH)(OR)_{13}(OOCR')_4$ $Ti_{17}O_{24}(OR)_{16}(OOCR')_4$ $Ti_{18}O_{25}(OR)_{12}(OOCR')_{10}$

$Ti_{28}O_{40}(OR)_{20}(OOCR')_{12}$ $Ti_{34}O_{50}(OR)_{30}(OOCR')_6$

Figure 1.1: *Cluster cores of different carboxylate titanium oxo (alkoxo) clusters.*

As can be seen in figure 1.1, some cores are formed from very similar building blocks, but have different nuclearities. The Ti_3O cluster core is built by a triangle with a central μ_3-oxygen. Three variations of the Ti_3O cluster core are known, all with a central μ_3-oxygen, but with a slightly different geometry due to a different ligand sphere, $Ti_3O(\mu_2\text{-}OR)_3(OR)_5(OOCR')_2$[160], $Ti_3O(\mu_2\text{-}OR)_2(OR)_6(OOCR')_2$[161,162] and $Ti_3O(\mu_2\text{-}OR)_2(OR)_5(OOCR')_3$[163]. The Ti_3O_2 cluster core can be described as a Ti_3O cluster with an μ_2-oxo bridge on one edge.[164,165] The tetrahedral Ti_4O_2 cluster core contains a μ_4-oxygen in the center of the tetrahedrally arranged titanium atoms.[166–168] Furthermore a μ_2-oxygen is bridging one edge of the tetrahedron. It is notable that other titanium oxo clusters containing a μ_4-oxo bridge have a nuclearity of 12 or higher.

Both the Ti_4O_2[3,169] cluster core and the Ti_6O_4[3,170–176] cluster core are flat, and in both structures two Ti_3O moieties can be found. In the case of the Ti_4O_2 cluster core, these two triangles are edge-sharing and in the case of the Ti_6O_4 cluster core the two triangles are bridged by two μ_2-oxygen atoms. The Ti_6O_4 cluster core was also obtained with a different ligand sphere (as $Ti_6O_4(OR)_{12}(OOCR')_4$) and therefore a slightly different geometry.

The titanium oxo cluster core with the highest number of published structures is that of Ti_6O_6.[161,163,166,168,174,177–185] This cluster has been obtained with different titanium alkoxides and many different carboxylic acids, also at elevated temperatures. The two Ti_8 clusters, although structurally completely different, are the only "pure" carboxylate titanium oxo clusters, meaning that only carboxylate ligands are coordinating. The Ti_8O_8 core is built up by eight $[Ti(\mu_2\text{-}O)(OOCR)_2]$ moieties forming an octagon.[186–188] The recently found Ti_8O_{10} cluster core was obtained in a solvothermal reaction. The core is in principle built by two flat Ti_4O_2 moieties which are aligned parallel, interconnected by six μ_2-oxo bridges.[189] Very similar to the Ti_8O_8 cluster core is that of Ti_9O_8, which was reported only once.[190] The ligand sphere of both Ti_9O_8 and Ti_8O_8 contain 16 carboxylate ligands, the Ti_9O_8 cluster also contains four alkoxo ligands, in contrast to the Ti_8O_8 cluster core.

Carboxylate titanium oxo clusters with a nuclearity higher than 10, like $Ti_{12}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_{10}\text{-}(\mu_2\text{-}OR)_4(OR)_{14}(OOCR')_6$[183] have been obtained less often. The $Ti_{14}O_{18}$ cluster core is in principle two Ti_7O_9 units which are linked by two alkoxo ligands.[184] The Ti_7O_9 units itself can be seen as the Ti_6O_6 cluster core capped by a titanium atom which is connected by three μ_2-oxo bridges. The cluster cores of $Ti_{14}(\mu_3\text{-}O)_{17}(\mu_2\text{-}O)_2(OH)(OR)_{13}(OOCR')_4$[191], $Ti_{18}(\mu_4\text{-}O)(\mu_3\text{-}O)_{20}(\mu_2\text{-}O)_4(OR)_{12}(OOCR')_{10}$[191,192] and $Ti_{28}(\mu_4\text{-}O)_2(\mu_3\text{-}O)_{32}(\mu_2\text{-}O)_6(OR)_{20}\text{-}(OOCR')_{12}$[192] are related to each other. The $Ti_{18}O_{25}$ cluster core is in the larger part (the left side of the core in fig. 1.1) analogous to the $Ti_{14}O_{19}$ cluster core with additionally condensed titanium atoms, while the $Ti_{28}O_{40}$ cluster core can be seen as a dimer of the $Ti_{14}O_{19}$ cluster core. The few $Ti_{17}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_{16}(\mu_2\text{-}O)_4(\mu_2\text{-}OR)_4\text{-}(OR)_{12}(OOCR')_4$ clusters were all obtained by substituting part of the alkoxo ligands of the $Ti_{17}O_{24}(OR)_{20}$ cluster.[191,192] The $Ti_{34}O_{50}$ cluster core can be seen as a dimer of the $Ti_{17}O_{24}$ cluster core and was obtained also by mixing the $Ti_{17}O_{24}(OR)_{20}$ cluster with carboxylic acid.[192]

It is interesting to note that no carboxylate-substituted titanium oxo cluster with a nuclearity of 5 or 7 has been obtained yet. While titanium oxo alkoxo clusters have been obtained with a nuclearity of 7, the nuclearity of 5 was only obtained with other ligands *e.g.* cyclopentadienyl ligands[193] or bis-aryloxo ligands[147,194].

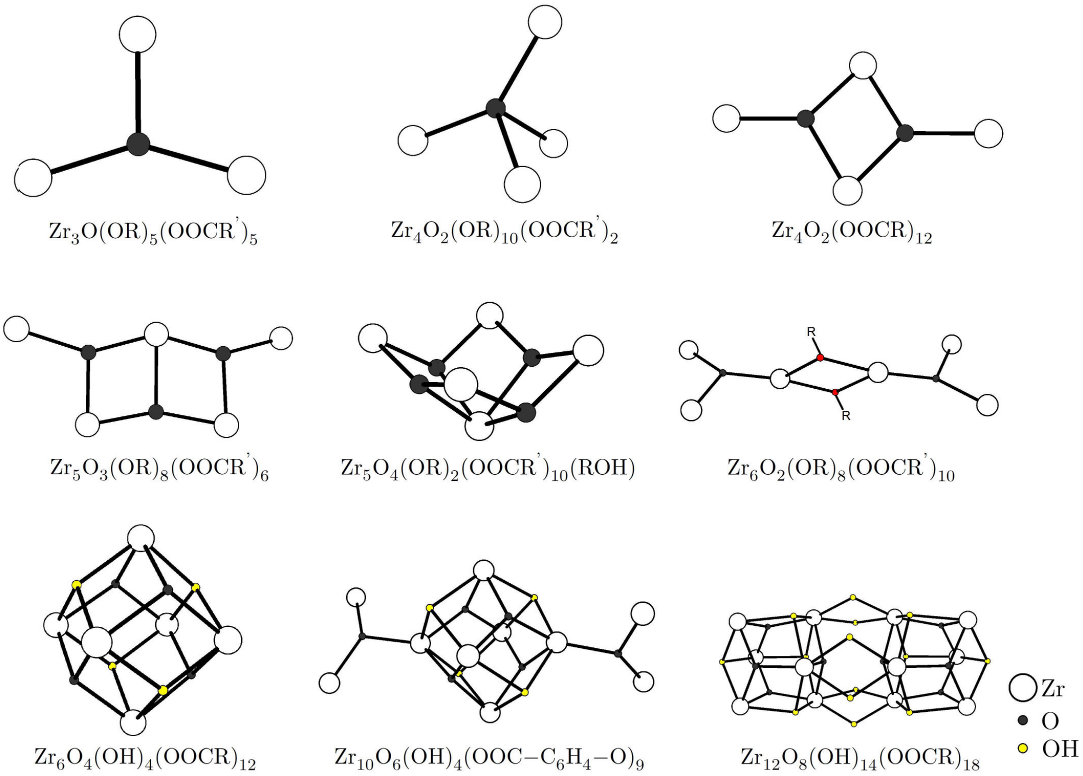
Table 1.1 shows the degree of condensation, degree of substitution and poisoning ratio of the different carboxylate titanium oxo clusters. The degree of condensation (O/Ti) is defined by the number of oxo bridges divided by the number of titanium atoms. It can thus be in the range between 0 and 2. The degree of substitution is given by the number of carboxylate groups divided by the number of titanium atoms. The poisoning ratio p is defined ”as the proportion of the metal coordination sphere occupied by terminal ligands that have reacted neither by hydrolysis/condensation nor by coordination polymerization.”[157] A higher poisoning ratio p may indicate a higher reactivity towards condensation reactions. The highest degree of condensation is found at higher nuclearities, while the highest degree of substitution (OOCR/Ti) is found at a nuclearity of 8. The two clusters without alkoxo groups also show the lowest poisoning ratio (0) since all carboxylates are bridging in these cases. The highest poisoning ratio (0.28) is found at the smallest oxo cluster, but it is not generally decreasing towards higher nuclearities.

Table 1.1: *A Comparison of degree of condensation (O/Ti), degree of substitution (OOCR/Ti) and poisoning ratio (p) of the different carboxylate titanium oxo clusters.*

Cluster core	O/Ti	OOCR/Ti	p
$Ti_3O(OR)_7(OOCR^{'})_3$	0.33	1.00	0.28
$Ti_3O_2Cl_3(OOCR)_5$	0.67	1.67	0.17
$Ti_4O_2(OR)_7(OOCR^{'})_2$	0.50	0.50	0.25
$Ti_4O_2(OR)_6(OOCR^{'})_6$	0.50	1.50	0.25
$Ti_6O_4(OR)_8(OOCR^{'})_8$	0.67	1.33	0.17
$Ti_6O_6(OR)_6(OOCR^{'})_6$	1.00	1.00	0.17
$Ti_8O_8(OOCR)_{16}$	1.00	2.00	0.00
$Ti_8O_{10}(OOCR)_{12}$	1.25	1.50	0.00
$Ti_9O_8(OR)_4(OOCR^{'})_{16}$	0.89	1.78	0.07
$Ti_{12}O_{12}(OR)_{18}(OOCR^{'})_6$	1.00	0.50	0.19
$Ti_{14}O_{18}(OR)_8(OOCR^{'})_{12}(ROH)_2$	1.29	0.86	0.10
$Ti_{14}O_{19}(OH)(OR)_{13}(OOCR^{'})_4$	1.36	0.29	0.16
$Ti_{17}O_{24}(OR)_{16}(OOCR^{'})_4$	1.41	0.24	0.20
$Ti_{18}O_{25}(OR)_{12}(OOCR^{'})_{10}$	1.39	0.56	0.09
$Ti_{28}O_{40}(OR)_{20}(OOCR^{'})_{12}$	1.43	0.43	0.13
$Ti_{34}O_{50}(OR)_{30}(OOCR^{'})_6$	1.47	0.18	0.17

1.4.4 Carboxylate-substituted zirconium oxo (alkoxo) clusters

Many carboxylate-substituted zirconium oxo clusters were obtained from the reaction of carboxylic acids with zirconium alkoxides. The reaction is similar to that of the titanium alkoxides (see eq. 1.3), but zirconium as central atom behaves differently. Both metals are in the +4 oxidation state but are different in the size of the cation and the coordination sphere (zirconium usually has a coordination number of 7-8, titanium usually has 6). In general, a lower number of carboxylate substituted zirconium oxo clusters compared to titanium derivatives is known. In figure 1.2 the known cluster cores of carboxylate-substituted zirconium oxo clusters are shown.



$Zr_3O(OR)_5(OOCR')_5$ $Zr_4O_2(OR)_{10}(OOCR')_2$ $Zr_4O_2(OOCR)_{12}$

$Zr_5O_3(OR)_8(OOCR')_6$ $Zr_5O_4(OR)_2(OOCR')_{10}(ROH)$ $Zr_6O_2(OR)_8(OOCR')_{10}$

$Zr_6O_4(OH)_4(OOCR)_{12}$ $Zr_{10}O_6(OH)_4(OOC{-}C_6H_4{-}O)_9$ $Zr_{12}O_8(OH)_{14}(OOCR)_{18}$

Figure 1.2: *Cluster cores of different carboxylate-substituted zirconium oxo alkoxo clusters.*

The smallest cluster shown in figure 1.2 has again a $Zr_3(\mu_3\text{-}O)$ core. Different to the zirconium oxo alkoxo clusters mentioned in section 1.4.2 the oxygen is in the plane of the zirconium triangle. The $Zr_4(\mu_4\text{-}O)(\mu_2\text{-}O)$ cluster core is similar to that of $Ti_4(\mu_4\text{-}O)(\mu_2\text{-}O)$, where all zirconium atoms are also 6-coordinated. In the flat $Zr_4(\mu_3\text{-}O)_2$ cluster core, the zirconium atoms have a higher coordination number of 7-8 compared to similar titanium species.

In contrast to the titanium oxo clusters, two carboxylate zirconium oxo clusters have been observed with a nuclearity of 5. The flat $Zr_5(\mu_3\text{-}O)_3$ cluster core consists of five zirconium atoms aligned almost in a plane. Of these zirconium atoms only the central zirconium atom is

7-coordinated while the other have an octahedral coordination sphere. The cluster $Zr_5(\mu_3\text{-}O)_4$ is built by four zirconium atoms forming a rectangle which are connected by four μ_3-oxygen atoms to the fifth zirconium atom which is out of the plane of the rectangle. The structure is similar to the later mentioned $Zr_6O_4(OH)_4$ cluster core, but with the top zirconium atom missing.

$Zr_6(\mu_3\text{-}O)_2$ is in principle a dimer of the Zr_3O cluster core and is more accurately described as $[Zr_3O]_2$. The most frequently obtained cluster core of carboxylate zirconium oxo clusters is that of $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4$.[175,195–198] This cluster core is built by octahedrally arranged zirconium atoms with alternating μ_3-oxo and μ_3-hydroxo groups on the faces of the octahedron. The core has been observed several times, sometimes with small differences in the arrangement of the ligands, but also in few cases with a different number of hydroxo ligands.[199–201] Dimeric structures were often obtained for this cluster core as well, with four carboxylate ligands bridging the two $Zr_6O_4(OH)_4$ entities.[176,196,202,203] Due to the similarities of these structures Puchberger *et al.* studied the behavior of the monomeric and the dimeric species in solution to see whether they can be converted into each other.[204] While they were able to exchange the carboxylate on the surface of the cluster, they were not able to synthesize the $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4$ cluster from the dimeric cluster or *vice versa.* The $Zr_6O_4(OH)_4$ cluster core has also been linked several times by dicarboxylic acids to form metal organic frameworks.[205–215] The last cluster core shown in figure 1.2, $Zr_{12}(\mu_3\text{-}O)_8(\mu_3\text{-}OH)_8(\mu_2\text{-}OH)_6$ is also a dimer of the $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4$ cluster core, bridged by six μ_2-hydroxo groups.[216]

Aside from $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_3]_2$ the highest nuclearity of known carboxylate substituted zirconium oxo clusters is $Zr_{10}(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_4$ which was obtained using salicylic acid.[217] The ligand has a different coordination behavior compared to other carboxylic acids due to the hydroxy group. In principle the core can be seen as that of $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4$ with two zirconium atoms connected by a μ_3-oxygen on each side.

1.4.5 Phosphonate substituted titanium oxo (alkoxo) clusters

Other ligands have also been used in the synthesis of titanium and zirconium oxo clusters besides carboxylates, *e.g.* oximate[218,219] and cyclopentadienyl ligands[220–225]. Another ligand known in oxo cluster chemistry are the aforementioned organophosphonates.

M. B. Dines *et al.*[226] showed that phosphonic acids react with titanium alkoxides very fast to result in a layered structure (in a ratio 1:1). Guerrero *et al.*[227] was the first to use a semi-stoichiometric amount of phosphonic acid to synthesize a titanium oxo cluster with phenylphosphonic acid. Although other phosphonates have then been used as ligands for titanium oxo clusters as well[228], and other reactions of phosphonic acids with titanium cyclopentadienyl derivatives[229,230] have been conducted, no functionalization thereof has yet been made. Hydrolysis was taking place in these reaction but the source of water was attributed to wet solvents or wet phosphonic acids[66,229,230] instead of an esterification reaction. The formula of all known phosphonate-substituted titanium oxo clusters is $Ti_4(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_5(O_3PR)_3(NL)$ with different organic substituents (R) and DMSO or THF as neutral ligand (NL) (see fig. 1.3).

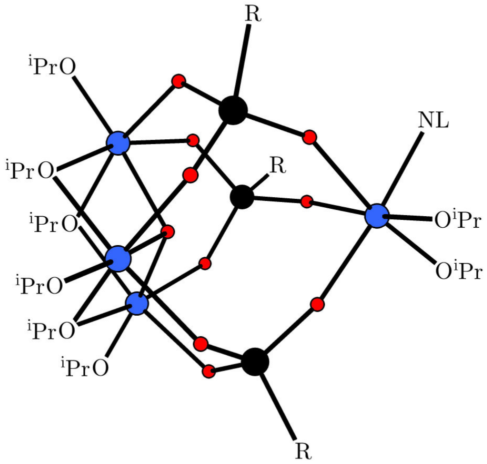


Figure 1.3: *General structure of all known phosphonate titanium oxo clusters.*

It can be seen that in this structure the phosphonates are all 3.111 (notation: see chapter 1.3) coordinated to the metal center. Furthermore, different binding modes of phosphonates were observed by Mehring *et al.*[228]. They also observed scrambling reactions between two different phosphonate groups, leading to an increase in the number of signals in the ^{31}P NMR spectrum. In another work it was shown that phosphonate-substituted titanium oxo clusters can be used in a sol-gel process retaining the Ti:P ratio.[231] In contrast to the titanium species, no phosphonate zirconium oxo cluster is known.

Apart from phosphonates, phosphates[232] and phosphinates[233] have also been used to create titanium oxo clusters with various structural motifs, the monoesters of the phosphates being similar to the structures of phosphonic acids, while the coordination of phosphinates is comparable to the coordination of carboxylates.

Chapter 2

Aim of the work

Zirconium and titanium oxo clusters are viable ”nano building blocks” (NBB) for the synthesis of class II hybrid materials due to their uniform size and shape. Class II hybrid materials require covalent bonds between the cluster and the matrix material. Therefore a functionalization of the clusters is needed. Polymerizeable ligands (*e.g.* methacrylic acid) enable copolymerization with organic monomers. For polymerization reactions it is desired to control the ligand sphere in order to tune the cross-linking properties of the cluster.

The aim of this work is the synthesis of new titanium and zirconium oxo clusters and the characterization thereof. One combination of titanium alkoxide and carboxylic acid should be studied to find a correlation between the precursor ratio and the product of the reaction. Another question was how cyclic anhydrides react with titanium alkoxides. Since no water can be formed *in situ*, a different result is expected. Based on the insight gained from the aforementioned experiments, a mixture of different carboxylic acids will be used to obtain mixed-ligand clusters. For additional control of the mixed-ligand sphere, sterically demanding ligands are to be used.

Carboxylate ligands on the surface of titanium and zirconium oxo clusters are often easily exchanged. Therefore other ligands, with stronger chemical bonds, will be used in the modification of oxo clusters, such as calixarenes or phosphonate ligands, which are used for stabilizing titania nanoparticles. Phosphonate ligands can easily be functionalized and provide three coordinating oxygens, thus enabling strong M-O-P bonds. Part of this work will be the synthesis of such functionalized and non-functionalized cluster compounds.

In extension of this work it would be interesting to gain insight into the reaction of a mixture of phosphonic acids and carboxylic acids with metal alkoxides. The question is whether phosphonates and carboxylates form mixed-ligand clusters or two separate cluster species. Both of these ligand types can coordinate to the cluster core, thus the results will show which ligand is preferentially coordinated and furthermore whether the addition of a carboxylic acid leads to a higher degree of condensation due to an easier esterification.

Part II

Results and Discussion

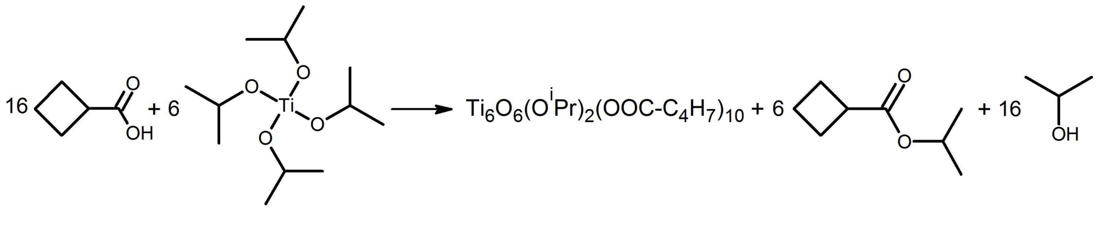
Chapter 3

Carboxylate substituted titanium and zirconium oxo clusters

3.1 New carboxylate substituted titanium and zirconium oxo clusters

Titanium and zirconium oxo clusters are interesting intermediates between molecules and nanoparticles. Unlike nanoparticles they are structurally defined and soluble compounds, the structure of which can be determined by single crystal XRD and NMR. In principle they are obtained by controlled condensation of the corresponding alkoxides or salts. One versatile route to metal oxo clusters are reactions of metal alkoxides with carboxylic acids. The metal alkoxides are partly hydrolyzed by water produced *in situ* through esterification of the acid. Controlled condensation is thus achieved, and well defined clusters are formed, which are stabilized by the carboxylate ligand sphere. A large quantity of titanium oxo clusters has thus been obtained using carboxylic acids in which they act as *in situ* water-source, ligand and (not in all cases) solvent.[234–239]

New titanium and zirconium oxo clusters can be easily generated. In a typical experiment, titanium isopropoxide was reacted with cyclobutanecarboxylic acid in a ratio of 1:4 (see equation 3.1).



(3.1)

The reaction led to the formation of $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_4(O^iPr)_2(\mu_2\text{-}OOCC_4H_7)_{10}$ (**TiCycloBu**, figure 3.1). This oxo cluster is isostructural to another flat Ti_6O_6 cluster with propionate ligands.[159] Other titanium clusters with a nuclearity of 6 exhibit a different core or a different degree of condensation.[240–246] There are many known oxo clusters with a Ti_6O_6 cluster core, but most of these oxo clusters have an octahedral arrangement of the titanium atoms.[163,168,177–185]

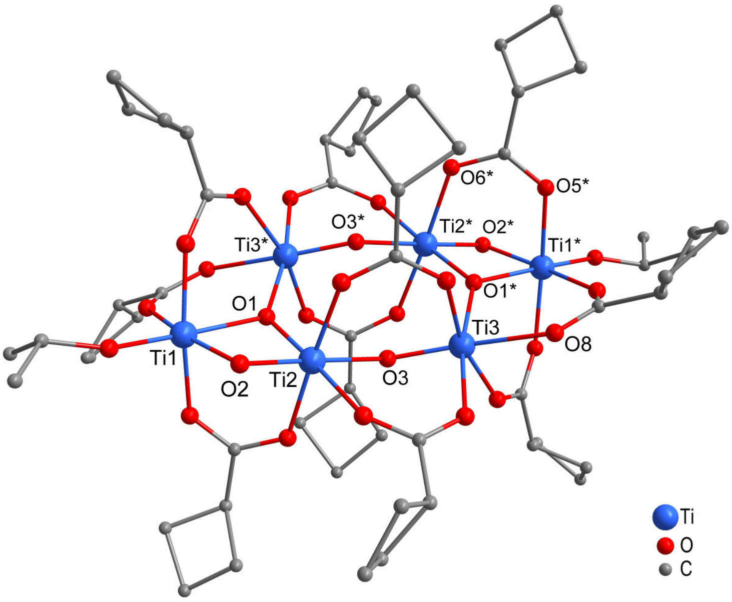


Figure 3.1: *Molecular structure of $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_4(O^iPr)_2(\mu_2\text{-}OOCC_4H_7)_{10}$ (**TiCycloBu**). Hydrogen atoms have been omitted for clarity.*

The structure consists of six titanium atoms which are roughly coplanar. Two Ti_3 triangles can be seen, which are bridged on two corners by each one μ_2-oxygen and two cyclobutanecarboxylates. The triangles are built by three titanium atoms which are bridged by a μ_3-oxygen. Ti1 and Ti2 are bridged by a μ_2-oxygen and one cyclobutanecarboxylate, Ti1 and Ti3 are bridged by two cyclobutanecarboxylates. Ti2 is not bridged to Ti3 on the same triangle but to Ti3* (* denotes the symmetry-related atom in the second Ti_3 triangle) on the second Ti_3 triangle.

The facile reaction as well as the crystallization from the mother liquid render the reaction of titanium alkoxides and zirconium alkoxides with carboxylic acids to the most common synthesis route to oxo clusters. Different carboxylic acids can be used, limited only by coordinating functionalities.

Functionalities which are not or weakly coordinating, such as double bonds or halogens are the easiest way to obtain functionalized titanium and zirconium oxo clusters. In an experiment, titanium isopropoxide was added to 4-chlorobenzoic acid in the ratio of 1:4 yielding $Ti_4(\mu_3\text{-}O)_2(O^iPr)_6(\mu_2\text{-}OOC{-}C_6H_4{-}Cl)_6$ (**TiBenzCl**, figure 3.2). Two other titanium oxo clusters are known which are isostructural to **TiBenzCl**, $Ti_4O_2(O^iPr)_6(OMc)_6$ and

$Ti_4O_2(O^iPr)_6(OOCCH{=}CH_2)_6$.[3] One more oxo cluster is isostructural, $Ti_4O_2Cl_6(O_2CPh)_6$, though in this structure the OR groups are replaced by Cl.[247] Carboxylate titanium oxo clusters with a nuclearity of 4 are also known. Some of these exhibit a μ_4-oxygen in the center of the structure[166–168] or have another coordinating functionality[248].

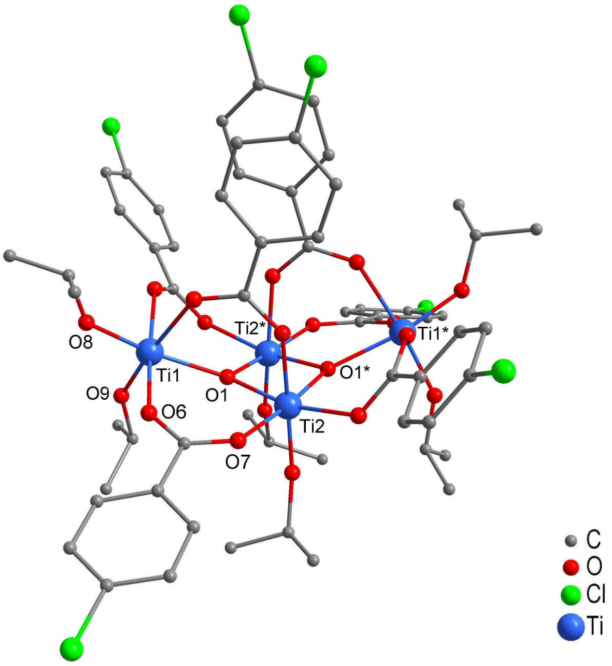


Figure 3.2: *Molecular structure of* $Ti_4(\mu_3\text{-}O)_2(O^iPr)_6(\mu_2\text{-}OOC{-}C_6H_4{-}Cl)_6)$ ***(TiBenzCl)****. Hydrogen atoms have been omitted for clarity.*

The structure of **TiBenzCl** is built up by four titanium atoms forming a butterfly structure. Six 4-chlorobenzoates are bridging the titanium atoms on the edges of the structure. In the center of the structure two μ_3-oxygens bridge between the titanium atoms. The outcome of the reaction shows that functionalization of oxo clusters can be achieved using organically functionalized carboxylic acids.

3.1.1 Adjusting the arrangement of ligands by means of steric hindrance

Oxo clusters with mixed ligands could be created using mixtures of less bulky and bulky carboxylic acids like a mixture of acetic acid and triphenylacetic acid (see figure 3.3). A limited number of bulkier ligands could then only occupy certain positions at the cluster surface, while the less bulky ligand could then fill the remaining coordination sites. The triphenylacetic acid was used to test this approach.

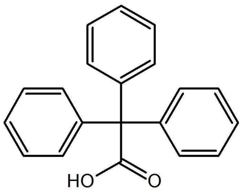
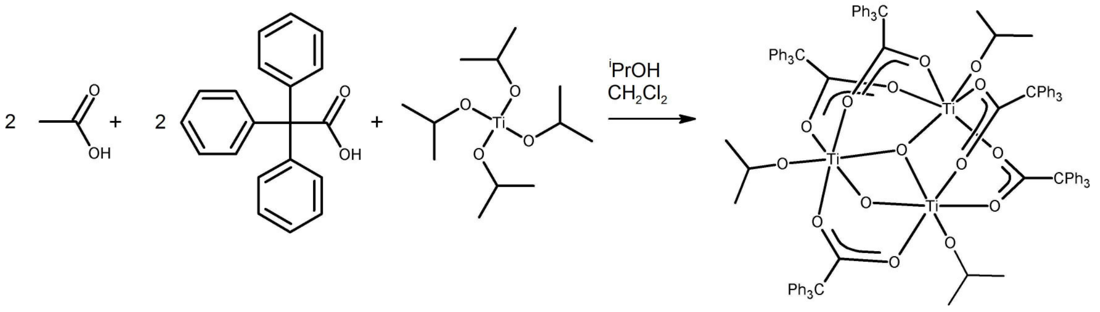


Figure 3.3: *Triphenylacetic acid.*

Sterically demanding carboxylic acids have a slower esterification rate than smaller carboxylic acids like acetic acid.[249–251] Therefore when reacting a mixture of triphenylacetic acid and acetic acid with $Ti(O^iPr)_4$, the latter should preferentially act as *in situ* water-source.

The outcome of the reaction (see equation 3.2) of triphenylacetic acid, acetic acid and titanium isopropoxide (molar ratio 2:2:1) was $Ti_3O_2(O^iPr)_3(OOCCPh_3)_5$ (**TiTPA**, figure 3.4). There are many known titanium oxo alkoxo clusters with a nuclearity of 3.[141,160–163,168] Although all of those have a μ_3-oxygen in the center of the triangle none of the structures shows an additional μ_2-oxygen as was found in the structure of **TiTPA**. The only structures with both of these features were $Ti_3Cl_3(OOC{-}C_6H_4{-}CH_3)_5$, obtained by Bashall *et al.*[164], and $Ti_3Cl_3(OOC{-}CH_2{-}CH_3)_5$ obtained by Barrow *et al.*[165]. Both have five carboxylate ligands, but chloro ligands are coordinating instead of the alkoxo ligands (**TiTPA**). The oxo cluster $Ti_3O(O^iPr)_8(OOCCPh_3)_2$ obtained by Senouci *et al.*[160] has a nucleardity of 3 and two coordinating triphenylacetate ligands.



(3.2)

The three titanium atoms of **TiTPA** are all octahedrally coordinated and form an isosceles triangle with Ti1-Ti2, Ti2-Ti3 and Ti1-Ti3 distances of 289 pm, 352 pm and 354 pm, respectively. In the center of the triangle a μ_3-oxygen is bound to all three titanium atoms. Ti1 and Ti3 are additionally bridged by a μ_2-oxygen, leading to the significantly smaller Ti-Ti distance. Between Ti1 and Ti2 as well as between Ti2 and Ti3 two triphenylacetates are bridging. In addition to the μ_2-oxo bridge between Ti1 and Ti3 one triphenylacetate is bridging. Ti-O bond distances of the triphenylacetate are in the small range of 200-205 pm, with the exception of the two bonds opposite to the Ti-O bond of the μ_2-oxygen (213 pm and 214 pm).

The initial aim of the reaction was to create a structure which consists of a mixed ligand sphere of triphenylacetates and acetates in an anisotropic arrangement. Due to the high steric demand

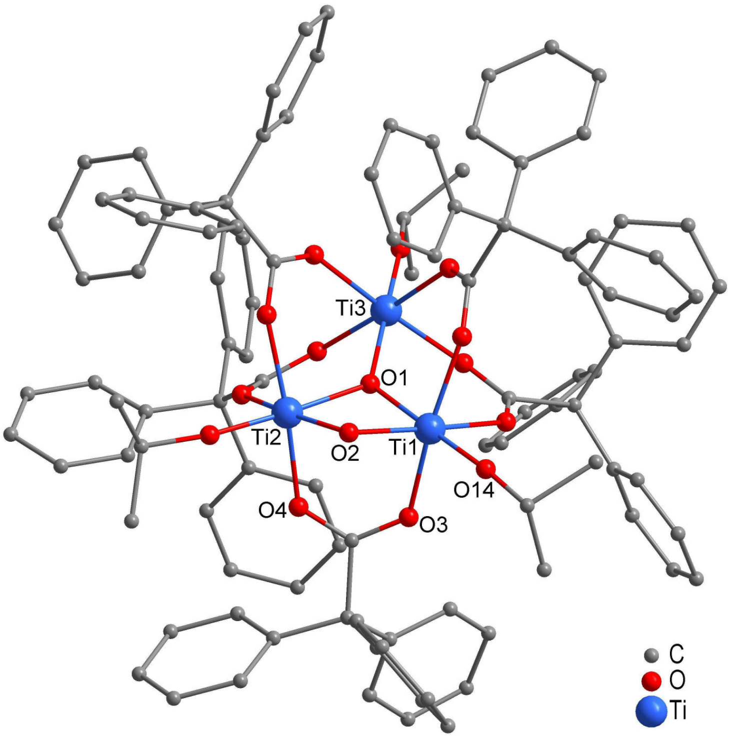
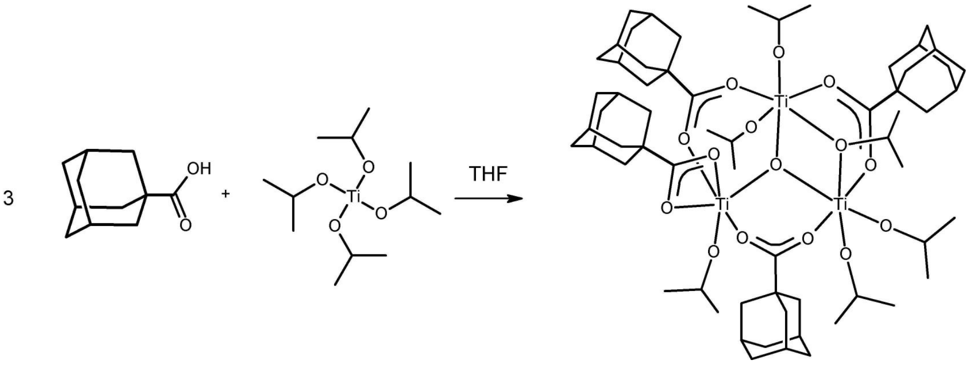


Figure 3.4: *Molecular structure of* $Ti_3O_2(O^iPr)_3(OOCCPh_3)_5$ ***(TiTPA)****. Hydrogen atoms have been omitted for clarity.*

of the triphenylacetic acid it was assumed that a high number of coordinating triphenylacetates was not possible. A small oxo cluster with no acetate ligands was obtained instead. The outcome of this simple reaction suggests that the approach of using a mixture of bulky and less bulky acids does not allow control of the ligand sphere.

The structure of **TiTPA**, however, shows that acetic acid is a suitable *in situ* source of water. It seems that acetic acid is esterified preferentially and faster, therefore leading to a different outcome than the reactions of triphenylacetic acid with $Ti(O^iPr)_4$. On the other hand when taking into account the total number of oxo bridges, only one third of acetic acid in total was consumed during the reaction. If all oxo bridges are obtained by esterification of acetic acid, the molar ratio of triphenylacetic acid to acetic acid is still 3:2 at quantitative yield. No acetates are coordinating, however, although a mixed ligand sphere was expected. Rather than the stoichiometry, the steric hindrance or acidity could play an important role here.

Another bulky acid is adamantylcarboxylic acid, which was reacted with $Ti(O^iPr)_4$ in a ratio of 3:1 (see equation 3.3). Different to **TiTPA** no acetic acid was added.



(3.3)

The outcome was another trinuclear titanium oxo cluster, $Ti_3O(\mu_2\text{-}O^iPr)(O^iPr)_5(OOC{-}adamantyl)_4$ (**TiAda**, figure 3.5). None of the known trinuclear titanium oxo clusters has the same number of carboxylate and alkoxo ligands as **TiAda**.[141,160–163,168] In the structure of **TiAda** all titanium atoms are octahedrally coordinated and form an isosceles triangle. The Ti-Ti distances are 318 pm for Ti1-Ti2, 351 pm for Ti2-Ti3 and 357 pm for Ti1-Ti3. Ti1 and Ti2 are bridged by a μ_2-isopropoxo ligand, thus explaining the lower Ti-Ti distance. On every edge of the triangle one carboxylate is bridging the two titanium atoms. One additional carboxylate is chelating Ti3, which is noteworthy since chelating carboxylates are not frequently found in titanium complexes. The coordination sphere of the titanium atoms is completed by terminal isopropoxo ligands, leading to a total of five terminal isopropoxo ligands (two coordinating to Ti1, two to Ti2 and one to Ti3).

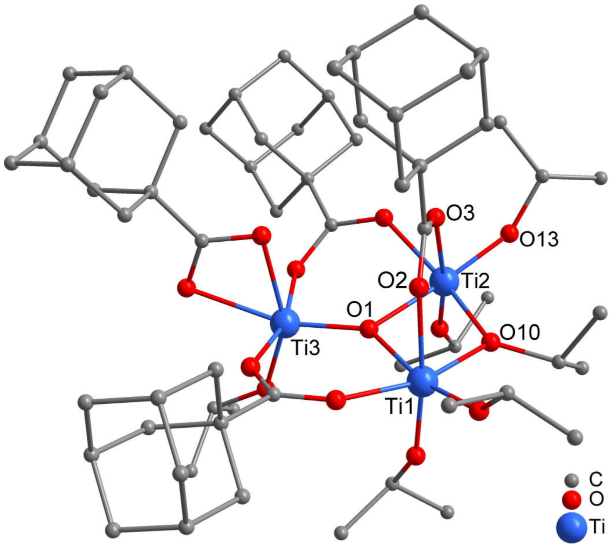


Figure 3.5: *Molecular structure of* $Ti_3O(\mu_2\text{-}O^iPr)(O^iPr)_5(OOC{-}adamantyl)_4$ *(**TiAda**). Hydrogen atoms have been omitted for clarity.*

Four carboxylates and one oxo bridge are less than the used stoichiometry (5:3 vs. 3:1), showing that some of the adamantylcarboxylic acid remains in the reaction mixture even at quantitative

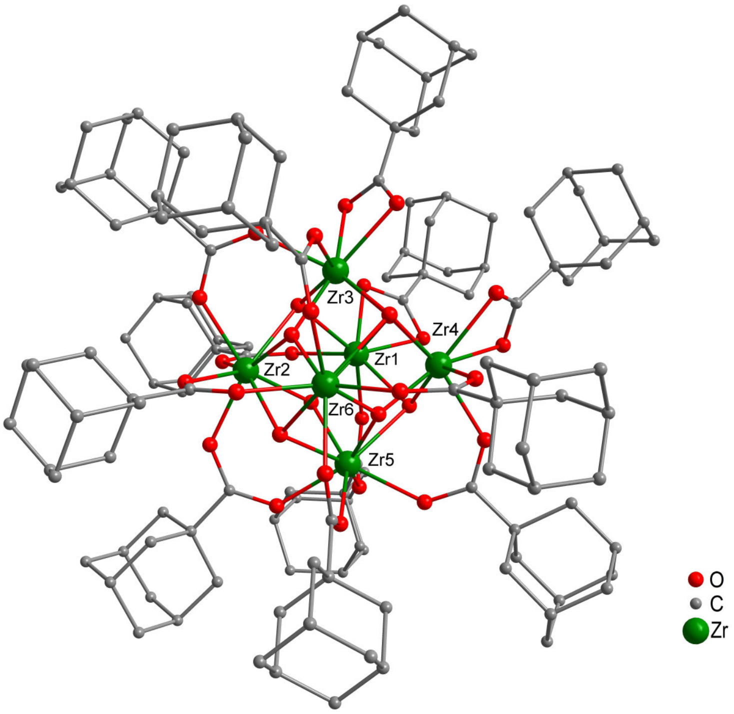


Figure 3.6: *Molecular structure of* $Zr_6O_4(OH)_4(OOC{-}adamantyl)_{12}$ (***ZrAda***). *Hydrogen atoms have been omitted for clarity.*

yield relative to Ti. **TiAda** shows a low number of oxo bridges and therefore a rather low degree of condensation (0.33). This was expected due to the size of the adamantylcarboxylic acid which lowers the rate of esterification, and it proves the role of the acetic acid in the reaction of **TiTPA**.

The reactivity and coordination sphere of zirconium alkoxides are different to that of titanium alkoxides. Therefore a reaction similar to that of **TiAda** was performed using adamantylcarboxylic acid and $Zr(O^nBu)_4$ in a ratio of 6:1. The outcome of this reaction is a zirconium oxo cluster with a nuclearity of 6, $Zr_6O_4(OH)_4(OOC{-}adamantyl)_{12}$ (**ZrAda**, figure 3.6). This cluster has the well known $Zr_6O_4(OH)_4$ cluster core,[175,195–201,252,253] which can also be found as a dimer[176,196,202–204,216]. Due to the high number of already published structures, it can be concluded that this core is thermodynamically favored.

The zirconium atoms in **ZrAda** form an octahedron with alternating μ_3-oxo and μ_3-hydroxo bridges on each face. The coordination number of all zirconium atoms is eight, with a square antiprism coordination polyhedron. Nine of the twelve coordinating adamantylcarboxylates are bridging between two zirconium atoms, on one face of the octahedron three chelating carboxylates are coordinating. One face with only chelating carboxylates is found in most of the other $Zr_6O_4(OH)_4$ structures[175,195–197] as well, only one structure, $Zr_6O_4(OH)_4(OOCC(CH_3)_3)_{12}$, is known[198] without this structural feature. The reason for the chelating carboxylate groups might be due to two adamantylic acid species which are each bonded by hydrogen bonds to one

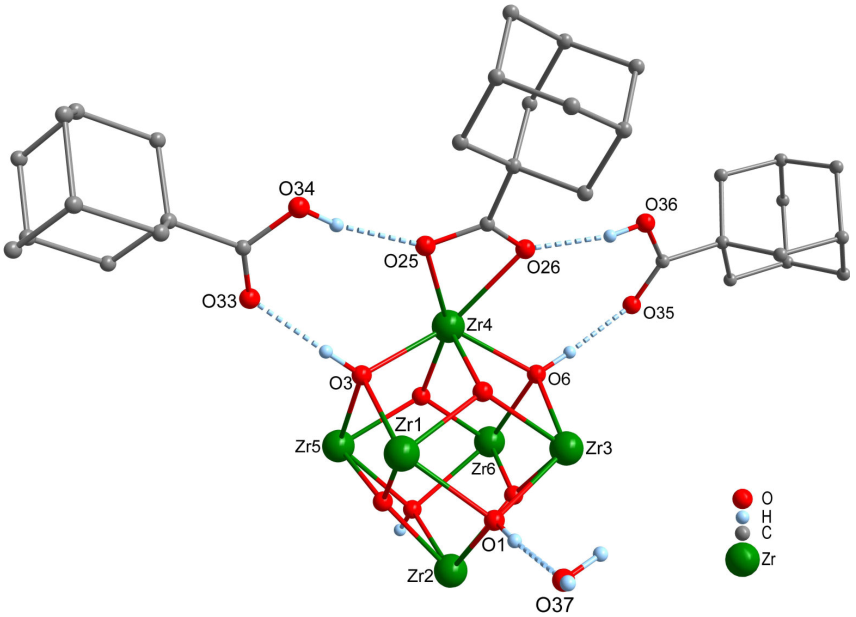


Figure 3.7: *Core of* ***ZrAda*** *with the hydrogen bonded adamantylcarboxylates and one water molecule. Non-relevant atoms have been omitted for clarity.*

Table 3.1: *Bond distances of hydrogen bonds in* ***ZrAda***

Donor Acceptor	Hydrogen Bond Distance [pm]
O3 - O33	274.1
O34 - O25	274.0
O6 - O35	274.1
O36 - O26	273.9
O1 - O37	285.7

OH group of the core and (surprisingly) the same adamantylcarboxylate (see figure 3.7). The Zr-O bond distances of this adamantylcarboxylate are thus slightly elongated from about 226 pm to 230 pm. Furthermore, one oxygen atom of a water molecule was found in the electron density map with a distance of 285.7 pm to O1. O1 is the oxygen of one OH group of the cluster core. Hydrogen bond distances are listed in table 3.1.

Since one water molecule can be found in the structure, it appears that the $Zr_6O_4(OH)_4$ core is to some extent stable in the presence of water. **ZrAda** is one of many zirconium oxo clusters with the $Zr_6O_4(OH)_4$ core, which is another indication for the stability of this core.

3.1.2 Oxo clusters obtained by using a low amount of carboxylic acid

Oxo cluster synthesis is conducted in general with a large excess of carboxylic acids in the reactions. The reason for this lies in the nature of the reaction. Since no water is added directly, the carboxylic acid serves as water-source, ligand and solvent. For titanium alkoxides, a stoichiometric amount of carboxylic acid leads to the formation of dimeric structures.[161,185] When 4-chloromethylbenzoic acid was reacted with titanium isopropoxide in 2-propanol, the dimeric structure, $Ti_2(O^iPr)_6(\mu_2\text{-OOC-}C_6H_4\text{-}CH_2Cl)(\eta_1\text{-OOC-}C_6H_4\text{-}CH_2Cl)(^iPrOH)$ (**TiBenzMeCl**, figure 3.8), was obtained.

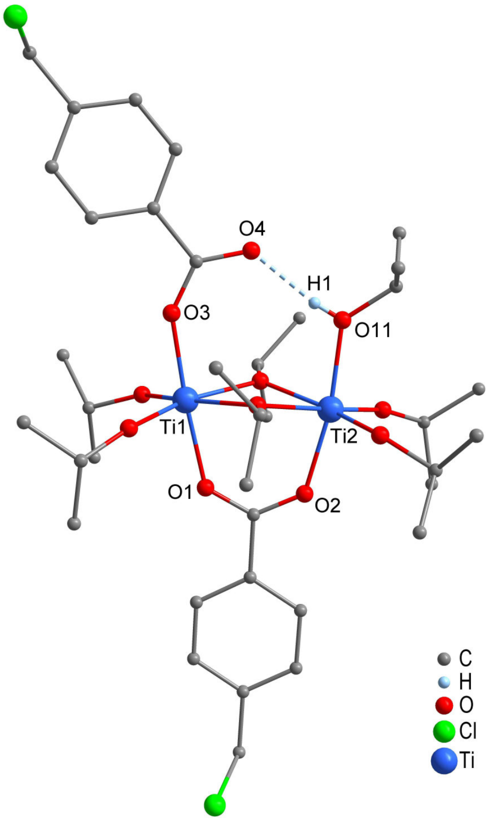
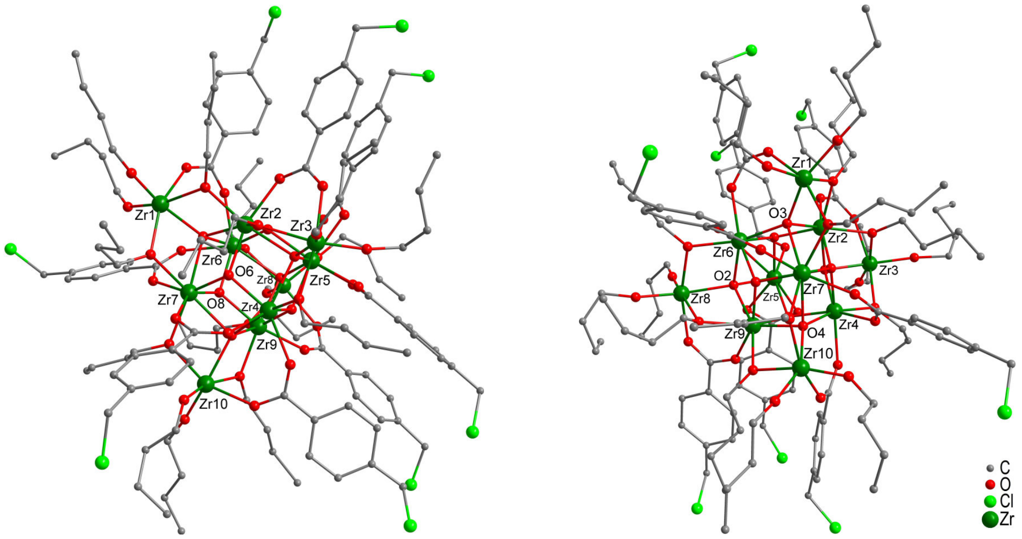


Figure 3.8: *Molecular structure of $Ti_2(O^iPr)_6(\mu_2\text{- OOC-}C_6H_4\text{-}CH_2Cl)(\eta_1\text{- OOC-}C_6H_4\text{-}CH_2Cl)$-$(^iPrOH)$ (**TiBenzMeCl**). Hydrogen atoms have been omitted for clarity.*

The same structure was obtained for methacrylic acid (figure 3.18) and phthalic anhydride (figure 4.1), therefore the structure will not be discussed in detail here. Thus it is predictable that reactions of titanium isopropoxide with simple carboxylic acids lead to this dimeric complex. This cannot be extended to functionalized carboxylic acids with possibly coordinating groups (see section 3.2). Furthermore, it shows that more than an equimolar amount of carboxylic acid or another water-source has to be added to obtain titanium oxo clusters.

The same reaction was performed for $Zr(O^nBu)_4$, leading to $Zr_{10}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(\mu_2\text{-}O^nBu)_8$-$(O^nBu)_8(\mu_2\text{-}OOC{-}C_6H_4{-}CH_2Cl)_6(OOC{-}C_6H_4{-}CH_2Cl)_2$ (**ZrBenzMeCl**, figure 3.9). Compared to other zirconium oxo clusters, **ZrBenzMeCl** has a high nuclearity and a moderate degree of condensation (0.8). This is in contrast to the dimer obtained with the titanium alkoxide.



(a) View along a-axis.

(b) View along c-axis.

Figure 3.9: *Molecular structure of* $Zr_{10}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(\mu_2\text{-}O^nBu)_8(O^nBu)_8$-$(\mu_2\text{-}OOC{-}C_6H_4{-}CH_2Cl)_6(OOC{-}C_6H_4{-}CH_2Cl)_2$ ***(ZrBenzMeCl)****. Hydrogen atoms have been omitted for clarity.*

The cluster core of **ZrBenzMeCl** can be described best as a tetrahedron (figure 3.10) with zirconium atoms on each edge and corner of the tetrahedron. In the center of the tetrahedron is the well known octahedral Zr_6O_8 ($Zr_6O_4(OH)_4$) cluster core (see figure 3.11).[175,195–201,252,253] Interestingly, the groups which would be OH in the $Zr_6O_4(OH)_4$ clusters are capped by zirconium atoms, thus forming the $Zr_{10}O_8$ cluster core. Thus, one can see this cluster core as $Zr_6O_4(OZr)_4$, but the "additional" (referred to as "terminal") zirconium atoms change the ligand sphere.

The average Zr-O bond distance of the μ_3-oxygens of the $Zr_{10}O_8$ cluster core is 205.7 ppm. This is comparable to the average Zr-O bond distances of the μ_3-oxygens of different $Zr_6O_4(OH)_4$ cluster cores, which are 206.5 ppm[195], 206.8 ppm[196] and 206.4 ppm[197] for different clusters. The average Zr-O bond distance of the μ_4-oxo bridges is 223.3 ppm in **ZrBenzMeCl** (without the "terminal" zirconium atoms), which is comparable to the average Zr-O bond distances of the μ_3-OH, which are 226.2 ppm[195], 227.2 ppm[196] and 227.2 ppm[197] for different clusters. With a average value of 213.9 ppm, the Zr-(μ_4-O) bond distances of the "terminal" zirconium atoms are significantly lower than the other Zr-(μ_4-O) bond distances in **ZrBenzMeCl**.

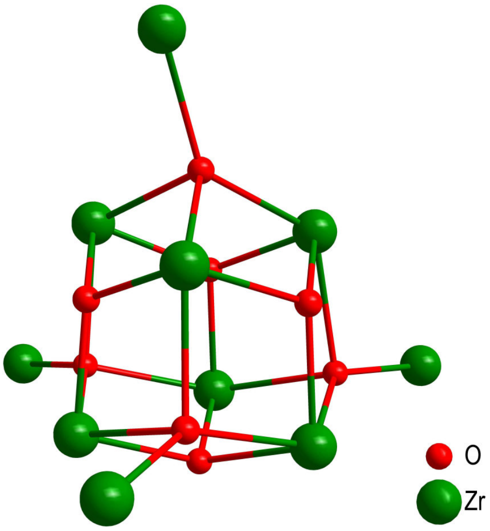


Figure 3.10: *Tetrahedral cluster core of **ZrBenzMeCl**. Hydrogen, carbon and chlorine atoms as well as ligand oxygen atoms have been omitted for clarity.*

The ligand sphere consists of sixteen butoxo ligands and eight 4-chloromethylbenzoates. It is notable that two of the 4-chloromethylbenzoates are chelating the same zirconium atom (as seen at the top in figure 3.11) while the other six 4-chloromethylbenzoates are bridging two zirconium atoms. The zirconium atoms show different coordination spheres. While the ”terminal” zirconium atoms are octahedrally coordinated, the other zirconium atoms are 7-fold coordinated with one exception. The zirconium atom with chelating 4-chloromethylbenzoates is 8-fold coordinated.

As for the outcome of the titanium complex, **TiBenzMeCl**, no oxo cluster was expected, because a low amount of carboxylic acid was used. The cluster **ZrBenzMeCl** crystallized several months after removal of the solvent. A Zr:OOCR ratio of 10:16 is found in the cluster (the number for OOCR includes the core oxygen atoms as they are formed through esterification). On the first glance this is in disagreement with the used precursor ratio of 1:1, but no quantitative yield was obtained. It could be possible, that about one third of the zirconium butoxide remains unreacted. Nevertheless, due to the long reaction time, it is possible that moisture is (part of) the water source.

ZrBenzMeCl has a C_2 axis through Zr5 and Zr7 and a nuclearity of 10. Only three zirconium oxo cluster cores are known in the literature with a nuclearity higher than 9. The $Zr_{13}O_8$ cluster core was found two times[151,152], while the $Zr_{10}O_6(OH)_4$ cluster core was only found for salicylic acid.[217] Another cluster core with a nuclearity higher than 9 is $Zr_{12}O_8(OH)_{14}$, but it can be seen as a dimeric structure of two $Zr_6O_4(OH)_4$ octahedra bridged by six OH groups.[216] There are many known clusters with a formal nuclearity of 12, but they are actually two $Zr_6O_4(OH)_4$ cluster cores bridged by carboxylates.[176,196,202–204] For titanium oxo clusters, high nuclearities were only found for oxo alkoxo clusters with no carboxylate ligand or a low number of carboxy-

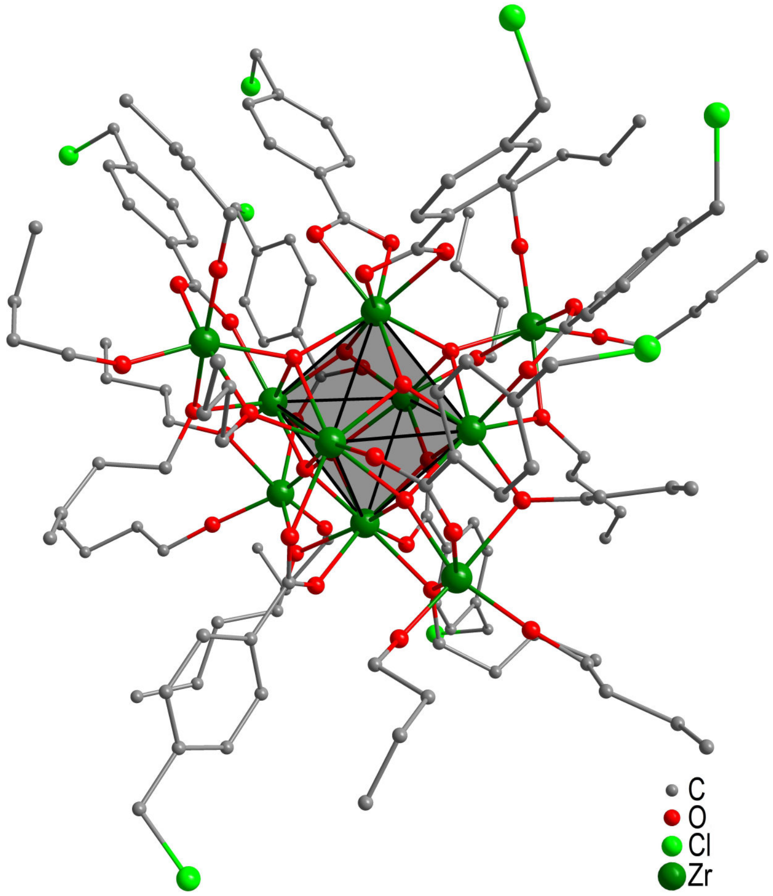
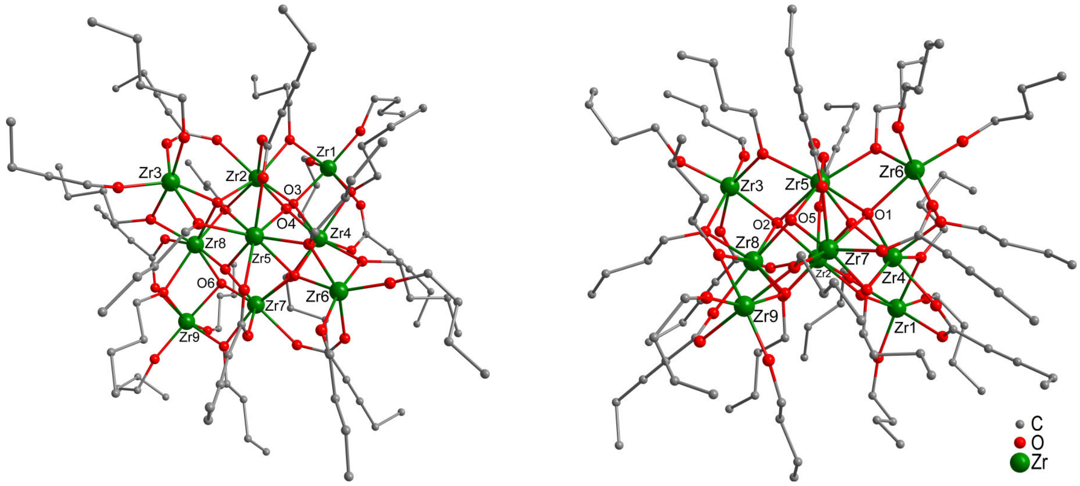


Figure 3.11: *Best projection of the zirconium oxo cluster* ***ZrBenzMeCl****. The central octahedron built by zirconium atoms has been highlighted. Hydrogen atoms have been omitted for clarity.*

late ligands.[139,140,142–144,168,183,184,191,192,241,244,254–258] Most of these structures were obtained by the direct addition of water, while others were obtained by the addition of low portions (max 1.3) of carboxylic acid to the titanium alkoxide and subsequent solvothermal synthesis.

To verify the obtained results for **ZrBenzMeCl**, another reaction was conducted using zirconium butoxide and pentinoic acid in a molar ratio of 1:1. In this case water (molar ratio 1:4, water:$Zr(O^nBu)_4$) diluted in 1-butanol was added directly to the reaction mixture to enable the formation of an oxo cluster. The outcome of the reaction, $Zr_9(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(\mu_2\text{-}O^nBu)_{10}\text{-}(O^nBu)_8(\mu_2\text{-}OOC{-}C\equiv C{-}CH_2CH_3)_6$ (**ZrPentin**, figure 3.12), is again a zirconium oxo cluster with a nuclearity higher than 6 (which represents the nuclearity of the frequently obtained $Zr_6O_4(OH)_4$ cluster core).

The shape of the core is again tetrahedral with zirconium atoms on each corner and on each but one edge of the tetrahedron (figure 3.13). The structure is related to **ZrBenzMeCl**, with the difference of the one missing zirconium on one edge of the tetrahedron. **ZrPentin** has a



(a) View along b-axis. (b) View along c-axis.

Figure 3.12: *Molecular structure of $Zr_9(\mu_4\text{-}O)_2(\mu_3\text{-}O)_4(\mu_2\text{-}O^nBu)_{10}(O^nBu)_8(\mu_2\text{-}OOC\text{-}C{\equiv}C\text{-}CH_2CH_3)_6$ (**ZrPentin**). Hydrogen atoms have been omitted for clarity.*

degree of condensation of 0.67, which is lower than the one of **ZrBenzMeCl** with 0.8. It is also notable that the one missing zirconium atom is part of the central octahedron related to the $Zr_6O_4(OH)_4$ core.

The average Zr-O bond distance of the μ_3-oxygens of the Zr_9O_6 cluster core is 207.8 ppm. They are comparable to the average Zr-(μ_3-O) bond distances of **ZrBenzMeCl** and $Zr_6O_4(OH)_4$ cluster cores (see above). The average Zr-(μ_4-O) bond distance of **ZrPentin** (again without the corner zirconium atoms) is 223.4 ppm, which is comparable to the average Zr-(μ_4-O) bond distances of **ZrBenzMeCl** and the average Zr-(μ_3-OH) bond distances of $Zr_6O_4(OH)_4$ cluster cores (see above). The corner zirconium atoms also have a shorter Zr-O bond distance of 214.2 ppm.

Water was added in a molar ratio of 0.25 relative to $Zr(O^nBu)_4$, covering 2.25 oxygens per cluster at quantitative yield. The precursor ratio ($Zr(O^nBu)_4$:pentinoic acid) was 1:1, the ratio of zirconium atoms to carboxylates (excluding oxo bridges in this case) in the final structure is 9:6. Part of the core oxygen can thus be provided by the esterification of carboxylic acid. Considering the yield of 37 %, the product is therefore in satisfying agreement with the precursor ratio.

The overall tetrahedral shape is highlighted in figure 3.14 and one can see on the bottom of the figure that one zirconium atom is missing for the octahedral center.

Only six pentinoate ligands are coordinating to the cluster core, while most of the cluster surface is covered by butoxo ligands. Ten of these butoxo ligands are bridging and eight are terminal, which are all coordinated to zirconium atoms on the corner of the tetrahedron. The pentinoates

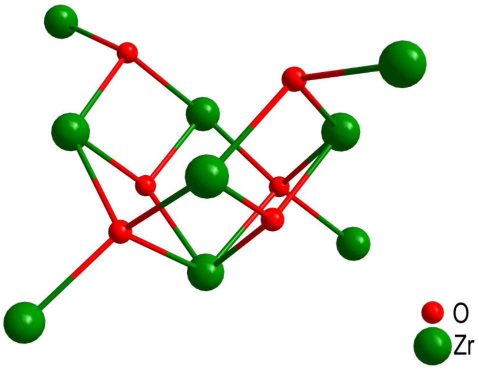


Figure 3.13: *Tetrahedral cluster core of* ***ZrPentin****. Hydrogen and carbon atoms as well as ligand oxygen atoms have been omitted for clarity.*

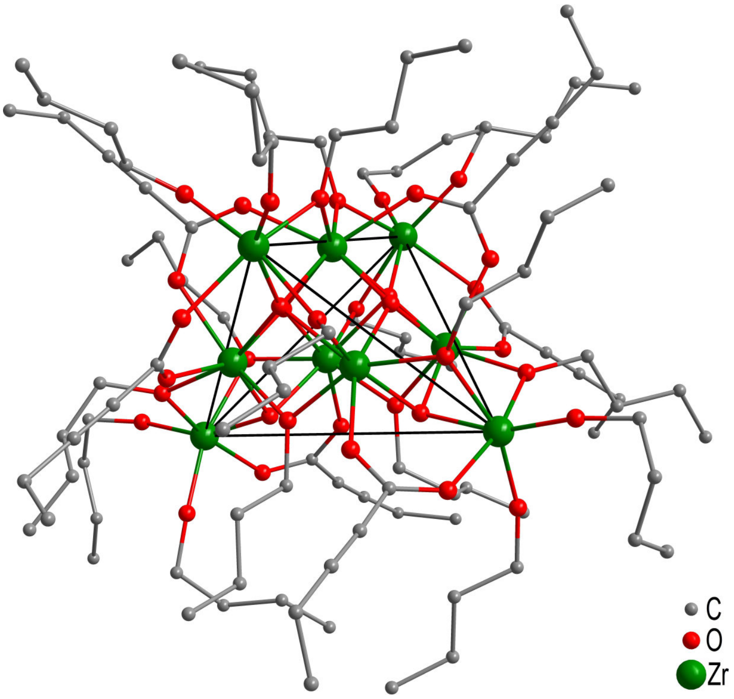


Figure 3.14: *Best projection of the zirconium oxo cluster* ***ZrPentin****. The overall tetrahedral shape of the cluster is highlighted. Hydrogen atoms have been omitted for clarity.*

are all bridging two zirconium atoms. Similar to the molecular structure of **ZrBenzMeCl**, the molecular structure of **ZrPentin** has a C_2 axis, passing through Zr5 and is parallel to b-axis.

The zirconium atoms which are located on the corner of **ZrPentin** are 6-fold (octahedrally) coordinated, while the zirconium atoms on the edges of the tetrahedron are 7-fold coordinated. The zirconium atom opposite to the zirconium free edge of the tetrahedron is an exception, as it is 8-fold coordinated.

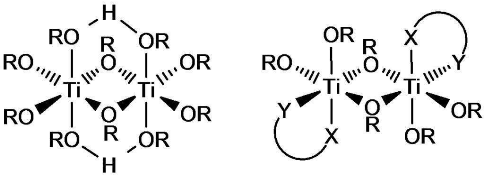
The two zirconium oxo clusters **ZrBenzMeCl** and **ZrPentin** were obtained with a low portion of carboxylic acid compared to other carboxylate oxo clusters. Furthermore, high nuclearities for titanium and zirconium oxo clusters were mainly obtained for low portions or even without carboxylic acid (see above). 33 titanium and 4 zirconium clusters are known with a nuclearity of 9 or higher. Of these oxo clusters only two are known, which were obtained with a ratio of carboxylic acid : metal alkoxide higher than 1:1. One was obtained by Kickelbick *et al.*[217] ($Zr_{10}O_6(OH)_4$(salicylato)$_{16}$) and the other by Piszczek *et al.*[216] ($Zr_{12}O_8(OH)_{14}(OOCC_5H_{11})_{18}$. Both can be seen as variation of the $Zr_6O_4(OH)_4$ cluster core. The $Zr_{12}O_8(OH)_{14}$ cluster core is in principle a dimer of the $Zr_6O_4(OH)_4$ cluster core bridged by six μ_2-OH groups. The $Zr_{10}O_6(OH)_4$ cluster core is probably obtained due to the OH group of the salicylic acid which enables a different binding mode.

The observations in the literature combined with these two new structures of zirconium oxo clusters allow the conclusion that high nuclearities of titanium and zirconium oxo clusters are preferentially obtained using low portions or no carboxylic acid at all. High portions of carboxylic acid appear to stabilize smaller oxo clusters. For **ZrPentin** water was added directly to enable condensation, while for **ZrBenzMeCl** water was probably diffusing into the reaction mixture. Nevertheless, for some experiments reported in the literature, the addition of a low portion of carboxylic acid was the sole source of water, leading to oxo clusters with a high nuclearity and a high degree of condensation, *e.g.* the $Ti_{17}O_{24}$ core.[144,191,192]

Both structures exhibit a tetrahedral shape, but while in **ZrBenzMeCl** the octahedral moiety of $Zr_6O_4(OH)_4$ can be seen, one zirconium atom of the octahedron is missing in **ZrPentin** even though the the structure is alike. In both cases the structure is not comparable to the $Zr_{13}O_8$ cluster core which has been obtained by the addition of water.[141,152]

3.2 A coordination polymer with unusual structural features from imidazolylbutyric acid and titanium isopropoxide

The chemistry of titanium alkoxide derivatives with organic co-ligands[49,113] is of topical interest because of the importance of such compounds in sol-gel and CVD processes. Two main types of derivatives are known: (a) adducts of neutral Lewis bases (LB) of the general composition $Ti(OR)_4(LB)$, and (b) derivatives $Ti(OR)_{4\text{-x}}(CL)_x$ where one or more OR groups of $Ti(OR)_4$ was substituted by a chelating ligand (CL) and which are prepared by reaction of $Ti(OR)_4$ with CL-H. The structures of mono-substituted derivatives $Ti(OR)_3(CL)$ with β-diketonates[259], aminoalcoholates[260,261], β-aminocarboxylates[262], oximates[218,263] and others as ligands are related to that of the adducts $Ti(OR)_4(LB)$ with alcohols[264–266] or amines as bases[267–271]. Both types are OR-bridged dimers with octahedrally coordinated titanium atoms. In the derivatives $Ti(OR)_3(CL)$, the neutral ligand and one neighboring OR group of $Ti(OR)_4(LB)$ are replaced by the chelating ligand CL (scheme 3.1).

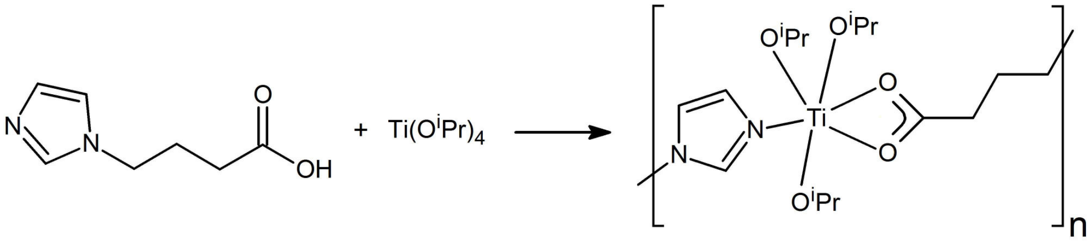


Scheme 3.1: *General structure of the adducts* $Ti(OR)_4(LB)$ *(left) and the mono-substituted derivatives* $Ti(OR)_3(CL)$ *(right,* $X \cap Y$ *= chelating ligand).*

Reactions of $Ti(OR)_4$ with carboxylic acids are special cases. In the first step, one OR group is substituted by a carboxylate ligand. The few derivatives which were isolated and structurally characterized have either the composition $[Ti(OR)_3(OOCR')]_2$, with bridging carboxylate ligands[161], or $[Ti(OR)_3(OOCR')(ROH)]_2$, where η_1-carboxylate ligands are hydrogen-bonded to the coordinated alcohol at the neighboring titanium atom[161,185]. In most reactions, however, carboxylate-substituted oxo/alkoxo clusters $Ti_aO_b(OR)_c(OOCR')_d$ were obtained[49,113]. This is due to ester formation between the alcohol cleaved in the first step and the employed carboxylic acid. The latter reaction produces water which is the source of the oxo ligands in the clusters.

In the light of the known structural chemistry of $Ti(OR)_4$ derivatives, the outcome of the reaction of $Ti(O^iPr)_4$ with 4-(imidazol-1-yl)-butyric acid is surprising, because the obtained coordination polymer has several unexpected features.[272]

$[Ti(O^iPr)_3(OOCCH_2CH_2CH_2C_3N_2H_3)]_n$ (**TiBuImid**, figure 3.15) was obtained by reaction of $Ti(O^iPr)_4$ with an equimolar amount of 4-(imidazol-1-yl)-butyric acid (**L**-H) in isopropanol (equation 3.4).



(3.4)

In the crystalline state, compound **TiBuImid** is a coordination polymer with mononuclear $Ti(O^iPr)_3$ units as connector and L as linker, coordinating through the carboxylate group to one Ti atom and the imidazolyl group to the next (figure 3.15). Although the alkyl chain is highly flexible, no back-biting of one of the imidazolyl nitrogen atoms to the same titanium atom was observed. The polymer chain extends parallel to the a-axis (figure 3.16). The titanium atoms are six-coordinate with a distorted octahedral coordination geometry and the O^iPr ligands in a *mer* arrangement. Distortion of the polyhedron is due to the chelating carboxylate group and results in O-Ti-O bond angles of the O^iPr ligands between 99.55 and 108.2 °. The coordinating nitrogen atom is slightly tilted towards the carboxylate ligand. The Ti1-N2 distance is distinctly shorter than that observed in the $Ti(OR)_4$(amine) adducts with primary amines, which are typically in the range 129-131 pm, or in $Ti(OR)_x$ derivatives with DHP ligands (226 pm, DHP-H2 = 4,6-dihydroxypyrimidine)[273].

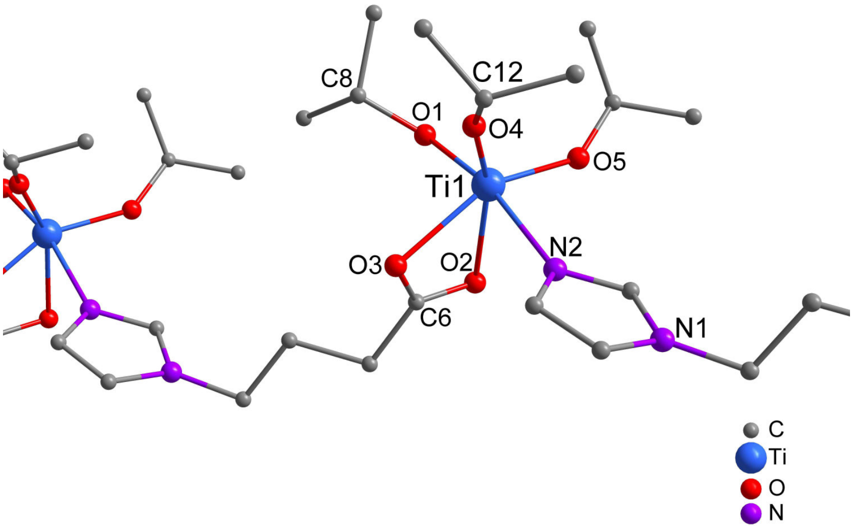


Figure 3.15: *Ball and stick plot of* ***TiBuImid****. Hydrogen atoms were omitted for clarity.*

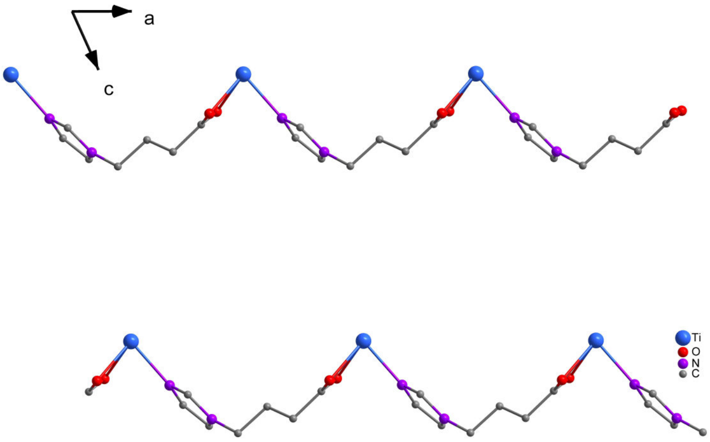


Figure 3.16: *Packing of the chains perpendicular to the b-axis. Isopropoxo ligands and hydrogen atoms were omitted for clarity.*

The FTIR-spectra (ATR) is in some parts similar to the spectra of titanium isopropoxide.[274] Additional peaks derive from the coordinating carboxylate (1540 cm^{-1}), as well as the imidazolyl group. The solution ^1H NMR spectrum shows one doublet at 1.22 ppm for the terminal CH_3 of the isopropoxy groups. The signals of the imidazolyl groups appear at 6.73, 7.19 and 7.59 ppm. In the aromatic region can be seen the resonances for the imidazolyl group. To verify the coordination behavior of the imidazolyl group in solution, 2D correlation spectra ($^1H/^{15}N$

HMBC) of the free ligand and the complex were recorded. The spectrum of the complex (figure 3.17) shows correlations at 152 ppm and 224 ppm, while the spectrum of the free ligand shows correlations at 153 ppm and 239 ppm. The shift difference of 15 ppm for one of the two nitrogen atoms is an indication for coordination in solution.

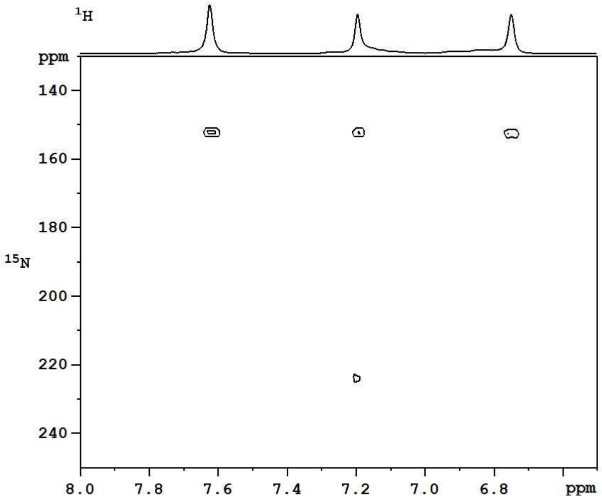


Figure 3.17: *$^1H/^{15}N$ HMBC NMR spectrum of the complex **TiBuImid** in CD_2Cl_2.*

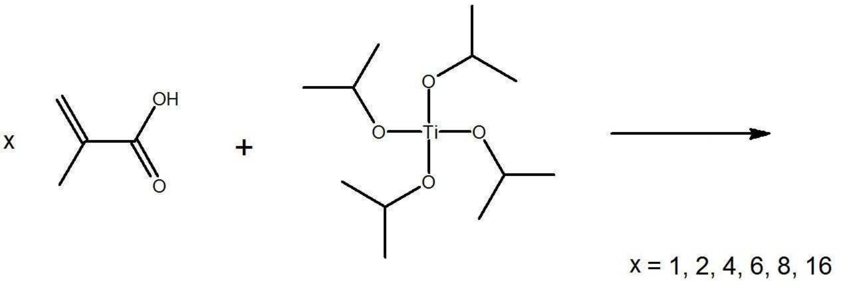
Reaction of $Ti(O^iPr)_4$ with 4-(imidazol-1-yl)-butyric acid resulted in the formation of the coordination polymer $[Ti(O^iPr)_3(OOCCH_2CH_2CH_2C_3N_2H_3)]_n$ (**TiBuImid**). Only few 1-dimensional titanium-containing coordination polymers were hitherto structurally characterized[275], among them also adducts of $Ti(OR)_4$ with diamines[269–271]. A metal-organic framework with terephthalate linkers and $Ti_8O_8(OH)_4$ units as connector was obtained from $Ti(O^iPr)_4$ and terephthalic acid[276], and materials at the borderline between sol-gel and metal-organic framework structures in the reaction with tri- and tetra-carboxylic acids[277]. On the other hand, amino-substituted carboxylic acids with rigid structures often give rise to the formation of coordination polymers[278].

Apart from the fact that a coordination polymer with $Ti(O^iPr)_3$ units was formed, compound **TiBuImid** shows several remarkable structural features. First, this is the first titanium alkoxide derivative with a chelating carboxylate group (in all other examples, the carboxylate group bridges two titanium atoms). Second, the fact that coordination of the imidazolyl group inhibits dimerization through alkoxo bridges is quite unusual, because completion of the octahedral coordination sphere of titanium through OR bridges is expected to be more favorable than coordination of a neutral nitrogen donor. A related example is $[Ti(OCH_2CMe_3)_3(py)]_2(\mu\text{-DHP})$ with very bulky OR ligands[273]. Third, no oxo cluster is formed. The formation of the coordination polymer apparently inhibits ester formation. This was already observed when $Ti(O^iPr)_4$ was reacted with di-, tri- and tetracarboxylic acids[276,277].

3.3 Elucidating the system $Ti(O^iPr)_4$ and methacrylic acid

Reactions of $Ti(OR)_4$ with carboxylic acids are particularly well investigated, and a great number of carboxylate-substituted titanium oxo clusters are known,[113,157,158] the majority of which have a mixed ligand shell of carboxylate and alkoxo groups. Many of those reactions, however, were focused on the reaction outcome of various alkoxides with a variety of carboxylic acids, while an analysis of the influence of the reaction parameters and stoichiometry is still missing.

Methacrylic acid (McOH) is one of the most frequently used carboxylic acids in oxo cluster chemistry due to its small rigid size and the polymerizeable group (for the preparation of class II hybrid materials). Four crystal structures using different titanium alkoxides and methacrylic acid were reported so far.[3,173,190] To shed further light on this system, solely $Ti(O^iPr)_4$ and methacrylic acid (McOH) were used and only their ratio was varied. (equation 3.5).



(3.5)

Crystals of reaction products obtained upon applying different ratios were obtained but unfortunately most crystals were of poor quality. Recrystallization may lead to different products than initially received. In addition, the solubility of the oxo clusters in this system is limited, for these reason recrystallization was not favored. The only structure known in the literature, obtained from titanium isopropoxide and methacrylic acid, is $Ti_4O_2(O^iPr)_6(OMc)_6$ of Moraru *et al.* (ratio 1: 2.3)[3].

When mixing $Ti(O^iPr)_4$ with methacrylic acid in the ratio 1:1 in 2-propanol, and crystallization at -10 °C the dimeric complex $Ti_2(\mu_2\text{-}O^iPr)_2(O^iPr)_4(\mu_2\text{-}OMc)(OMc)(^iPrOH)$ was isolated (**TiOMc1**, figure 3.18). When warming the complex in the reaction solution from -10 °C to room temperature, it dissolved and after 48 h at room temperature it did not crystallize again when cooled to -10 °C. The complex **TiOMc1** consists of two titanium atoms which are bridged by two isopropoxo and one methacrylate ligands. A second methacrylate is η_1-coordinated to one titanium atom. Both titanium atoms are octahedrally coordinated, the coordination sphere of Ti1 is filled by two terminal isopropoxo ligands and the η_1-coordinated methacrylate ligand, while the coordination sphere of Ti2 is filled by two terminal isopropoxo ligands and a coordinating isopropanol. A hydrogen bond is formed between the coordinating isopropanol and the η_1-coordinated methacrylate. The structure is isostructural to **TiBenzMeCl** (see chapter 3.1.2), **TiPhthal1** (see chapter 3.2) and the known dimeric carboxylate titanium complex, $Ti_2(O^iPr)_6(OOC{-}C(CH_3)_3)_2(^iPrOH)$[161]. The structure has a ratio of 1:1 for titanium atoms to methacrylate ligands, which is the same ratio as was used initially. No esterification occurred, which could be due to the lowered temperature of -10 °C.

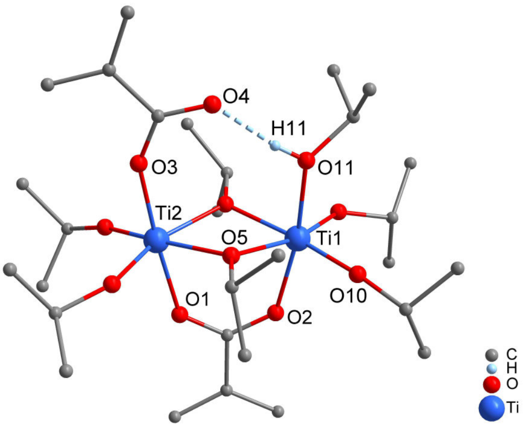


Figure 3.18: *The complex $Ti_2(\mu_2\text{-}O^iPr)_2(O^iPr)_4(\mu_2\text{-}OMc)(OMc)(^iPrOH)$, **TiOMc1**. Hydrogen atoms except H11 have been omitted for clarity.*

A 1:2 mixture of $Ti(O^iPr)_4$ and McOH resulted in $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O^iPr)_2(O^iPr)_6(\mu_2\text{-}OMc)_8$ instead (**TiOMc2**, figure 3.19). Clusters exhibiting the same core were previously obtained with other combinations of alkoxo and/or carboxylate ligands.[3,170–176,279–281] It consists of six nearly coplanar titanium atoms forming two inversion-related Ti_3O moieties. The three titanium atoms are aligned in a triangle and bridged by one μ_3-oxygen atom. The edge of the triangle between Ti1 and Ti2 is bridged by one methacrylate and one isopropoxo ligand, and Ti2 and Ti3 are bridged by one methacrylate, while Ti1 and Ti3 are not bridged. Four methacrylate and two μ_2-oxo bridges in total connect the two triangles between Ti1 and Ti3* (*denotes the symmetry-related atoms) and Ti3 and Ti1*. All three titanium atoms have an octahedral coordination sphere, which is completed at Ti2 by two and at Ti3 by one terminal isopropoxo ligand.

The product's stoichiometry reflects the used precursor ratio, since for each titanium atom there are 1.33 methacrylate ligands in the structure as well as 0.67 oxo bridges. The oxo bridges are formed by esterification of cleaved isopropanol with methacrylic acid which is then of course not available as ligand anymore. With this in mind, lower portions of methacrylic acid should lead to a different outcome or lead to unreacted $Ti(O^iPr)_4$.

The reactions of $Ti(O^iPr)_4$ with McOH in a ratio of 1:4 or 1:6 led to $Ti_9(\mu_3\text{-}O)_2(\mu_2\text{-}O)_6(O^iPr)_4\text{-}(\mu_2\text{-}OMc)_{16}$ (**TiOMc6**, figure 3.20), a cluster with an unusual ring structure[190]. This cluster has the same structure core as has been found by Kickelbick *et al.* for $Ti(O^nPr)_4$ and methacrylic acid (ratio 1:4)[190]. The structure is also similar to the known Ti_8O_8-core[186–188,237], which was also received for ratios of 1:8 and higher (see below).

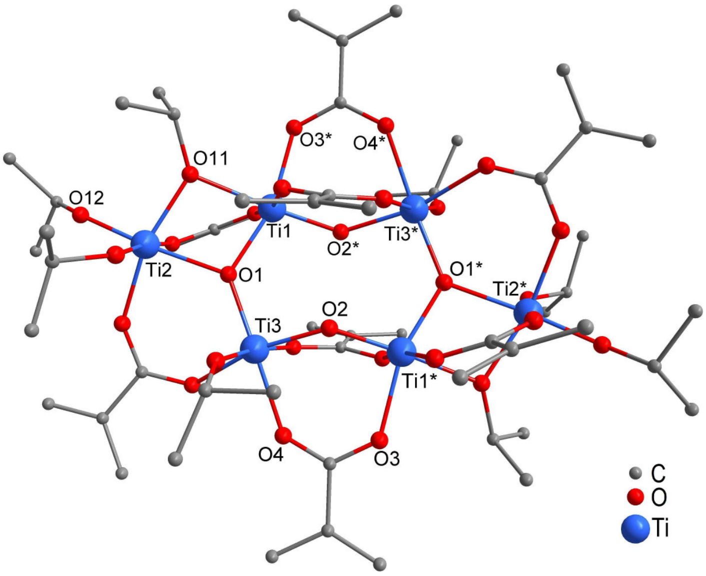


Figure 3.19: *The structure of* $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O^iPr)_2(O^iPr)_6(\mu_2\text{-}OMc)_8$, ***TiOMc2****. Hydrogen atoms have been omitted for clarity.*

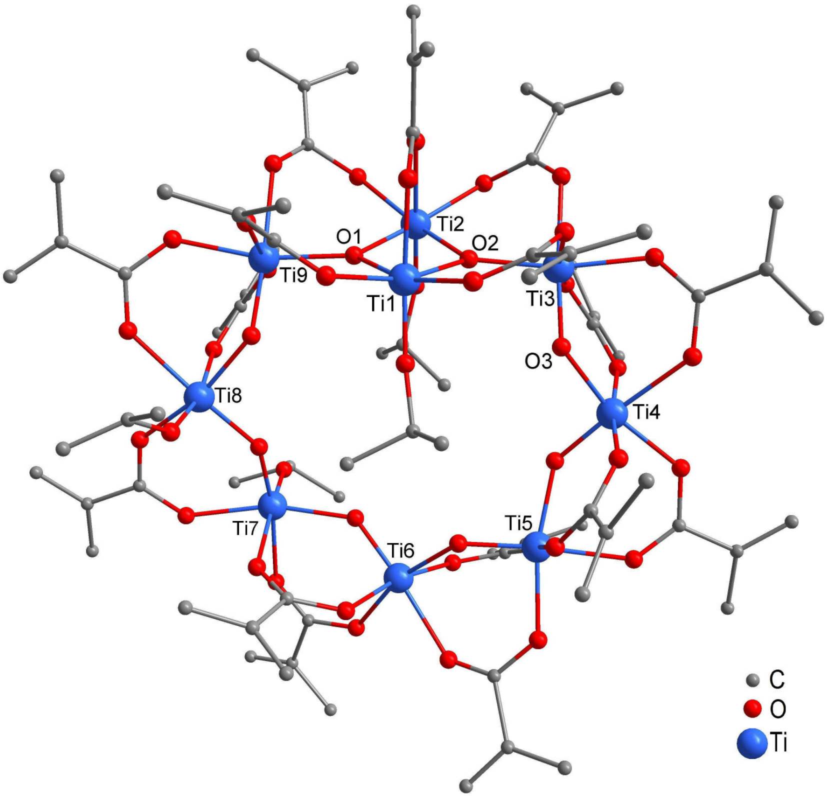
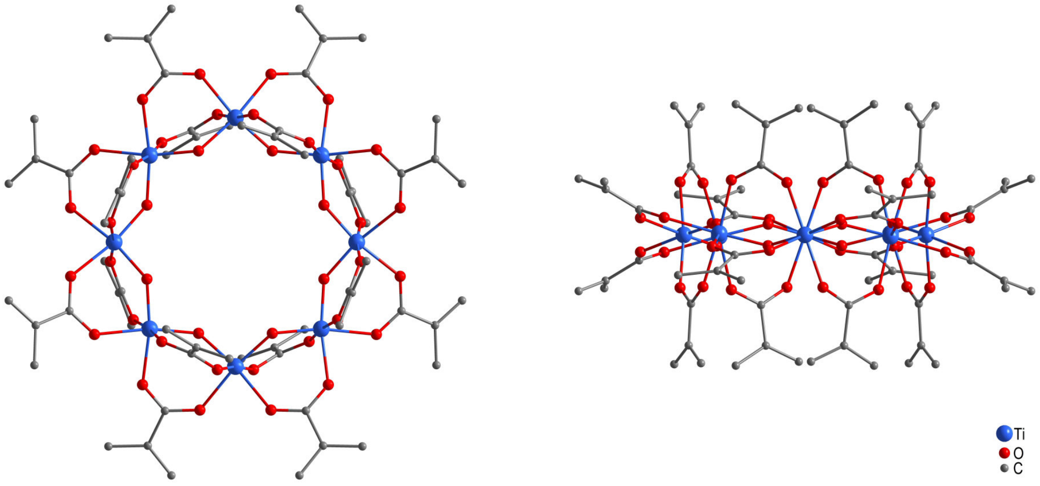


Figure 3.20: *The structure of* $Ti_9(\mu_3\text{-}O)_2(\mu_2\text{-}O)_6(O^iPr)_4(OMc)_{16}$, ***TiOMc6****. Hydrogen atoms and solvent molecules have been omitted for clarity.*

The structure of **TiOMc6** consists of nine octahedrally coordinated titanium atoms. From Ti3 to Ti7 the titanium atoms are bridged by two methacrylates and one μ_2 oxygen each. Ti7 and Ti8 have one terminal isopropoxo ligand each which are located in opposite directions perpendicular to the ring and are therefore only bridged by one μ_2-oxygen and one methacrylate ligand. Ti8 is again bridged to Ti9 by two methacrylates and one μ_2-oxygen. Between the two titanium atoms Ti3 and Ti9, the two titanium atoms Ti1 and Ti2 are aligned perpendicular to the plane of the ring, forming a rhombus with Ti3 and Ti9. One μ_3-oxygen bridges each of the triangles formed by Ti1, Ti2 and Ti9; and Ti1, Ti2 and Ti3. Each edge of the rhombus is bridged by a methacrylate ligand. Furthermore Ti1 and Ti2 are bridged by one methacrylate ligand, and one terminal isopropoxo ligand completes the coordination sphere of Ti1 and Ti2. These isopropoxo ligands point in the direction of the center of the ring and fill part of the space opened by the ring structure.

While for the ratio of 1:2 the stoichiometry of the final product corresponds perfectly with the precursor ratio used, this is not the case for the ratio 1:6 (or 1:4). Calculating the ratio of used titanium to used McOH, one finds a ratio of 1:2.67 (1.78 for the methacrylates and 0.89 for the oxo-bridges) in the final molecular structure. On one hand this means it is impossible to obtain this cluster using a ratio of 1:2 (provided quantitative yield), on the other hand it means that part of the methacrylic acid remains unreacted.

Even higher portions of methacrylic acid (ratio 1:8) led to the formation of $Ti_8(\mu_2\text{-}O)_8(\mu_2\text{-}OMc)_{16}$ (**TiOMc8**, figure 3.21), with the known cluster core, Ti_8O_8.[186–188,237] The molecular structure has a C_{4v} symmetry.



(a) View along b-axis.

(b) View along c-axis.

Figure 3.21: *The titanium-oxo-cluster obtained from $Ti(O^iPr)_4$ and McOH (1:8), $Ti_8(\mu_2\text{-}O)_8(\mu_2\text{-}OMc)_{16}$,* ***TiOMc8****. Hydrogen atoms and solvent molecules have been omitted for clarity.*

This symmetric ring (C_{4v}) is built from eight [Ti(μ_2-O)(μ_2-OMc)$_2$] units forming this octanuclear ring structure. One moiety consists of one titanium atom which is bound to the next titanium atom (of the next unit) by one μ_2-oxo bridge and two bridging methacrylates. One of these methacrylate ligands is in the plane of the ring while the second one is perpendicular to the plane alternating in opposite directions.

Until recently, when Frot *et al.* found $Ti_8O_{10}(OOC{-}CCl_3)_{12}$,[189] the Ti_8O_8 cluster core represented the only carboxylate titanium oxo cluster without alkoxo ligands. The degree of condensation is 1 for **TiOMc8**, which is higher than in most carboxylate titanium oxo alkoxo clusters. The structure exhibits a ratio of used titanium to used methacrylic acid of 1:3 (2 for the methacrylates and 1 for the oxo-bridges). Similar to this, when $TiCl_4$ was reacted with C_6F_5COOH and in a ratio of 1:3 this eight membered ring was obtained.[186] The reaction of $Ti(O^iPr)_4$ with methacrylic acid in the ratio of 1:4 (or 1:6) led to **TiOMc6** instead.

The same cell dimensions as for **TiOMc8** were obtained when using a ratio of 1:16, or when using $Ti(O^iPr)_4$, methacrylic acid and acetic acid in a ratio of 1:40:4. Some titanium oxo alkoxo clusters with a degree of condensation higher than 1 are known[140,143,144,282] but only few with carboxylates. A Ti_7O_9-cluster core[184] was obtained using 2,2-dimethylbutyric acid, and a Ti_8O_{10} cluster-core[283] was obtained using citric acid in air. The $Ti_8O_8(OH)_4$ units found in a metal-organic-framework using terephthalic acid are also similar to **TiOMc8**.[276] Some carboxylate titanium oxo alkoxo clusters have been prepared from the $Ti_{17}O_{24}$ cluster core[144] and subsequent modification with carboxylic acids[168,192]. The cluster $Ti_8O_{10}(OOCH(CH_3)_2)_{12}$ was obtained by reaction of $Ti(O^iPr)_4$ with isobutyric acid in excess under solvothermal conditions.[189] This Ti_8O_{10} cluster core is the only cluster obtained from an excess of carboxylic acid with a degree of condensation higher than 1 (1.25) without alkoxo ligands.

TiOMc8 can also be seen as an oligomer of the [Ti(μ_2-O)(μ_2-OAc)$_2$]$_n$ polymer, which was found before.[157,284] In the work of Doeuff *et al.*[284] a large excess of acetic acid was used and the same basic moiety was found, which is another indication that higher degrees of condensation cannot be achieved when reacting $Ti(O^iPr)_4$ with a simple carboxylic acid.

In continuation of this work one cluster was obtained by reacting acetic acid, methacrylic acid and $Ti(O^iPr)_4$ in ratio 4:4:1. The outcome of this reaction was the desired Ti_8O_8 cluster core with a mixed ligand sphere consisting of acetates and methacrylates. Single crystal XRD data and NMR data are in good agreement and show a statistical distribution of ligands with a methacrylate to acetate ratio of about 4 : 1. This is in good agreement with other results (see section 3.1.1) where acetic acid was used as *in situ* water-source.

Starting from the ratio 1:1 over 1:2 and 1:4 (or 1:6) to 1:8 (or higher) the degree of condensation rises from 0 over 0.67 and 0.89 up to 1 (see table 3.2). The poisoning ratio p, on the other hand decreases from 0.5 over 0.167 and 0.074 down to 0. These few data points (including $Ti_4O_2(O^iPr)_6(OMc)_6$, $p = 0.25$, O/Ti = 0.5) show that the poisoning ratio p depends on the condensation degree (O/Ti) by the equation $2 \cdot p + \mathrm{O/Ti} = 1$.

Table 3.2:** Comparison of the oxo clusters **TiOMc1**, **TiOMc2**, **TiOMc6** and **TiOMc8

ratio of McOH : $Ti(O^iPr)_4$	obtained cluster	formula	degree of condensation O/Ti	poisoning ratio p
1 : 1	**TiOMc1**	$Ti_2(O^iPr)_6(OMc)_2{}^iPrOH$	0	0.5
2 : 1	**TiOMc2**	$Ti_6O_4(O^iPr)_8(OMc)_8$	0.67	0.167
4 : 1 or 6 : 1	**TiOMc6**	$Ti_9O_8(O^iPr)_4(OMc)_{16}$	0.89	0.074
8 : 1	**TiOMc8**	$Ti_8O_8(OMc)_{16}$	1	0

Reaction of different portions of methacrylic acid with $Ti(O^iPr)_4$ showed a correlation between used portion of methacrylic acid and degree of condensation as well as the poisoning ratio. The relationship of the initial stoichiometry ($Ti(O^iPr)_4$: McOH) and the stoichiometry in the final product (Ti : (OMc + O)) is retained for the products of the ratios 1:1 and 1:2, **TiOMc1** and **TiOMc2**, respectively. For the ratio 1:8, **TiOMc8**, the structure, $Ti_8O_8(OMc)_{16}$ was obtained, which exhibits the already known eight-membered ring.[186–188,237,239] This regular octagon is built up by $[TiO(OOCR)_2]$ units, which were found before[284], and shows no more coordinating alkoxo ligands. For the ratio 1:4 (or 1:6) **TiOMc6**, $Ti_9O_8(O^iPr)_4(OMc)_{16}$, was found, a structure which is related to **TiOMc8**.

Chapter 4

Carboxylate substituted titanium oxo clusters obtained from anhydrides

4.1 Reaction of titanium alkoxides with anhydrides

4.1.1 Reaction with phthalic anhydride

Reacting titanium isopropoxide, $Ti(O^iPr)_4$, with carboxylic acids (equimolar or in excess) results in the formation of oxo clusters with carboxylate ligands[150,161,163,176,177,285]. When using anhydrides instead of the acids, the formation of oxo clusters should be inhibited since no water can be formed *in situ*.[185]

The first reaction using anhydrides was done using $Ti(O^iPr)_4$ with an equimolar amount of phthalic anhydride. It resulted in the transfer of an isopropoxo group from the metal to one carbonyl group of the anhydride and coordination of the thus formed monoester to titanium. The outcome, $Ti_2(O^iPr)_6(\mu_2\text{-}OOC{-}C_6H_4{-}COO^iPr)(\eta_1\text{-}OOC\text{-}C_6H_4\text{-}COO^iPr)(^iPrOH)$ (**TiPhthal1**, figure 4.1), is analogous to that of $Ti_2(O^iPr)_6(\mu_2\text{-}OOC{-}R)(\eta_1\text{-}OOC{-}R)(^iPrOH)$, **TiBenzMeCl** (see section 3.1.2) and **TiOMc1** (see section 3.3).[161] The two titanium atoms in the asymmetric dimer are bridged by two O^iPr ligands and one phthalate monoester ligand. The octahedral coordination of Ti1 is completed by coordination of an η_1-phthalate monoester and two terminal O^iPr ligands, and that of Ti2 by two terminal O^iPr ligands and one ^iPrOH ligand. No oxo bridges were formed and the yield was quantitative, which implies that no di-isopropyl ester is formed. This is interesting since it was shown recently by Wu *et al.* that phthalic acid and $Ti(O^iPr)_4$ in a ratio 3:2 react to a dicarboxylate titanium oxo cluster, depending on the solvent.[238] Using toluene a Ti_6O_4 cluster core with two mono-isopropyl phthalates and two not-esterified phthalates was obtained. Using ^iPrOH as solvent a Ti_6O_3 cluster core with only two not-esterified coordinating phthalates was obtained. Not only the possibility of *in situ* water formation through esterification is hindered using anhydrides, but also cleavage of the anhydride is favored and a monoester and a coordinating carboxylate is obtained.

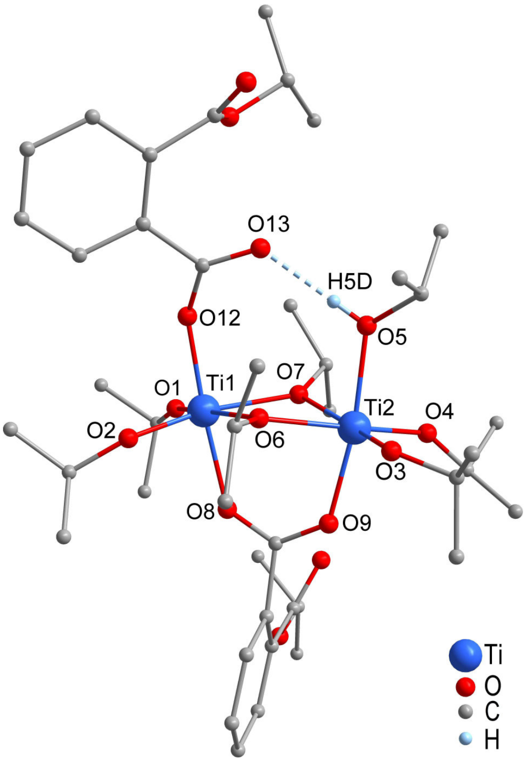
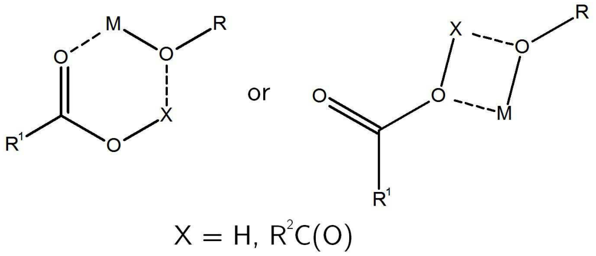


Figure 4.1: *Molecular structure of $Ti_2(O^iPr)_6(\mu_2\text{- }OOC{-}C_6H_4{-}COO^iPr)(\eta_1\text{- }OOC^{-}C_6H_4\text{-}COO^iPr)$-$(^iPrOH)$ (**TiPhthal1**). Hydrogen atoms have been omitted for clarity.*

Because of the bridging carboxylate ligand in **TiPhthal1**, the $[TiO_6]$ coordination octahedra are slightly tilted towards this ligand. The carbonyl oxygen O13 of the η_1-phthalic ester and that of the adjacent O^iPr ligand O5 at the neighboring titanium atom are clearly connected through a hydrogen bridge [O5$\cdots$O13 260.3(2) pm]. The hydrogen atom was located in difference Fourier maps, and was close to O5 of the O^iPr ligand [O5 - H5D 81(3) pm] corresponding to a coordinated ^iPrOH molecule, the O5-H5D-O13 angle was 175(3)°. This can also be concluded from the Ti2-O5 distance [207.20(12) pm] which is much longer than that of the Ti-O distances of the other terminal O^iPr ligands (177.8 - 181.9 pm). Furthermore, the C33-O13 distance is 124.2(2) pm, which is only slightly longer than that of the ester CO group in the bridging ligand [C29-O11 120.4(2) pm]. The stabilization of an η_1-carboxylate ligand by means of a hydrogen bridge to the oxygen atom of an adjacent ligand was also observed in $Zr_6O_4(OH)_4(\text{iso}{-}\text{butyrate})_{12}(HX)$ ($HX = H_2O$ or BuOH).[197]

Although the general structure type represented by **TiPhthal1** has been observed before (see above), the formation of **TiPhthal1** is remarkable. Substitution of metal alkoxides is usually performed by reaction with protic compounds (HY) during which the proton of HY is transferred to an OR group with subsequent elimination of ROH (see scheme 4.1, X = H, for Y = OOCR'). In a similar manner, an alkoxo group could be transferred to the R'C(O) moiety of the anhydride with concomitant formation of an ester (see scheme 4.1, X = R'CO). The resulting carboxylate group is coordinated to titanium. If a cyclic anhydride is used, as in the case of phthalic anhydride, the ester and carboxylate groups remain of course attached to each other.



Scheme 4.1: *Possible substitution intermediates.*

No protic compounds are involved in the reaction with phthalic anhydride. No water or hydroxo groups can therefore be formed, and hence no oxo/hydroxo clusters. To gain further insight into the role of carboxylic acids in reactions with metal alkoxides, the reaction was modified. An equimolar amount of acetic acid was added to the isopropanol solution of $Ti(O^iPr)_4$ and phthalic anhydride. This allowed a competition between a carboxylic acid and a carboxylic acid anhydride as potential sources for carboxylate ligands.

After a long reaction period, crystals of the centrosymmetric cluster $Ti_6O_6(O^iPr)_6(OOC{-}C_6H_4\text{-}COO^iPr)_6$ (**TiPhthal2**, figure 4.2) were isolated. The IR spectrum of the supernatant solution showed a broad peak at 1723 cm^{-1} indicating ester formation. For comparison: the ν_{CO} band of isopropyl acetate is at 1735 cm^{-1} and that of acetic acid at 1710 cm^{-1}. The cluster core of **TiPhthal2** can be described as a Ti_6 octahedron in which six of the eight triangular faces are capped by μ_3-oxygen atoms or as a slightly distorted hexagonal prism with alternating titanium and oxygen atoms. The six phthalic isopropyl ester ligands bridge the six four-membered Ti_2O_2 rings of the hexagonal prism. Each titanium atom is octahedrally coordinated by two phthalic ester groups, one terminal O^iPr ligand and three μ_3-oxygen atoms. The terminal OR ligands are oriented perpendicular to the slightly puckered Ti_3O_3 rings. This structural motif was already found in other Ti_6O_6 clusters with either carboxylate[113,161,163,166,168,174,177–184] or oximate ligands[218].

Compound **TiPhthal2** only contains phthalate monoester ligands but no acetate ligand. This is remarkable because two potential sources for carboxylate ligands were present in the reaction mixture. It is rather obvious that the phthalate monoester ligands were formed by the same reaction as in **TiPhthal1**. On the other hand, the μ_3-oxygen atoms in **TiPhthal2** must be due to esterification of acetic acid. Since formation of **TiPhthal2** was much slower than that of **TiPhthal1**, it can be assumed that reaction of the anhydride (giving the phthalate monoester ligands) is faster than that of acetic acid (resulting in partial hydrolysis). Although no other species were found in the reaction solution, it appears that the role of acetic acid was to provide the water for hydrolysis of part of the alkoxo groups (through formation of isopropylacetate), while phthalate anhydride served to substitute part of the alkoxo groups.

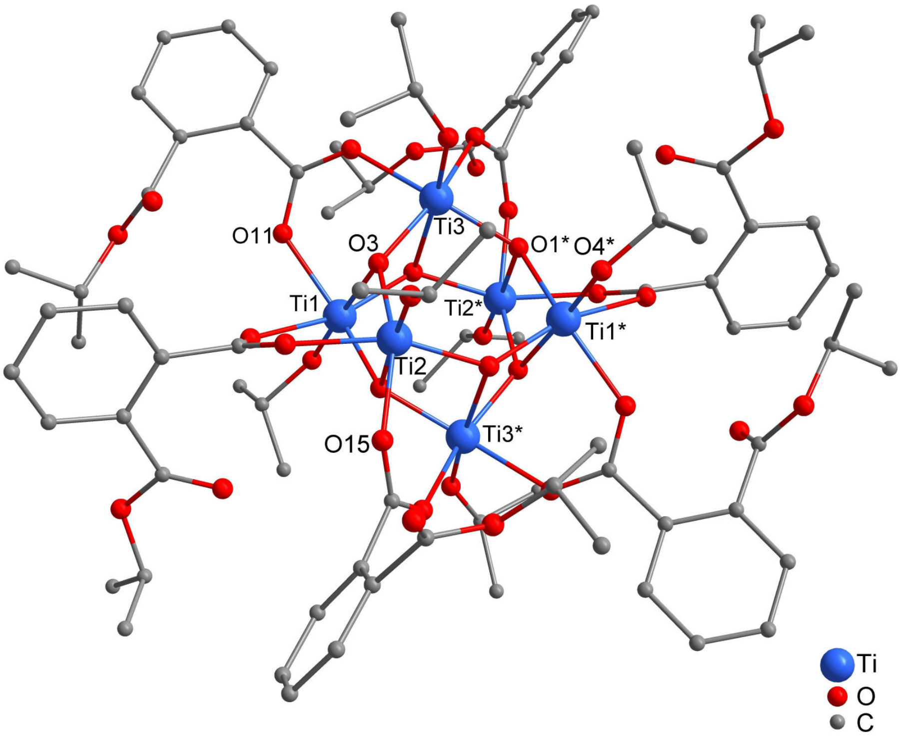


Figure 4.2: *Molecular structure of $Ti_6O_6(O^iPr)_6(OOC-C_6H_4-COO^iPr)_6$ (**TiPhthal2**). Hydrogen atoms have been omitted for clarity.*

These results strongly support the notion that the first step of the reaction of $Ti(OR)_4$ with carboxylic acids is the formation of carboxylate-substituted titanium alkoxides $Ti(OR)_{n-x}(OOCR')_x$ (x = 1 or 2). In the case studied here, *i.e.* the reaction of a carboxylic acid anhydride, the carboxylate group was formed by a route that excludes the formation of water or OH species and thus the formation of oxo/hydroxo clusters. The carboxylate group, which eventually was coordinated to titanium, was generated by OR group transfer from the metal to the other CO group of the anhydride. Formation of **TiPhthal1** was a surprisingly fast and quantitative process.

When the system was modified in a way that slow internal water production was possible, an oxo/alkoxo cluster (**TiPhthal2**) was obtained instead (with otherwise the same reaction conditions). The added acetic acid is the only possible source of the oxo groups. If one assumes that formation of **TiPhthal1** is the first step in the formation of **TiPhthal2** (because formation of **TiPhthal1** is very fast), two O^iPr ligands must be subsequently replaced by one oxo groups, while the Ti : OOCR ratio is retained.

The formal equation $2\ O^iPr^- + CH_3COOH \xrightarrow{\quad} CH_3COO^iPr + {}^iPrOH + O^{2-}$ shows that one molar equivalent of acetic acid per Ti is sufficient to explain the outcome of the overall reaction.

4.1.2 Reaction with maleic anhydride

The reaction of phthalic acid with $Ti(O^iPr)_4$ in ^iPrOH mentioned before leads to $Ti_6O_3(OOC-C_6H_4-COO)_2(O^iPr)_{14}$.[238] An oxo cluster was also obtained when reacting maleic anhydride with $Ti(O^iPr)_4$, $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)(\mu_2\text{-}O^iPr)_4(O^iPr)_{10}(OOC-CH=CH-COO)_2$ (**TiMal**, figure 4.3) in low yield. This cluster consists of two Ti_3O moieties which are connected by the two maleates and one μ_2-oxo bridge. The Ti_3O moieties are built up by three titanium atoms which form an almost isosceles triangle with a μ_3-oxo bridge in the center. Bridging isopropoxo ligands are coordinating on two edges, while the maleate is bridging the third edge. One terminal O^iPr ligand is coordinating to each of the central titanium atoms Ti3 and Ti4, while two O^iPr ligands are coordinating at each of the remaining titanium atoms. Ti1, Ti2, Ti4 and Ti5 are octahedrally coordinated while Ti3 and Ti6 have a trigonal bipyramidal coordination polyhedron.

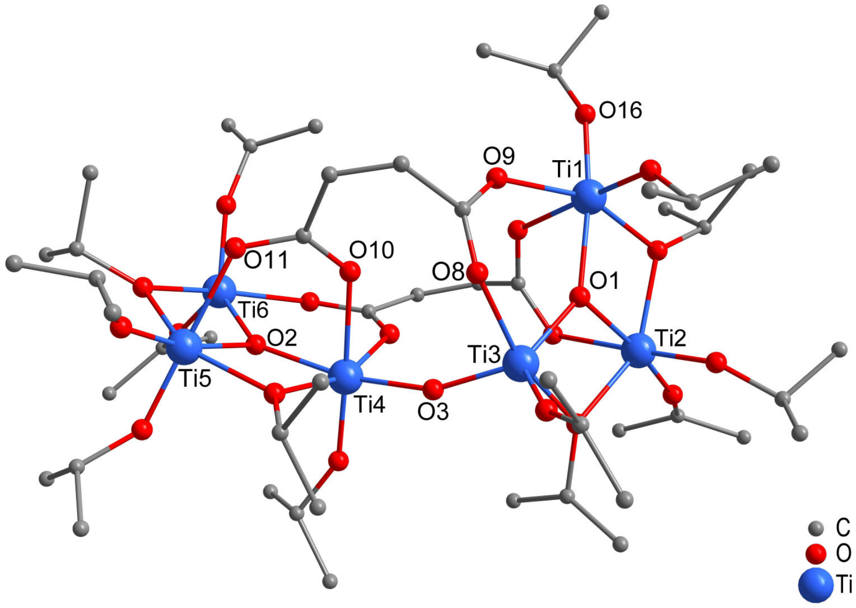
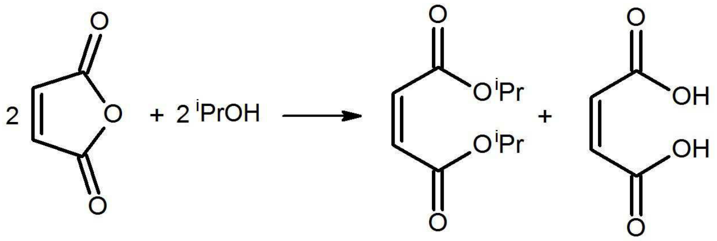


Figure 4.3: *Molecular structure of $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)(\mu_2\text{-}O^iPr)_4(O^iPr)_{10}(OOC-CH=CH-COO)_2$ (**TiMal**). Hydrogen atoms have been omitted for clarity.*

No monoester was found in the structure, instead the maleate is coordinating with both carboxylic groups to two different Ti_3O moieties. This is noteworthy because for **TiPhthal2** and **TiPhthal1** only monoester species were found. The comparable reaction leading to **TiPhthal1** resulted in a dimeric structure without oxo bridges in less than 24 hours in quantitative yield. For the maleic anhydride the reaction time was 16 weeks and the yield lower than 15 %. The only differences in both reactions are the type of anhydride and the amount of solvent. There are in principle two different possible sources of water, which is needed for condensation: (a) esterification of the monoester to the diester or (b) moisture diffusing into the reaction solution. Low yield indicates esterification and thus the formation of the diester as byproduct, while the long reaction time would allow diffusion to take place. The even more interesting question is the origin of the dicarboxylate. Reaction of the phthalic anhydride with $Ti(O^iPr)_4$ led to the quantitative formation of the isopropyl monoester in less than 24 hours. In the case of **TiMal** a different reaction (see equation 4.1) has to take place.



(4.1)

The reaction of titanium alkoxides with anhydrides showed some unexpected results. *In situ* production of water through esterification is not possible, but through esterification of the monoester the formation of oxo bridges is at least possible. No oxo cluster has been found for the reaction of phthalic anhydride with titanium isopropoxide. Instead the monoester easily formed in quantitative yield resulting in coordinating phthalate monoesters. Adding acetic acid to the reaction showed that acetic acid is esterified to provide water *in situ* for condensation, as intended. An oxo cluster is thus formed, which exhibits six coordinating monoisopropylphthalates, which is in good agreement with the first reaction. In contrast, monoisopropylcarboxylates have not been found in the case of maleic anhydride. This seems at first to contradict the assumption that monoesters are formed fast and quantitatively. But titanium alkoxides are well known transesterification catalysts[130], which allows consideration of a quantitative reaction to the monoester (fast) followed by a transesterification reaction of two monoesters to a diester and a dicarboxylate.

Chapter 5

Titanium oxo clusters with other ligands

5.1 The use of calix[4]arenes

Calixarenes are macrocyclic compounds synthesized from a phenol and an aldehyde.[286] Gutsche *et al.* brought further insight into this class of molecules making them readily available in good quality and high yield.[287] Other literature describes the functionalization at the so called lower rim[288,289] (the oxygen atoms) or the upper rim[290,291] (reactions on the aromatic ring position opposite to the oxygen). ^{t}Butyl-calix[4]arene (Calix^{tBu}(OH)$_4$) (shown in figure 5.1) was used in this work as a tetraphenolic ligand for titanium and zirconium alkoxides. The molecule can coordinate with all four oxygens, thus exhibiting strong bonding to the metal atom. Moreover, for ^{t}butyl-calix[4]arene all hydroxo groups are oriented in the same direction and thus bind to the same metal atom or at least to the same cluster, inhibiting the formation of *e.g.* a coordination polymer. With four phenolic groups and therefore four ^{t}butyl groups, the molecule is bulky enough to prohibit nucleophilic attacks on the central metal atom.

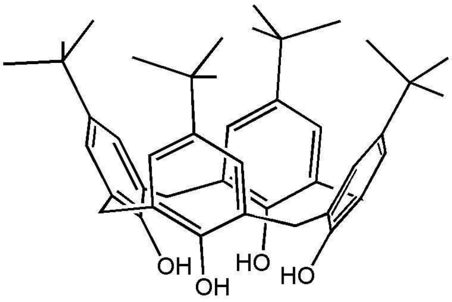


Figure 5.1: *Skeletal formula of* ^{t}*butyl-calix[4]arene(Calix*^{tBu}*(OH)*$_4$*).*

Reacting ^{t}butyl-calix[4]arene with $Zr(O^{n}Bu)_4$ in a ratio of 1:4 led to the formation of $Zr_3(O^{n}Bu)_8(Calix^{tBu}O_4)$ (**Zr3Calix**, figure 5.2). This complex crystallized after 16 hours in good yield. **Zr3Calix** consists of three zirconium atoms, which form a triangle. Two butoxo ligands are located below and above the center of the triangle, coordinating to all three zirconium atoms. Three oxygen atoms of the $Calix^{tBu}O_4$ ligand are bonded to one of the three zirconium atoms, Zr1 through Zr-O bonds. The fourth oxygen atom of the $Calix^{tBu}O_4$ ligand is bridging Zr1 and Zr2. The coordination sphere of Zr1 is completed by one ^{n}butoxo group which is bridging Zr1 and Zr3. Another ^{n}butoxo ligand is bridging Zr2 and Zr3. Their coordination spheres are completed by two ^{n}butoxo ligands, respectively. The coordination polyhedron of Zr1 is a distorted square face monocapped trigonal prism, while the coordination polyhedra of Zr2 and Zr3 are distorted octahedra. There are not many known zirconium complexes with calixarenes[292–295] and to the authors knowledge no zirconium alkoxides have been reacted with calixarenes and characterized by single crystal XRD.

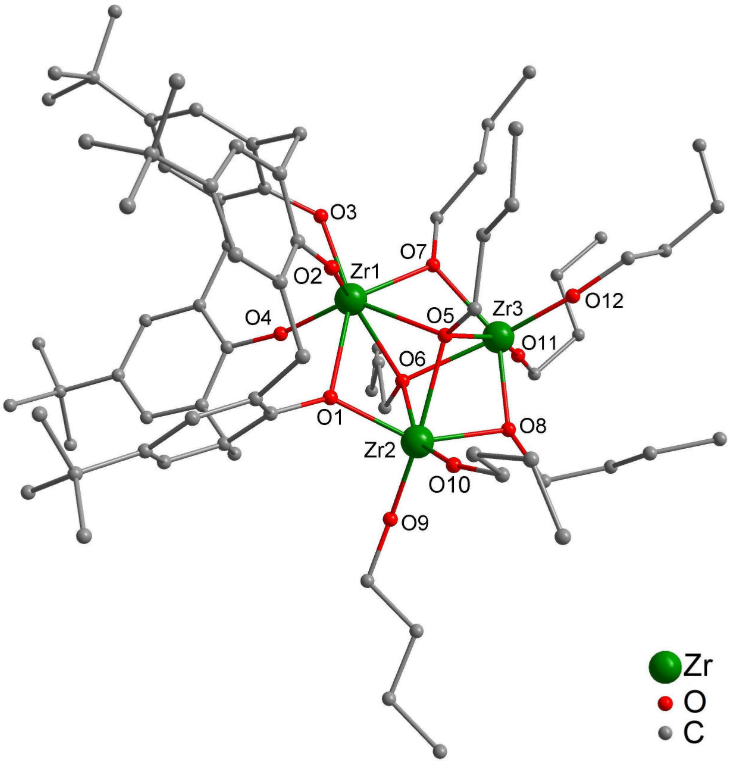


Figure 5.2: *Molecular structure of* $Zr_3(O^{n}Bu)_8(Calix^{tBu}O_4)$ *(**Zr3Calix**). Hydrogen atoms have been omitted for clarity.*

The overall charge of the complex is zero. All OH groups of ^{t}butyl-calix[4]arene are deprotonated. As no carboxylic acid or water was added, no condensation took place and therefore no oxo cluster was obtained. Nevertheless, it was shown that $Calix^{tBu}O_4$ is a suitable ligand for the modification of zirconium alkoxides.

Zr3Calix has a local C_s symmetry. In the ^1H NMR spectrum, two signals were found for the ^{t}butyl groups of the ($Calix^{tBu}O_4$) ligand at 0.93 and 1.02 ppm, and one signal for the other two symmetry-related ^{t}butyl groups at 1.59 ppm. The hydrogen atoms of the CH_2 of the calixarene show geminal coupling with a large shift between axial and equatorial. Four different doublets can thus be found in the NMR spectrum (at 3.59, 3.64, 5.23 and 5.32 ppm) with a coupling constant of around 12 Hz. Therefore, it can be assumed that the C_s symmetry is retained in solution. In the ^{13}C NMR spectrum the number of signals of the calixarene ligand reflects the mirror symmetry (one signal overlaps with the C_6D_6 resonance). The signals of the O^nBu ligands partly overlap in the ^1H and ^{13}C NMR spectra. A lower number of signals than expected were therefore observed in the latter.

The reactions of various titanium compounds with calix[4]arenes have been studied, but until now no structure of the reaction of a titanium alkoxide with calix[4]arenes has been published.[292,296–301] Reaction with titanium butoxide resulted in $Ti_2(O^nBu)_2(Calix^{tBu}O_3(OH))_2$ (**TiCalix**, figure 5.3). Adding the titanium butoxide to the ^{t}butyl-calix[4]arene lead to an immediate formation of a yellow solution of which red crystals formed within a week. The structure differs significantly from the zirconium equivalent. The two titanium atoms are both octahedrally coordinated and bridged by two ^{n}butoxo ligands. The two $Calix^{tBu}O_3(OH)$ ligands are chelating one titanium atom. One of the four oxygen atoms coordinates as phenolic group, while the other three are deprotonated. The position of the phenolic group was identified by the Ti-O bond length. While Ti1-O1, Ti1-O2 and Ti1-O3 have bond lengths of 180 pm, 181 pm and 194 pm, respectively, Ti1-O4 has a bond length of 224 pm. The structure is similar to the monomethyl derivative which has been reported by Dubberley *et al.*.[292] The methoxybenzolic group in the latter structure is coordinating similarly as the phenolic group in the structure of **TiCalix**.

Although a ratio of 1:4 (^{t}butyl-calix[4]arene:$Ti(O^nBu)_4$) was used, the final molecule has a ratio of 1:1. Due the difference in coordination behavior the titanium species cannot result in the same final structure as the zirconium species (sevenfold coordination is unfavorable for titanium). Furthermore, a monomeric titanium species would be even less favorable in terms of charge.

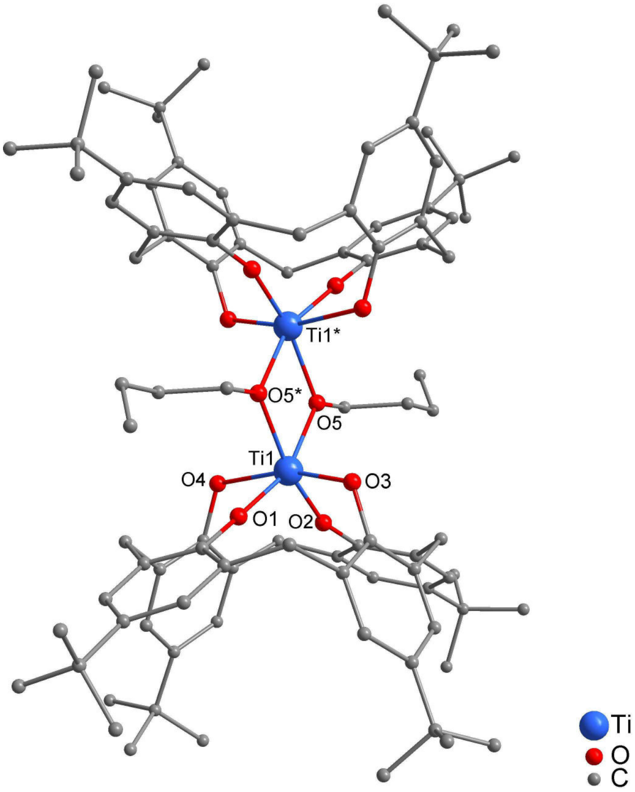


Figure 5.3: *Molecular structure of* $Ti_2(O^nBu)_2(Calix^{tBu}O_3(OH))2$ *(**TiCalix**). Hydrogen atoms have been omitted for clarity.*

To obtain a zirconium oxo cluster of ^{t}butyl-calix[4]arene, the reaction of zirconium butoxide with ^{t}butyl-calix[4]arene was repeated in the presence of acetic acid (ratio 4:1:4). This led to the formation of the zirconium oxo cluster $Zr_4(\mu_3\text{-}O)(O^nBu)_6(Calix^{tBu}O_4)(^nBuOH)_2$ (**Zr4Calix2**, figure 5.4). It is built from four zirconium atoms which are forming a distorted rhombus. Zr1, Zr2 and Zr3 form a regular triangle which is capped on two sides by μ_3-^{n}butoxo ligands. The forth zirconium atom, Zr4, is bound by a μ_3-oxo bridge to Zr2 and Zr3. There are two positions for Zr4 in this cluster, which are shown in figure 5.5 as Zr4A and Zr4B. Due to this positional disorder, the three ^{n}butoxo groups and the coordinating ^{n}butanol group are disordered as well. Zr4A (or Zr4B) is connected to Zr2 (or Zr3) by one bridging phenoxy group of one $Calix^{tBu}O_4$ ligand. This way, one of the two $Calix^{tBu}O_4$ ligands is coordinated to two and the other is coordinated to three zirconium atoms.

In contrast to **Zr3Calix**, two $Calix^{tBu}O_4$ ligands are coordinating. This was surprising since the same ratio was used. Furthermore, no acetate is coordinating, although it was used equimolar to $Zr(O^nBu)_4$. This shows that $Calix^{tBu}O_4$ are preferred ligands compared to carboxylic acids. The outcome of the reaction of $Zr(O^nBu)_4$, ^{t}butyl-calix[4]arene and water (diluted in THF) in a ratio of 8:1:4 was the same oxo cluster. This is proof that acetic acid acts as an *in situ* water source.

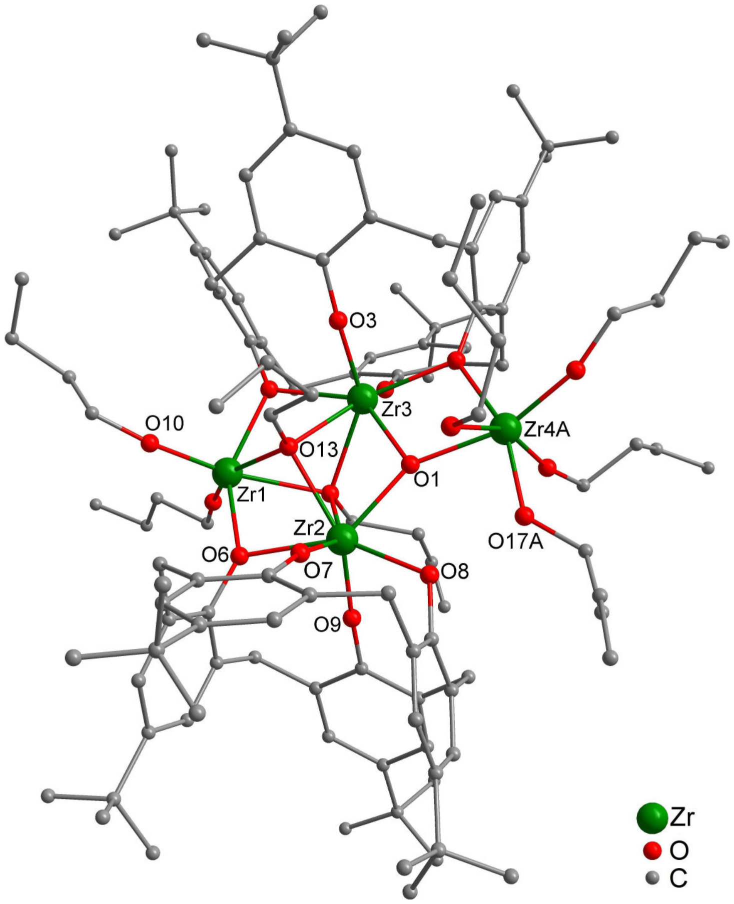


Figure 5.4: *Molecular structure of* $Zr_4(\mu_3\text{-}O)(O^nBu)_6(Calix^{tBu}O_4)_2(^nBuOH)_2$ *(**Zr4Calix2**). Hydrogen atoms and disordered atoms have been omitted for clarity.*

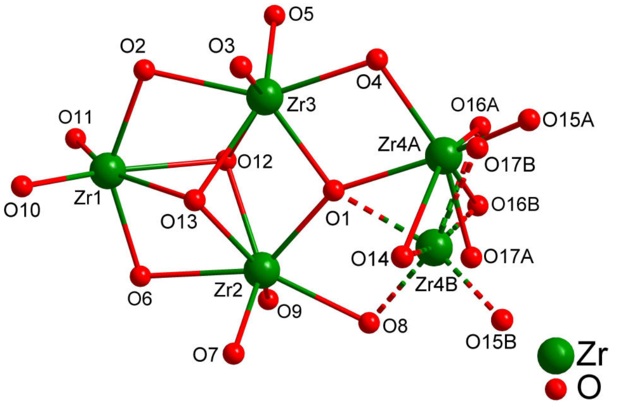


Figure 5.5: *Cluster core of **Zr4Calix2** including the positional disorder of Zr4. Ligand atoms have been omitted for clarity.*

5.2 An unusual cluster formed by 1,2-cyclohexanedione dioxime

Oximes[218,219,263,302–311] as well as dioximes[308,312,313] have been used in a variety of reactions as ligands for titanium and zirconium complexes. Baumann *et al.* described two oximate titanium oxo clusters and one oximate zirconium oxo cluster.[218,314]. Partial hydrolysis was achieved by the addition of water through air moisture.

1,2-Cyclohexanedioxime is an interesting compound since both oximes in the molecule are oriented in the same direction. This lowers the possibility of generating a coordination polymer or a metal-organic framework. The ring and the C=N double bond prevent the two functional groups from rotating and fix the distance between the two oximes. Thus, a zirconium oxo cluster was obtained upon reacting the oxime with zirconium ^{n}butoxide and acetic acid. It has been shown that acetic acid can be used to obtain oxo clusters of various ligands due to its reactivity towards esterification.[315] The obtained cluster $Zr_{10}(\mu_4\text{- }O)_2(\mu_3\text{- }O)_2(\mu_2\text{- }On^nBu)_{10}(O^nBu)_8(\mu_3\text{- }(ON)_2C_6H_{10})_2$-($\mu_2$- $(ON)_2C_6H_{10})_2(\mu_2OAc)_4(OAc)_2$ (**ZrHexOx**) is shown in figure 5.6.

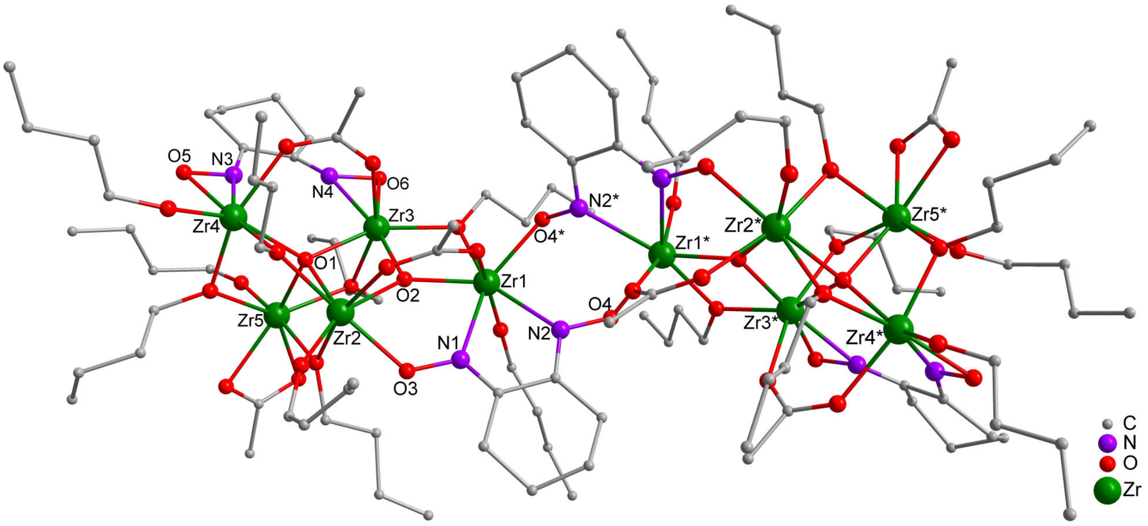


Figure 5.6: *Molecular structure of the cyclohexandioximate acetate zirconium oxo cluster (**ZrHexOx**). Hydrogen atoms have been omitted for clarity.*

ZrHexOx is formed from two Zr_5O_2-moieties which are interconnected by two dioximates. Each Zr_5O_2 moiety consists of one Zr_4 tetrahedron with one μ_4-oxygen in the center. The tetrahedron is connected through one edge to the one of the central zirconium atoms by a μ_3-oxygen, a bridging butoxo ligand, a bridging acetate and an oximate group. Four dioximate and six acetate ligands coordinate to the cluster core in total. The dioximate ligands have different binding modes (similar to the notation for phosphonate coordination modes[74], w.xy refers to the number of metal atoms to which the oximate ligand is coordinated [w], and the number of metal atoms to which each N-O group is coordinated [x,y]). While the central dioximates bind 3.22, the dioximates on one edge of the Zr_4O-tetrahedron bind 2.11. The acetates also differ in coordination behavior. Four are bridging and two are chelating. It is interesting that every zirconium atom is bound to one acetate, and all but two zirconium atoms (Zr5 and the inversion symmetry related Zr5*) are bound to an oximate. Every zirconium atom in this structure is 7-coordinated, with a distorted pentagonal bipyramidal coordination geometry. The coordination sphere of the zirconium atoms are completed by butoxo ligands of which ten are bridging and eight are terminally coordinating.

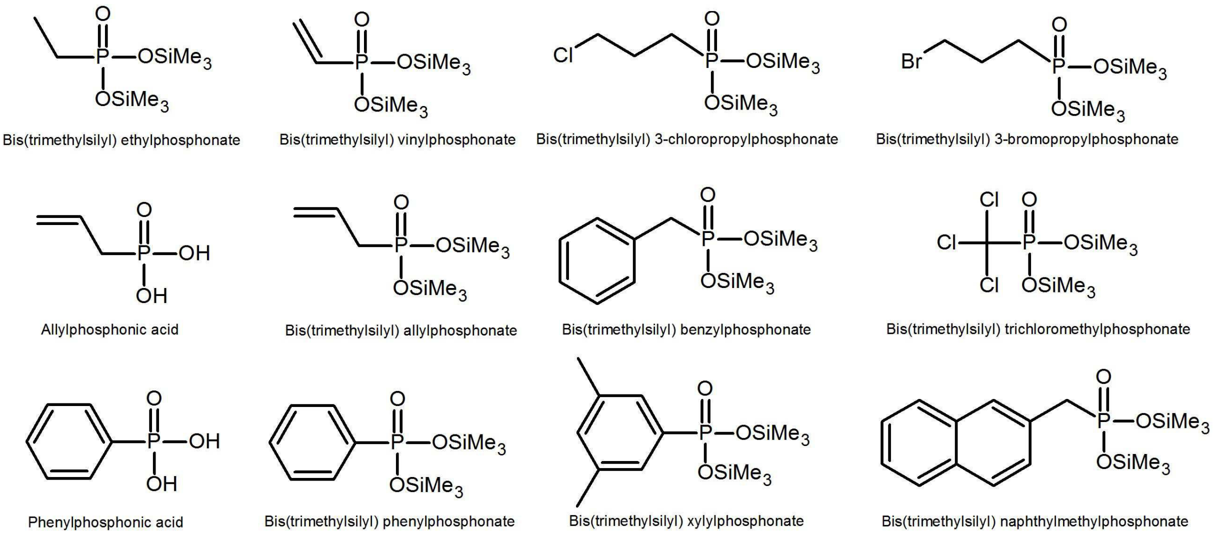
In principle, this structure is another example for the possibility of using acetic acid as an *in situ* water-source. The final structure consists of 10 zirconium atoms, 4 dioximates and 10 acetates (acetates are counted including the number of oxo bridges, which originate from the esterification of acetic acid). This is in good agreement with the used precursor ratio $Zr(O^{n}Bu)_4$:1,2-cyclohexanedioxime:AcOH of 10:5:10.

Chapter 6

Phosphonate substituted titanium and zirconium oxo clusters

6.1 Higher binding energies? - The use of phosphonic acids and its derivatives

Since the tetradentate calix[4]arenes show interesting binding to the metal oxo cluster surface, another class of ligands was researched which has a tridentate binding mode. The use of phosphonic acids is apparent when looking at the chemistry of titania and zirconia nanoparticles (oxo clusters can be seen as small, very defined metal oxide nanoparticles).[59,61,62] For both oxides phosphonic acids are used to stabilize the particles, thus generating a phosphonate ligand shell.[316] The grafting of phosphonates onto titania surfaces has been studied intensively, leading to numerous applications.[58,63,73,317–319] One can conclude that phosphonate ligands are also suitable for titanium and zirconium oxo clusters. Surprisingly, the number of known phosphonate titanium oxo clusters is small.[227,228,233] In these oxo clusters the formation of the oxo groups was rather attributed to residual moisture in the solvents or phosphonic acids[227,233] than esterification reaction. Phosphinates seem viable as well although structures obtained with phosphinates are comparable to carboxylate-substituted derivatives.[227,228,230,233] One problem regarding phosphonic acids is their solubility in common organic solvents. Due to their high polarity, they are only soluble in polar solvents. Bis(trimethylsilyl) esters of phosphonic acids are sometimes obtained as intermediates in the synthesis of functional phosphonic acids. In contrast to their parent acid the esters are often liquids and miscible in common organic solvents like 2-propanol or dichloromethane. These esters can be converted to the phosphonic acids by methanolysis.[76–78] Bis(trimethylsilyl) esters of different phosphonic acids were synthesized in this work (see scheme 6.1) and used to generate new titanium oxo clusters.



Scheme 6.1: *Phosphonic acids and phosphonates used to obtain new phosphonate oxo clusters of this thesis.*

6.1.1 Phosphonate titanium oxo clusters

The phosphonate-substituted oxo clusters $Ti_4(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_5(O_3PR)_3(DMSO)$ (R = Ph, Me, ^{t}Bu, 4-NC-C_6H_4) were obtained by Guerrero *et al.*[227] and Mehring *et al.*[228] from the reaction of $Ti(O^iPr)_4$ with $RP(O)(OH)_2$. The structure of this cluster type consists of a symmetric $Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_3$ triangle in which three octahedrally coordinated Ti atoms are bridged by a μ_3-oxygen. The titanium atoms of the triangle are additionally bridged by three μ_2-O^iPr ligands, and each titanium atom is coordinated by a terminal O^iPr ligand. The forth ("capping") Ti atom is connected to this triangular unit by the three phosphonate ligands. The vacant coordination sites at the forth titanium atom are occupied by two terminal O^iPr groups and one DMSO molecule. DMSO was used as solvent due to the low solubility of phosphonic acids in organic solvents.

An oxo cluster (**TiDMSOAllylPA**) of the same structure was obtained when reacting $Ti(O^iPr)_4$ with allylphosphonic acid in DMSO (figure 6.1)[320]. The average Ti-O distances of the phosphonate groups is 197 pm, with the exception of the Ti-O bond at Ti1 *trans* to the terminal O^iPr ligands (204 pm). The Ti-O bond distances of the μ_2-O^iPr groups are 202 pm in the average, and that of the terminal O^iPr ligands 180 pm.

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^iPr signals, and the ^{13}C NMR spectrum six doublets for phosphorous-coupled carbon atoms of the allyl group.

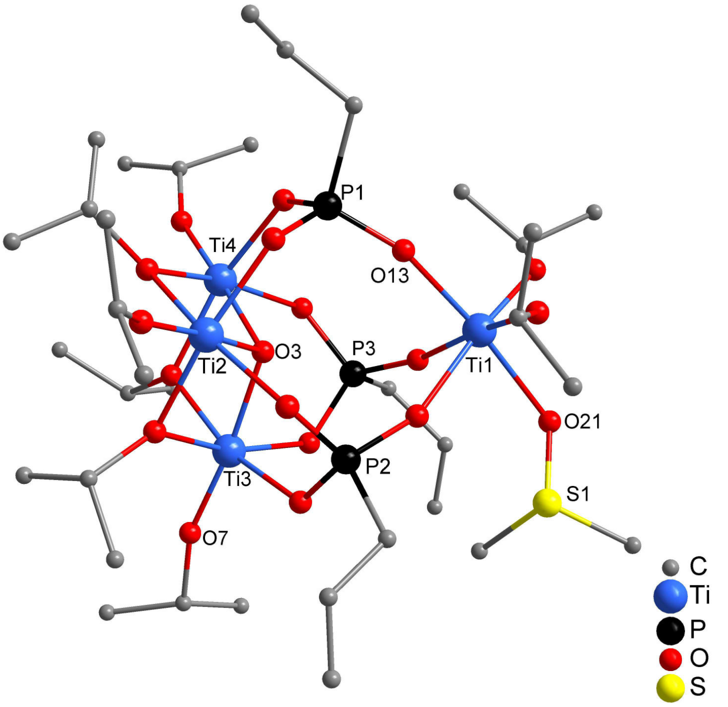


Figure 6.1: *Molecular structure of* $Ti_4(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_5(O_3P{-}allyl)_3(DMSO)$ *(**TiDMSOAllylPA**). Hydrogen atoms have been omitted for clarity.*

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

When bis(trimethylsilyl) allylphosphonate was reacted with $Ti(O^iPr)_4$ in a 1:2 ratio in isopropyl alcohol, the cluster $Ti_8(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_6(O^iPr)_8(O_3P{-}allyl)_6(O_2P(O^iPr)allyl)_2$ (**TiAllylPP**) was formed (figure 6.2). Cluster **TiAllylPP** consists of two Ti_4O units [= $Ti_4(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3$-$(O^iPr)_4(O_3P{-}allyl)_3$] as in **TiDMSOAllylPA**, which are, however, 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^iPr ligand and the oxygen atoms of two allylphosphonate ester groups (instead of two terminal O^iPr ligands and a DMSO molecule in **TiDMSOAllylPA**).

The bond lengths in **TiAllylPP** are similar to that of **TiDMSOAllylPA**, with an average Ti-O bond distance of 197 pm for the phosphonate groups. An exception is again the Ti-O bond *trans* to the terminal O^iPr ligand on the capping titanium atom (204 pm). The bridging O^iPr groups have an average Ti-O bond distance of 203 pm and the terminal of 178 pm.

The synthesis of **TiAllylPP** was repeated several times, and either triclinic (space group $P\bar{1}$, denoted as **TiAllylPP**) or monoclinic crystals (space group $P2_1$/n, denoted as **TiAllylPP2**)

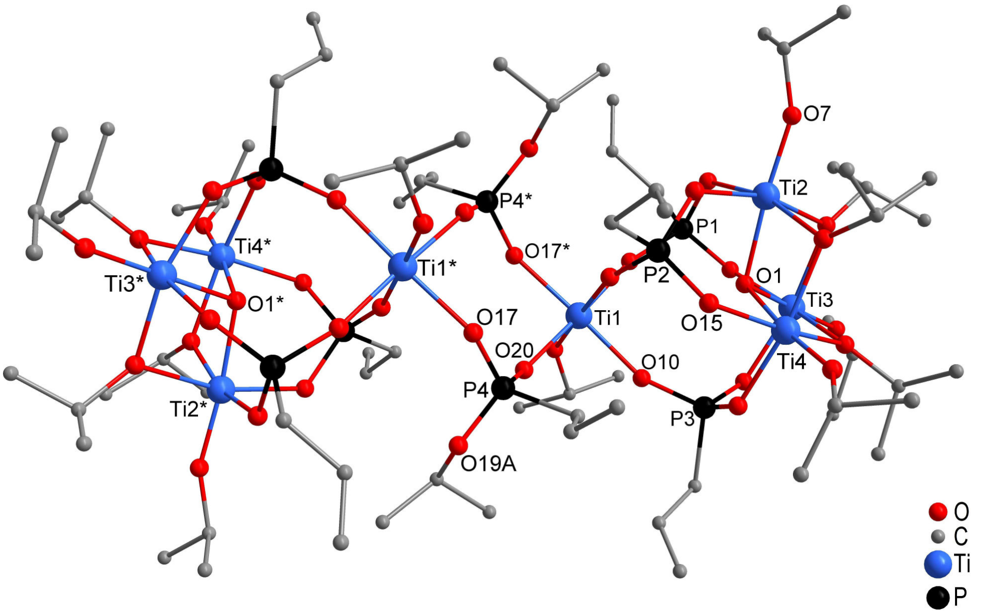


Figure 6.2: *Molecular structure of* $Ti_8(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_6(O^iPr)_8(O_3P\text{–}allyl)_6(O_2P(O^iPr)allyl)_2$ *(**TiAllylPP**). Hydrogen and disordered atoms have been omitted for clarity.*

were obtained. The molecular structure was the same in both cases and the bond distances and angles are similar, but the packing of the clusters was different. The clusters are parallel to each other in **TiAllylPP** and aligned with a 58.2 ° angle in **TiAllylPP2**.

The most remarkable feature of **TiAllylPP** is the phosphonic acid isopropyl ester groups. The formation of a phosphonic acid isopropyl ester indicates that similar to the reaction of carboxylic acids, esterification of the (non-coordinated or coordinated) phosphonic acid could also be the source of the oxo groups, especially since the ester:(μ_3-O) ratio in **TiAllylPP** is one. Reaction of bis(trimethylsilyl) phosphonates with alcohols leads to the corresponding phosphonic acid and alkoxytrimethylsilane[77] in a fast reaction.[321] Use of the trimethylsilyl esters thus allows generating the phosphonic acid *in situ*, which may substitute part of the O^{i}Pr groups of Ti(O^{i}Pr)$_4$. The (coordinated or non-coordinated) phosphonic acid could then react with isopropanol, possibly catalyzed by Ti(O^{i}Pr)$_x$ moieties,[130] to produce water for condensation and the found isopropyl monoester.

Crystals of **TiAllylPP** (or **TiAllylPP2**) were soluble in common organic solvents. NMR data, however, were ambiguous. In the ^{31}P NMR spectrum five peaks were found. Interpretation of the ^{1}H NMR data was limited due to the high number of chemically similar groups. The integrals fitted well, but multiplicity and overlapping led to very broad and indistinct signals. ^{13}C NMR spectra also showed five doublets for the allyl groups, but overlapping led again to a spectrum from which the symmetry of **TiAllylPP** in solution was difficult to elucidate.

Reaction of bis(trimethylsilyl) ethylphosphonate with Ti(O^{i}Pr)$_4$ in isopropyl alcohol resulted in $Ti_8O_2(O^iPr)_{14}(O_3P\text{–}Et)_6(O_2P(O^iPr)Et)_2$ (**TiEtPP**), which is isostructural with **TiAllylPP**.

The bond distances and angles were the same within the error limits. ^{31}P NMR data of **TiEtPP** were in agreement with the solid state structure. ^{1}H NMR and ^{13}C NMR spectra confirmed the structural data in a general manner, with the limitations already pointed out for **TiAllylPP**.

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, bis(trimethylsilyl) 3-chloropropylphosphonate was reacted with $Ti(O^iPr)_4$ in isopropyl alcohol, and $Ti_7O_2(O^iPr)_{12}$-$(O_3PCH_2CH_2CH_2Cl)_6$ (**TiClPrPP**) (figure 6.3) was obtained. The structure of **TiClPrPP** is again based on Ti_3O units [$= Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_3(O_3P{-}R)_3$]. Contrary to **TiAllylPP** and **TiEtPP**, the two Ti_3O units are connected by a single titanium atom, i.e. a sandwich structure is formed, with Ti4 as the central atom and the Ti_3O units as "ligands" (in this way of looking at the structures, **TiDMSOAllylPA** would be a half-sandwich structure). The bond distances are similar to **TiDMSOAllylPA**. 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.

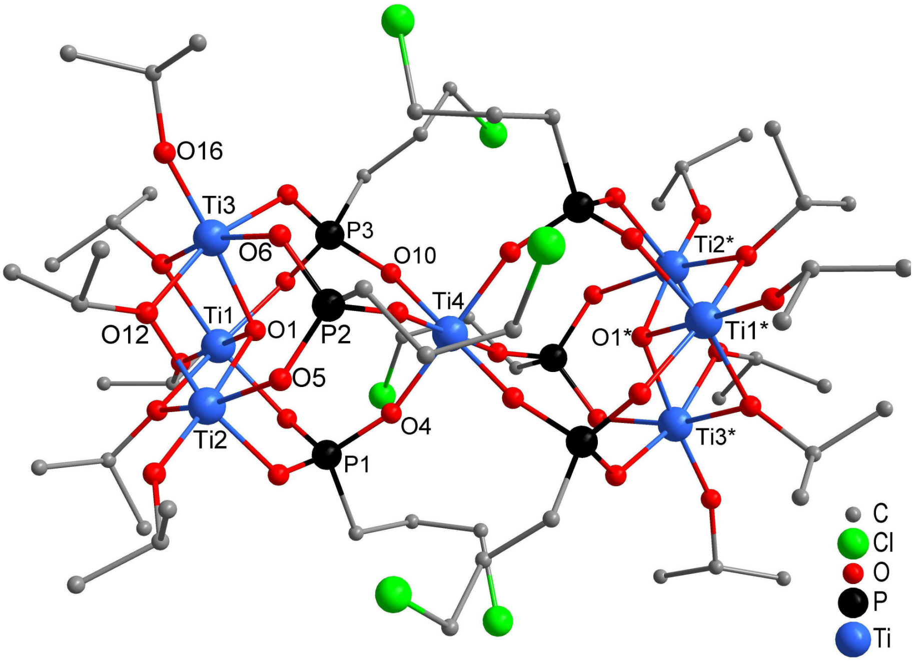


Figure 6.3: *Molecular structure of* $Ti_7O_2(O^iPr)_{12}(O_3PCH_2CH_2CH_2Cl)_6$ *(**TiClPrPP**). Hydrogen and disordered atoms have been omitted for clarity.*

The ^{31}P NMR spectrum showed only one peak, indicating the high symmetry and stability of this cluster in solution. This was also seen in the ^{1}H NMR spectrum where only two different signals for O^iPr groups were found. The ^{13}C NMR spectrum confirmed this observation, where also J_{PC} was seen. Smaller additional signals indicated the presence of a side product, where Cl is replaced by Br. This was already observed in the spectra of the precursors. Since 1-bromo-3-chloropropane was used for the preparation of bis(trimethylsilyl)

3-chloropropylphosphonate, both halogens can react with dimethylphosphite, and therefore a small amount of 3-bromopropylphosphonate was also formed. The presence of some bromine (replacing Cl) was also seen in the electron density map of the single crystal measurements.

Reaction of bis(trimethylsilyl) benzylphosphonate with $Ti(O^iPr)_4$ yielded $Ti_7O_2(O^iPr)_{12}(O_3P\text{-}CH_2C_6H_5)_6$ (**TiBzlPP**) which is isostructural to **TiClPrPP**. The arrangement of the benzyl groups in the center of the structure is paddle wheel-like. Another isostructural cluster was received upon reaction of bis(trimethylsilyl) 3-bromopropylphosphonate with $Ti(O^iPr)_4$, $Ti_7O_2(O^iPr)_{12}(O_3PCH_2CH_2CH_2Br)_6$ (**TiBrPrPP**).

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 question, phosphonate ligands with sterically more demanding groups were included in this study. Furthermore, aromatic phosphonic acids are slightly more acidic. Reaction of bis(trimethylsilyl) xylylphosphonate and $Ti(O^iPr)_4$ led to the formation of $Ti_4O(O^iPr)_8(O_3P\text{-}xyl)_3(^iPrOH)$ (**TiXylPP**) (figure 6.4). The structure is analogous to that of **TiDMSOAllylPA**, the neutral ligand at the capping titanium atom being isopropyl alcohol (instead of DMSO in **TiDMSOAllylPA**).

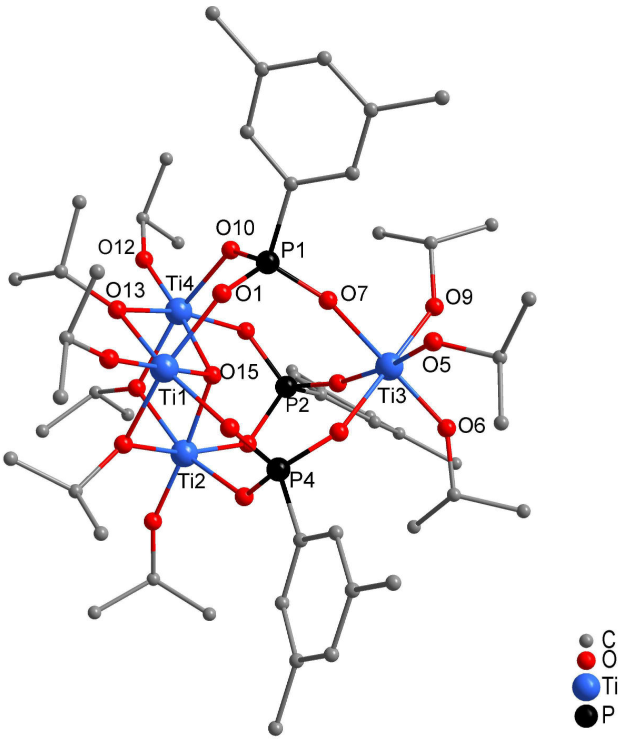


Figure 6.4: *Molecular structure of* $Ti_4O(O^iPr)_8(O_3P{-}xyl)_3(^iPrOH)$ (***TiXylPP***)*. Hydrogen and disordered atoms have been omitted for clarity.*

The appearance of only one signal in the ^{31}P NMR spectrum indicated that cluster **TiXylPP** has C_3 symmetry also in solution. This was confirmed by the ^{1}H NMR data were 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 were detected. The proton of the coordinated isopropyl alcohol exchanges easily on the NMR time scale since only averaged signals of the isopropyl alcohol and the O^{i}Pr groups were observed.

Reaction of a phosphonate with an even bulkier substituent, *viz.* bis(trimethylsilyl) naphthylmethylphosphonate resulted in the complex $Ti_4(\mu_2\text{-}O^iPr)(O^iPr)_7(O_3PMeNp)_4(^iPrOH)_2$ (**TiNpMePP**, figure 6.5). In **TiNpMePP**, two of the O^{i}Pr ligands of $Ti(O^iPr)_4$ were substituted by one O_3PMeNp ligand [formal composition $Ti(O^iPr)_2(O_3PMeNp)$], but no partial hydrolysis took place. This is in contrast to the reactions with the other bis(trimethylsilyl) phosphonates described in this article. Different to the other clusters reported in this article, the crystallization time of **TiNpMePP** was much faster. Compound **TiNpMePP** could therefore represent the structure of an initially formed substitution product, which possibly crystallized easier from the isopropyl alcohol solution due to the apolarity of the naphthyl group and thus escaped hydrolysis.

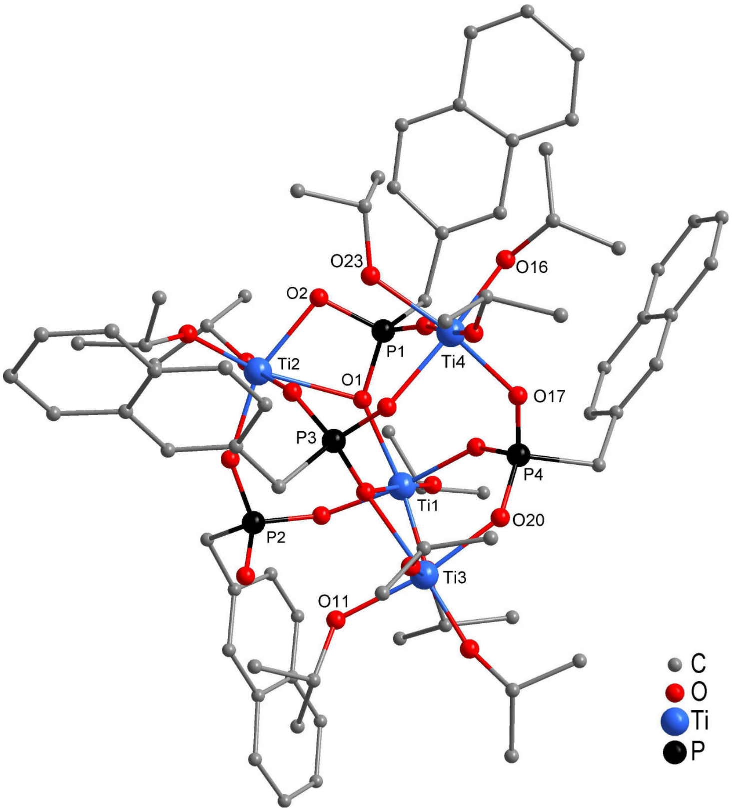


Figure 6.5: *Molecular structure of* $Ti_4(\mu_2\text{-}O^iPr)(O^iPr)_7(O_3PMeNp)_4(^iPrOH)_2$ ***(TiNpMePP)****. Hydrogen and disordered atoms have been omitted for clarity.*

The structure of **TiNpMePP** consists of four octahedrally coordinated titanium atoms arranged in an irregular shape. In contrast to all other structures, where all the phosphonates are binding in a 3.111 mode (w.xyz refers to the number of metal atoms to which the phosphonate ligand is coordinated [w], and the number of metal atoms to which each oxygen is coordinated [x,y,z][74]), in **TiNpMePP** just one phosphonate (P4) is coordinating 3.111. The other phosphonates coordinate as 4.211 (P3), 3.211 (P1) and 2.110 (P2). Due to the high connectivity of the phosphonates, there is only one bridging O^iPr ligand.

NMR measurements are in good agreement with the crystal structure. Four signals were 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 were detected in the ^{13}C NMR spectrum, while four were expected. One of these doublets has a higher intensity, indicating an overlap of signals.

Another structure similar to **TiDMSOAllylPA** was obtained when reacting bis(trimethylsilyl) trichloromethylphosphonate with titanium isopropoxide, $Ti_4(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_5(O_3P\text{-}CCl_3)_3(DMF)$ (**TiCl3MePP**, figure 6.6). The reaction was done using DMF as second solvent, since the product formed precipitated within one minute without DMF. The DMF acted as a neutral ligand, leading to the same Ti_4O-core as in **TiDMSOAllylPA**. The differences between these two structures is the neutral ligand and the organic substituent on the phosphorous atom.

The obtained structure is again built up by the $Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_3$ unit which is linked by three 3.111 coordinating phosphonates to a fourth titanium atom. The coordination sphere of this separated titanium atom is filled by two terminal isopropoxo ligands and one coordinating DMF.

Although the bis(trimethylsilyl) ester of the phosphonic acid was used, the same cluster core as in **TiDMSOAllylPA** and **TiXylPP** was obtained if a neutral ligand was provided. All three structure have a different neutral ligand: **TiDMSOAllylPA** has DMSO coordinating, at **TiXylPP** an isopropanol is coordinating and at **TiCl3MePP** the added DMF is coordinating. It seems that one can prevent the "dimerization" of the Ti_4O moieties (e.g. at **TiAllylPP**, **TiClPrPP**) by providing a strongly binding neutral ligand which can complete the octahedral coordination sphere of the separated titanium atom (Ti4).

Reacting bis(trimethylsilyl) vinylphosphonate with $Ti(O^iPr)_4$ in a ratio of 1:1 in 2-propanol, led to the formation a gel in which crystals of $Ti_8(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_6(O^iPr)_8(PO_4)_2(O_3P(vinyl))_4\text{-}(^iPrOH)_2$ (**TiVinylPP**, figure 6.7) were grown. The structure of **TiVinylPP** consists of two Ti_3O moieties which are each bridged by a phosphate and two vinylphosphonates to two central titanium atoms. Similar to **TiAllylPP** it can be seen as two Ti_4O moieties with the difference of the bridging phosphate instead of two monoisopropyl phosphonates.

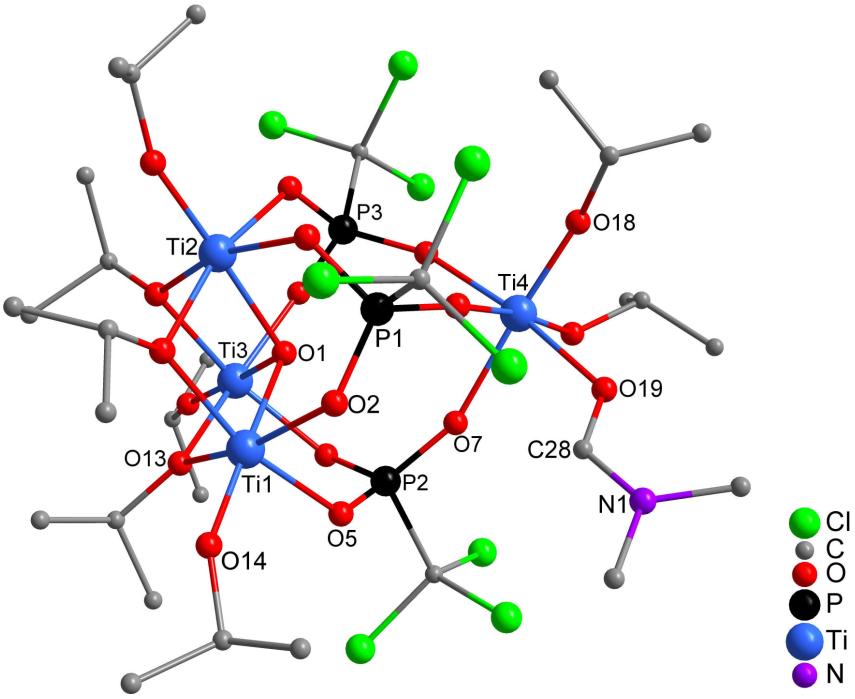


Figure 6.6: *Molecular structure of* $Ti_4(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_5(O_3PCCl_3)_3(DMF)$ (***TiCl3MePP***). *Hydrogen and disordered atoms have been omitted for clarity.*

The most remarkable feature of the structure is the phosphate. While for **TiAllylPP** and **TiEtPP** monoisopropyl esters of the corresponding phosphonate were found, the formation of a phosphate renders octahedral coordination of the central titanium atoms in **TiAllylPP** possible. Taking the overall charge into account, two 2-propanol have to be coordinating to the structure. These can be identified by the increased Ti-O bond length of 215 pm, at the central titanium atoms (Ti4). The Ti-O bond lengths of the other terminal isopropoxo ligands are between 176 and 178 pm. The outcome is the first titanium phosphate phosphonate oxo cluster which has a hydrolysis ratio of 0.25. This cluster is functionalized by four polymerizable vinyl groups and can therefore be used as precursor for class II hybrid materials.

The origin of the phosphate is debatable. Unfortunately no NMR data of the gel are available. However the existence of a phosphate evidences that the phosphorus - carbon bond is broken and the vinyl group is replaced by an oxygen (bound to titanium) or a hydroxide. C-P bond cleavage is known for phosphonates,[322–325] and a similar observation was done with the related compound tetraethyl ethylidenebis(phosphonate).[326] A mechanism cannot be postulated at this stage. Nevertheless vinylphosphonic acid has been proven to be a versatile ligand for titanium oxo clusters. In terms of reactivity the vinyl group is superior to that of the allyl group and therefore it is favorable to further investigate this topic.

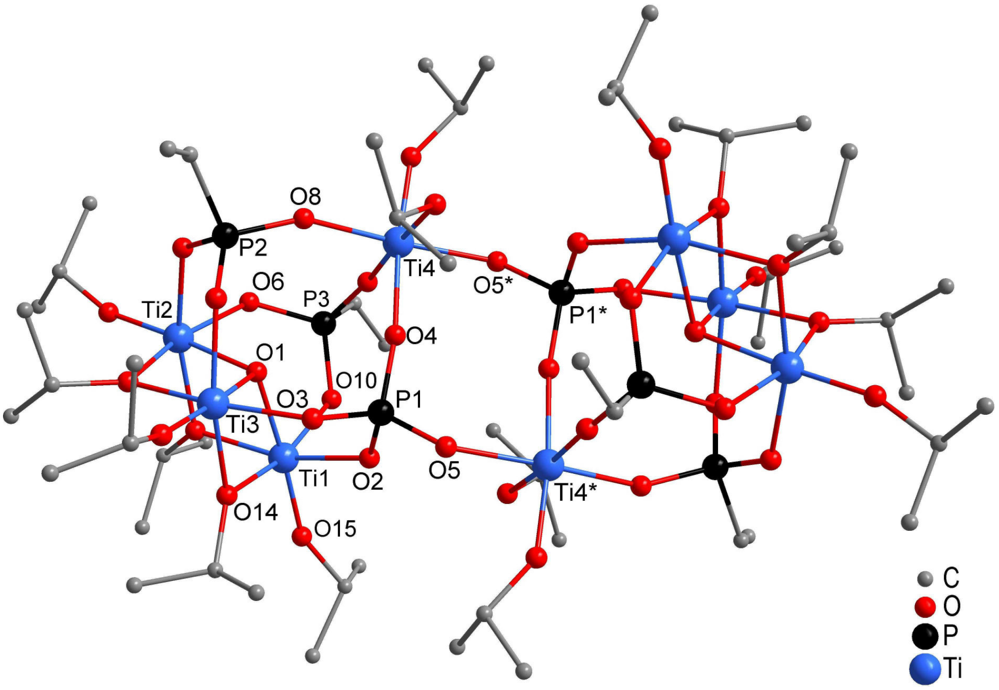


Figure 6.7: *Molecular structure of* $Ti_8(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_6(O^iPr)_8(PO_4)_2(O_3P(vinyl))_4(^iPrOH)_2$ (***TiVinylPP***). *Hydrogen and disordered atoms have been omitted for clarity.*

In summary it can be said that trimethylsilylesters of phosphonic acids are preferable precursors for the preparation of phosphonate-substituted titanium oxo clusters, due their better solubility, as already stated in earlier work.[233,327] This renders the reactions more reliable, and crystals of good quality are obtained easily.

It was proposed that metal alkoxides may react with P-O-$SiMe_3$ in nonhydrolytic condensation processes.[327] The results presented in this work indicate that another possibility must also be considered. Reaction of bis(trimethylsilyl) phosphonates with isopropyl alcohol liberates phosphonic acid, which could substitute part of the O^iPr groups of $Ti(O^iPr)_4$. The latter reaction must also be fast, because otherwise the (sparingly soluble) acids would precipitate. The formation of **TiNpMePP** indicates that introduction of phosphonate ligands is not necessarily coupled to the formation of oxo groups. The latter might be due to esterification of (coordinated or non-coordinated) phosphonic acid as it is the case with carboxylic acids. This possibility is strongly supported by the presence of isopropyl phosphonate ligands in **TiAllylPP** and **TiEtPP**.

Formation of the oxo clusters, or at least their crystallization from solution, is a very slow process, although the clusters can be obtained reproducibly in sufficient yields. The slow crystallization may be due to the good solubility of the clusters in organic solvents. NMR measurements indicate that most, but not all cluster structures are retained in solution.

The synthesis of **TiDMSOAllylPA**, **TiAllylPP** and **TiVinylPP** shows that titanium alkoxo derivatives with polymerizable organic groups can be prepared, where the organic groups are linked to Ti by means of robust phosphonate ligands. Due to the presence of both organic double bonds and Ti-OR groups in **TiAllylPP** this derivative appears suitable for the preparation of hybrid materials, similar to alkoxysilanes $(RO)_3$Si-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, which is $Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_3\text{-}(O_3P{-}R)_3$. This Ti_3O motif is varied in a variety of ways and thus appears to be a rather robust building block.

6.1.2 The first phosphonate-substituted zirconium oxo cluster

Apart from functionalizing titania nanoparticles phosphonic acids are also frequently used to modify zirconium oxide nanoparticles.[59,63,73,328–332] In contrast to titanium clusters, no zirconium oxo cluster functionalized with phosphonate ligands is known.

Therefore, reactions of zirconium alkoxides with phosphonates were also performed. In the reaction of $Zr(O^nBu)_4$ with bis(trimethylsilyl) phenylphosphonate (ratio 2:1) crystals were obtained after several months and removal of the solvent. The outcome, $Zr_6(\mu_3\text{-}O)_2(\mu_2\text{-}O^nBu)_6(O^nBu)_6(O_3P{-}Ph)_4$ (**ZrPhPP**, figure 6.8), represents the first crystallographically characterized phosphonate substituted zirconium oxo cluster.

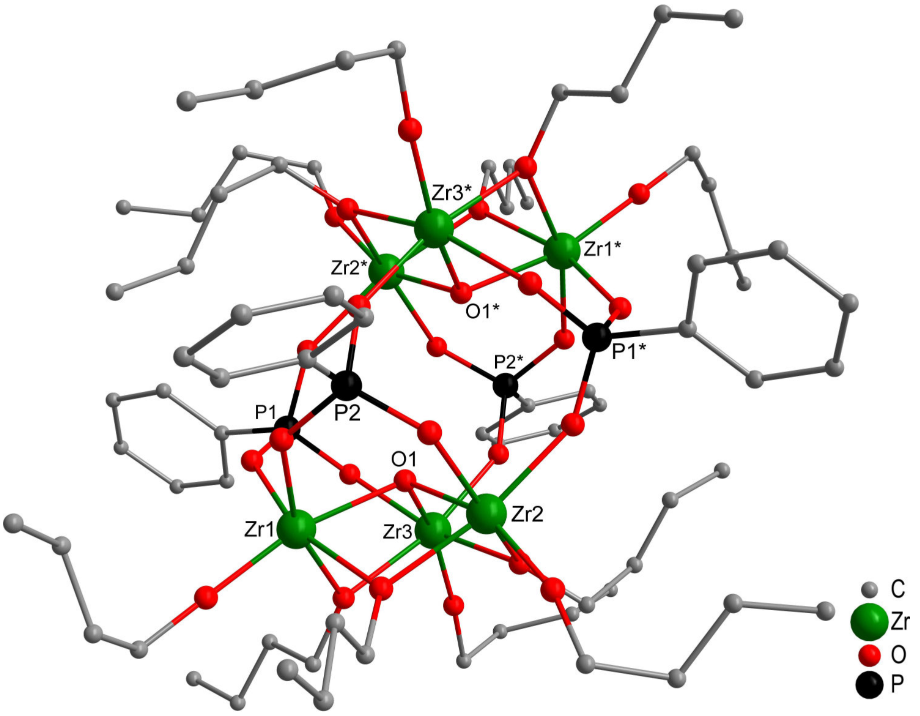


*Figure 6.8: Molecular structure of $Zr_6(\mu_3\text{-}O)_2(\mu_2O^nBu)_6(O^nBu)_6(O_3P{-}Ph)_4$ (**ZrPhPP**). Hydrogen and disordered atoms have been omitted for clarity.*

ZrPhPP consists of six zirconium atoms which are aligned in two Zr_3O triangles. As for the phosphonate-substituted titanium oxo clusters the phosphonate-substituted zirconium oxo cluster is built by two $Zr_3O(\mu_2\text{-}O^nBu)_3(O^nBu)_3$ moieties which are interconnected with each other. In contrast to the titanium counterparts, these two Zr_3O moieties are connected with each other by four (instead of three) phenylphosphonates. These are bridging three zirconium atoms each. One can see in figure 6.9 that two phosphonates are each binding to two zirconium atoms of one Zr_3O triangle and one zirconium atom of the other Zr_3O triangle. These phosphonates are arranged up, up, down, down rather than alternating up and downwards.

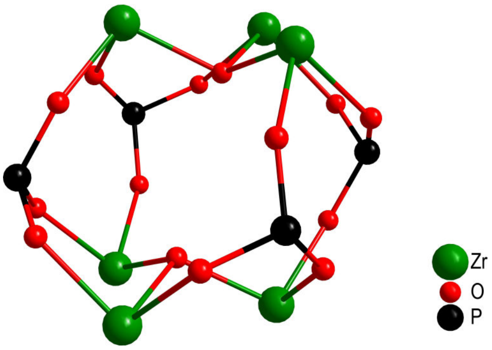


Figure 6.9: *The cluster core* $Zr_6O_2(O_3P)_4$ *of* ***ZrPhPP****, including the phosphonate groups. Hydrogen and carbon atoms as well as ligand oxygen atoms have been omitted for clarity.*

Although all zirconium atoms are octahedrally coordinated, forming the two $Zr_3O(\mu_2\text{-}O^nBu)_3(O^nBu)_3$ moieties, the bridging between the two Zr_3O moieties is different to the corresponding titanium clusters. Instead of three, four phosphonates are bridging and there is no equivalent to the ”capping” titanium atom. The reason for this behavior ought to be the different ionic radius of Zr^{4+} (87 pm) and Ti^{4+}(74.5 pm).[333]

6.1.3 Phosphonate acetate titanium oxo clusters

Carboxylic acids are often used in the preparation of oxo clusters, due to the simple synthesis. In many cases the acids are used as solvent, ligand and *in situ* source of water. While carboxylate-substituted titanium oxo/alkoxo clusters are particularly well investigated,[113,157] only few phosphonate-substituted derivatives are known (see above).[227,228,233,320] Those phosphonate titanium oxo clusters are interesting for hybrid materials because of the strong Ti-O-P bonds, especially if phosphonate ligands with functional organic groups are employed.[69,71,334]

It was observed above that (coordinated or non-coordinated) phosphonic acids generate oxo groups *in situ* by esterification, as in the case of carboxylic acids. But when comparing the reaction of bis(trimethylsilyl) phosphonates with $Ti(OR)_4$ and the reactions of carboxylic acids with $Ti(OR)_4$, it is evident that carboxylic acids lead to higher degrees of condensation, in many cases also in a faster reaction. Carboxylic acids are frequently used in excess, while this is not possible for phosphonates since a molar ratio of 1:1 of $Ti(OR)_4$:phosphonate (or higher phosphonate content) leads to the precipitation of an insoluble amorphous white solid. However, esterification of phosphonic acids appears to be slow and oxo clusters with a low degree of condensation (O:Ti ratio of the Ti/O core[141]) (0.25 or 0.29) were obtained.

Considering this and knowing that acetic acid can be used as *in situ* source of water (see section 5.2 or section 3.1.1), $Ti(O^iPr)_4$ was reacted with mixtures of various bis(trimethylsilyl) esters of phosphonic acids and acetic acid. The basic idea was to increase the proportion of *in situ* generated water taking advantage of the easier ester formation of acetic acid. This should lead to titanium oxo clusters, possibly substituted by both phosphonate and acetate ligands, with an increased degree of condensation.

Reaction of one molar equivalent of bis(trimethylsilyl) ethylphosphonate with two equivalents of acetic acid and four equivalents of $Ti(O^iPr)_4$ led to the centrosymmetric cluster $[Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O^iPr)_4(O^iPr)_6(OAc)_2(O_3PEt)_2]$ (**TiOAcEtPP**, figure 6.10). The degree of condensation of this cluster (0.67) is the highest among phosphonate-substituted titanium oxo clusters known until present. The cluster is also the first mixed carboxylate-phosphonate substituted titanium oxo cluster.

This new cluster type consists of a Ti_6O_4 cluster core with two parallel Ti_3O triangles which are connected by μ_2-oxo and phosphonate bridges. The nearly cubic $Ti_6P_2O_{10}$ core resembles that of polyhedral oligomeric silsesquioxanes (POSS) with a Si_8O_{12} core. The titanium and phosphorus atoms form a distorted parallelepiped (figure 6.11).

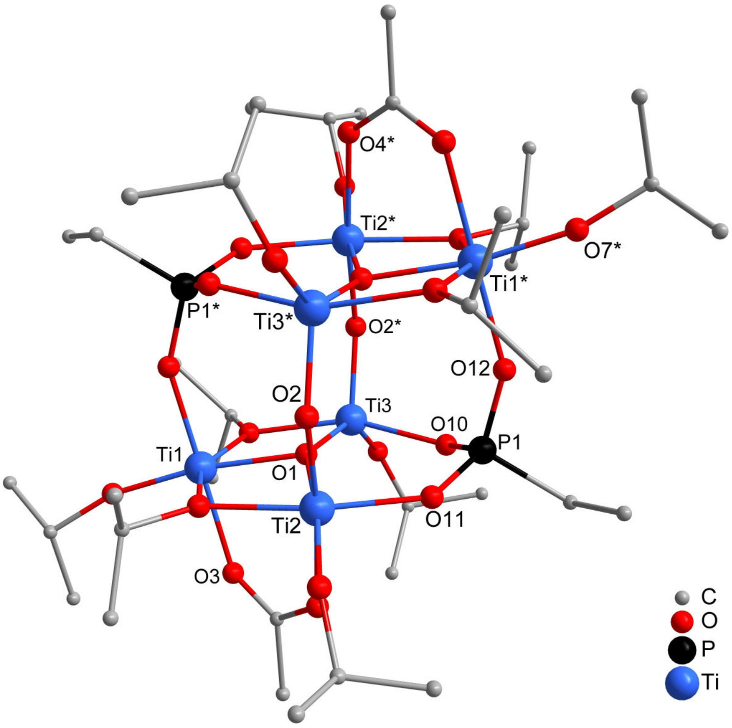


Figure 6.10: *Molecular structure of* $[Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O^iPr)_4(O^iPr)_6(OAc)_2(O_3PEt)_2]$ *(**TiOAcEtPP**). Hydrogen atoms are omitted for clarity.*

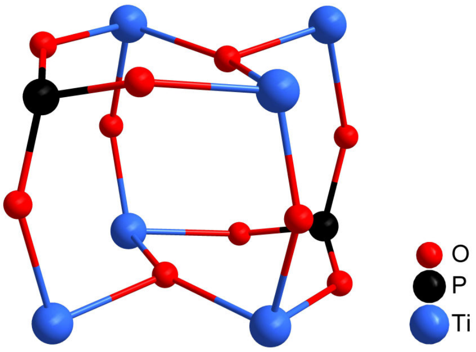
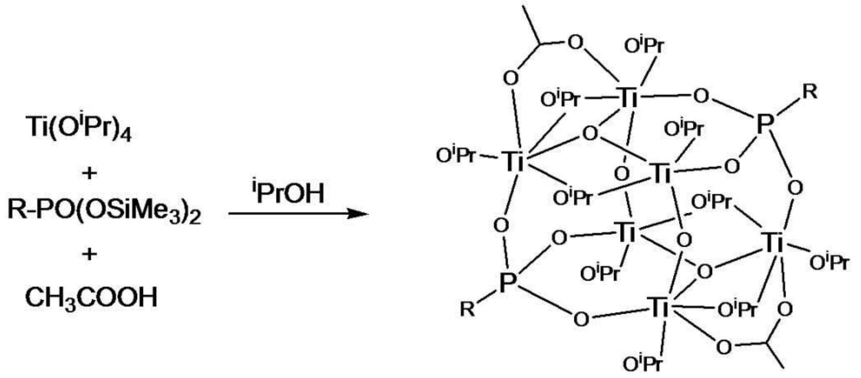


Figure 6.11: *Core structure of the carboxylate-phosphonate-substituted titanium oxo clusters **TiOAcEtPP**, **TiOAcNpMePP**, **TiOAcVinylPP**, **TiOAcAllylPP**, **TiOAcClPrPP**, **TiOAcBzlPP** and **TiOAcBrPrPP**. Isopropoxo and acetate ligands as well as the substituents at the phosphorus atoms were omitted for clarity.*

Contrary to the previously obtained clusters with symmetrical, phosphonate-substituted $Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_3$ units as the basic structural motif,[227,228,233,320] the structure of **TiOAcEtPP** is based on unsymmetrically substituted $Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_2(O^iPr)_3(\mu_2\text{-}OAc)$ units. Two Ti atoms (Ti1 and Ti2) of this unit are bridged by both an O^iPr and an acetate ligand, while Ti1 and Ti3 are singly bridged by a μ_2-O^iPr group. A terminal O^iPr ligand is coordinated to each Ti atom. The two Ti_3O triangles are connected through a μ_2-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, while Ti3 has a distorted trigonal bipyramidal coordination sphere.

The μ_3-oxygen (O1) is not in the center of the triangle because of the asymmetric substitution of the Ti_3O 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 5-coordinate Ti3 are longer than the corresponding distances of Ti1 and Ti2. The core of the structure of **TiOAcEtPP** is comparable to that of $[Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O^iPr)_4(O^iPr)_6(O_3SiFlMe)_2(PhNH_2)_2]$ (Fl = 9-methyl-fluorenyl),[335] although all titanium atoms in the titanasiloxane structure are five-coordinated.

Contrary to reactions of $Ti(O^iPr)_4$ with bis(trimethylsilyl) phosphonates in the absence of acetic acid,[320] a series of isostructural clusters $[Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PR)_2]$ was obtained both with much bulkier groups at the phosphorous atom, such as R = CH_2naphthyl (**TiOAcNpMePP**), and with functional organic groups, such as R = vinyl (**TiOAcVinylPP**), allyl (**TiOAcAllylPP**), or $CH_2CH_2CH_2Cl$ (**TiOAcClPrPP**) (see equation 6.1). This cluster type therefore appears to be rather robust. With one exception (see below) this cluster type was obtained for the RPO_3H:HOAc:$Ti(O^iPr)_4$ ratio of 1:1:2. In some cases this ratio was varied for the preparation of **TiOAcEtPP**, **TiOAcNpMePP**, **TiOAcVinylPP**, **TiOAcAllylPP** and **TiOAcClPrPP** slightly, from 1:1:2 to 1:2:3 and 1:2:4, but the same cluster was always obtained. It is noteworthy that in each case the molar ratio of (RPO_3H + HOAc) did not exceed that of $Ti(O^iPr)_4$.



(6.1)

Table 6.1: *Ratios used in the equation 6.1.*

	R	RPO_3H : HOAc : $Ti(O^iPr)_4$
TiOAcEtPP	Et	1:1:2, 1:2:4
TiOAcNpMePP	CH_2naphthyl	1:1:2
TiOAcVinylPP	Vinyl	1:1:2
TiOAcAllylPP	Allyl	1:1:2, 1:2:3
TiOAcClPrPP	$CH_2CH_2CH_2Cl$	1:1:2, 1:2:4
TiOAcBzlPP	Benzyl	1:2:3
TiOAcBrPrPP	$CH_2CH_2CH_2Br$	1:2:4, 1:2:3

The clusters **TiOAcEtPP**, **TiOAcNpMePP**, **TiOAcVinylPP**, **TiOAcAllylPP** and **TiOAcClPrPP** crystallized from the reaction mixture at room temperature within several weeks. To get the cluster faster and in higher yield, the synthesis of **TiOAcEtPP** and **TiOAcAllylPP**, as examples, were repeated by refluxing the reaction mixture (1:2:3) overnight. The NMR spectra of the resulting powder were the same as that of the sample prepared at room temperature.

The white powder obtained from bis(trimethylsilyl) allylphosphonate and $Ti(O^iPr)_4$, was recrystallized from CH_2Cl_2 resulted in crystals of high quality. The outcome was the same molecular structure of the cluster, but in a different crystal structure (**TiOAcAllylPP2**). Both structures are triclinic, but the unit cell volume of **TiOAcAllylPP2** is about two times the unit cell volume of **TiOAcAllylPP**. The mutual orientation of the molecules is different. While the clusters are aligned parallel in **TiOAcAllylPP** there are two differently orientated molecules in the unit cell of **TiOAcAllylPP2**.

With this faster preparation process, the isostructural clusters **TiOAcBzlPP** ($R = CH_2Ph$) and **TiOAcBrPrPP** ($R = CH_2CH_2CH_2Br$) were additionally obtained. Cluster **TiOAcBrPrPP** was only obtained for RPO_3H:HOAc:$Ti(O^iPr)_4$ ratios of 1:2:4 or 1:2:3; for a 1:1:2 ratio another cluster was surprisingly obtained (see below for cluster **TiOAcBrPrPP2**).

Since phosphonic acids are often more easily accessible than their bis(trimethylsilyl)esters, an experiment was conducted using phenylphosphonic acid, acetic acid and $Ti(O^iPr)_4$ in a ratio of 1:2:3. This acid was also used in the first titanium phosphonate oxo cluster experiment conducted by Guerrero *et al.*[227] $Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PR)_2$ (**TiOAcPhPA**) was indeed obtained after refluxing for 16 hours and subsequent recrystallization from CH_2Cl_2.

The clusters **TiOAcEtPP**, **TiOAcNpMePP**, **TiOAcVinylPP**, **TiOAcAllylPP**, **TiOAcClPrPP**, **TiOAcBzlPP** and **TiOAcBrPrPP** are well soluble in organic solvents. Their NMR spectra are very similar, and they correspond to the solid-state structures. This shows that the clusters are stable in solution and are not in equilibrium with other structures. The ^1H NMR data of **TiOAcEtPP**, **TiOAcNpMePP**, **TiOAcVinylPP**, **TiOAcAllylPP**,

TiOAcClPrPP, **TiOAcBzlPP** and **TiOAcBrPrPP** show five doublets for the CH_3 of the O^iPr ligands, although the signals of two bridging O^iPr ligands are overlapping at about 1.7 ppm. The other three doublets are partly overlapping at 1.3-1.5 ppm. For the CH group of the O^iPr ligands three different multiplets were found, in few cases two of them were partly overlapping. 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 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 $Ti(O^iPr)_4$ in a 1:1:2 ratio, another cluster type was only obtained in one case. Reaction of bis(trimethylsilyl) 3-bromopropylphosphonate at room temperature resulted reproducibly in the cluster $[Ti_5(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_4(O^iPr)_7(OAc)(O_3PCH_2CH_2CH_2Br)_3]$ (**TiOAcBrPrPP2**), the structure of which (figure 6.12) is related to that of the previously found clusters $[Ti_4(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_5(O_3PR)_3L]$ (L = neutral ligand).[227,228,233,320] The latter consist of a symmetrical $Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_3$ unit to which a $Ti(O^iPr)_2L$ 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.

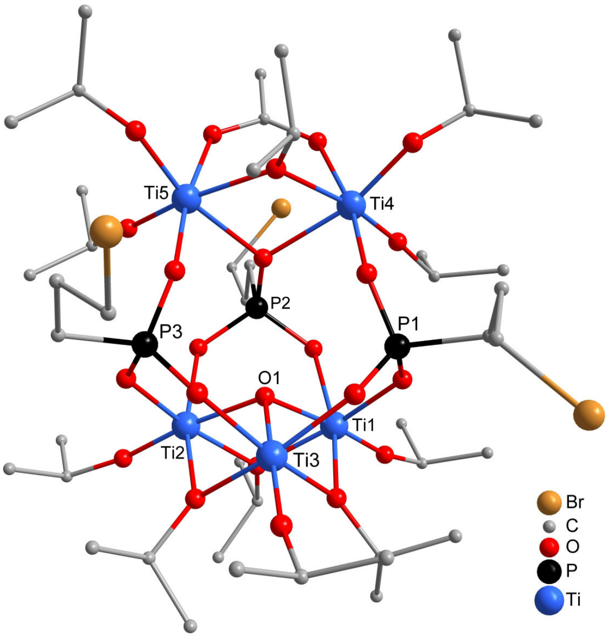


*Figure 6.12: Molecular structure of $[Ti_5(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_4(O^iPr)_7(OAc)(O_3PCH_2CH_2CH_2Br)_3]$ (**TiOAcBrPrPP2**). Hydrogen atoms are omitted for clarity.*

In **TiOAcBrPrPP2**, the capping $Ti(O^iPr)_2L$ group is replaced by a $Ti_2(\mu_2\text{-}O^iPr)(O^iPr)_4(\mu_2\text{-}OAc)$ moiety. Two of the phosphonate ligands are coordinated to only one titanium atom of the Ti2 unit, while 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][74]) while the other two phosphonate ligands, as well as those in the cluster **TiOAcEtPP**, **TiOAcNpMePP**, **TiOAcVinylPP**, **TiOAcAllylPP**, **TiOAcClPrPP**, **TiOAcBzlPP** and **TiOAcBrPrPP**, have a 3.111 binding mode. The $Ti_2(\mu_2\text{-}O^iPr)(O^iPr)_4(\mu_2\text{-}OAc)$ moiety in **TiOAcBrPrPP2** is structurally related to $Ti_2(OR)_6(\mu_2\text{-}OOCR')_2$.[161,185]

The solution ^{1}H NMR spectrum showed several overlapping signals in the region of 1.2-2.0 ppm, which can be assigned to the CH_3 groups of O^iPr as well as to the PCH_2 group. The CH signals of O^iPr appear at 4.6-5.4 ppm as five multiplets. The two well separated triplets for the CH_2Br group at 3.52 and 3.71 ppm have an intensity ratio of 1:2. The same is true for the two resonances at 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 data confirm the ^{1}H NMR 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 group; the signals of the P-CH_2 groups could not be unequivocally assigned.

Another titanium oxo cluster with a nuclearity of 5 was obtained from the reaction of bis(trimethylsilyl) 3,5-dimethylphenylphosphonate with $Ti(O^iPr)_4$ and acetic acid (1:2:2). $[Ti_5(\mu_3\text{-}O)_2\text{-}(\mu_2\text{-}O)(\mu_2\text{-}O^iPr)_2(O^iPr)_4(OAc)_4(O_3P\text{−}xylyl)_2]$ (**TiOAcXylPP**, figure 6.13) consists of five octahedrally coordinated titanium atoms which form two corner-sharing Ti_3O triangles (Ti1, Ti2, Ti3 and Ti3, Ti4, Ti5), tilted by 52.2 °C. The cluster has a non-crystallographic C_2 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 $Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)(O^iPr)_2(\mu_2\text{-}OAc)_2$ and can be derived from the basic structural motif $Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_3$ in the previously obtained acetate-free clusters[227,228,233,320] and in **TiOAcBrPrPP2**, and the mono-substituted unit $Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_2(O^iPr)_3(\mu_2\text{-}OAc)$ in **TiOAcEtPP**. 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 by that of just one phosphonate ligand.

Cluster **TiOAcXylPP** has another degree of condensation (0.6) and a higher proportion of acetate ligands than the Ti_5 cluster **TiOAcBrPrPP2** or the Ti_6 clusters **TiOAcEtPP**, **TiOAcNpMePP**, **TiOAcVinylPP**, **TiOAcAllylPP**, **TiOAcClPrPP**, **TiOAcBzlPP** and **TiOAcBrPrPP**. 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 reacted with $Ti(O^iPr)_4$, the steric bulk of the phosphonate substituents had a significant influence on the cluster structure.[320]

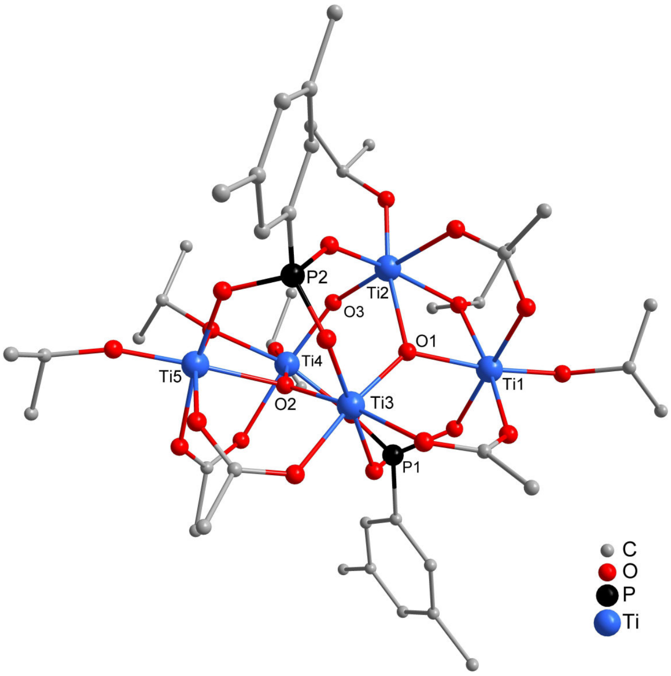


Figure 6.13: *Molecular structure of* $Ti_5(\mu_3\text{- }O)_2(\mu_2\text{- }O)(\mu_2\text{- }O^iPr)_2(O^iPr)_4(\mu_2\text{- }OAc)_4(\mu_3\text{- }O_3P{-}xylyl)_2$ *(**TiOAcXylPP**). Hydrogen atoms are omitted for clarity.*

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 showed three singlets for the xylyl CH groups at 6.91, 8.03 and 8.08 ppm and three multiplets for the isopropoxo CH groups at 5.07, 5.22 and 5.66 ppm. One singlet at 2.18 ppm was assigned to the CH_3 groups of the xylyl moieties and two singlets at 1.95 and 1.98 ppm to the two acetate ligands. These signals agree in shift, number and intensity with the solid state structure.

Five doublets were found for the CH_3 groups of the O^iPr ligands. Their total intensity corresponds to the expected value, but only three doublets were expected because of the C_2 symmetry. Two doublets at 1.90 and 1.91 ppm are overlapping with a shift difference of only 0.01 ppm and can be assigned to the two bridging O^iPr 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 1.46 and 1.51 ppm. The other two terminal O^iPr ligands show a doublet at 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 the sterically hindered rotation of the O^iPr groups.

The experiments conducted in this section show that addition of acetic acid to the 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 to 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 with a mixed ligand sphere containing carboxylate, phosphonate and alkoxo ligands.

While 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,[113,157] reaction with various phosphonates and acetic acid led to the same cluster type $[Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PR)_2]$ (**TiOAcEtPP**, **TiOAcNpMePP**, **TiOAcVinylPP**, **TiOAcAllylPP**, **TiOAcClPrPP**, **TiOAcBzlPP** and **TiOAcBrPrPP**) 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. Since phosphonate ligands with functional organic groups are easily introduced, reactions of these groups will be possible, *e.g.* polymerization, thiol-en or addition reactions, by which chains of clusters and hybrid materials with anisotropic structures could be generated.

6.1.4 Reaction of titanium alkoxides with phosphonates under the presence of water

Reacting bis(trimethylsilyl)esters of different phosphonic acids with titanium alkoxides resulted in the formation of titanium oxo clusters with a relatively low degree of condensation (0.25-0.28). Condensation can easily be achieved by the addition of water to the reaction mixture, therefore a reaction using bis(trimethylsilyl) phenylphosphonate, $Ti(O^iPr)_4$ and water in ratio 2:4:1 was performed, leading to $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O^iPr)_4(O^iPr)_6(\mu_3\text{-}O_3P{-}Ph)_2(\mu_2\text{-}O_2(O^iPr)P{-}Ph)_2$ (**TiOPhPP**, figure 6.14). The addition of water led indeed to a higher degree of condensation and a different cluster core. **TiOPhPP** is isostructural to the different $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2\text{-}(\mu_2\text{-}O^iPr)_4(O^iPr)_6(\mu_3\text{-}O_3P{-}R)_2(\mu_2\text{-}OAc)_2$ clusters shown in the last section (section 6.1.3).

TiOPhPP is very similar to **TiOAcEtPP** and will not be described here (see section 6.1.3). The differences to **TiOAcEtPP** are the organic substituent on the phosphorous atom and that a monoisopropyl phenylphosphonate is coordinating instead of the acetate. This monoisopropyl ester is coordinating in the same manner as the acetate. Although water was added, the added water would not be enough to obtain **TiOPhPP** in quantitative yield without another source of water. It seems that part of the oxo bridges are obtained from esterification of the phosphonate, as it has been seen for **TiAllylPP**. It shows that monoesters of phenylphosphonates exhibit a similar coordination behavior as carboxylates. Furthermore it shows that steric hindrance in the position of the acetate does not play a crucial role in the formation of the cluster.

The formation of the cluster in the presence of water proves in a different way that the acetic acid acts as water source in the reactions of section 6.1.3. The yield of the reaction was very low, so no NMR data have been obtained.

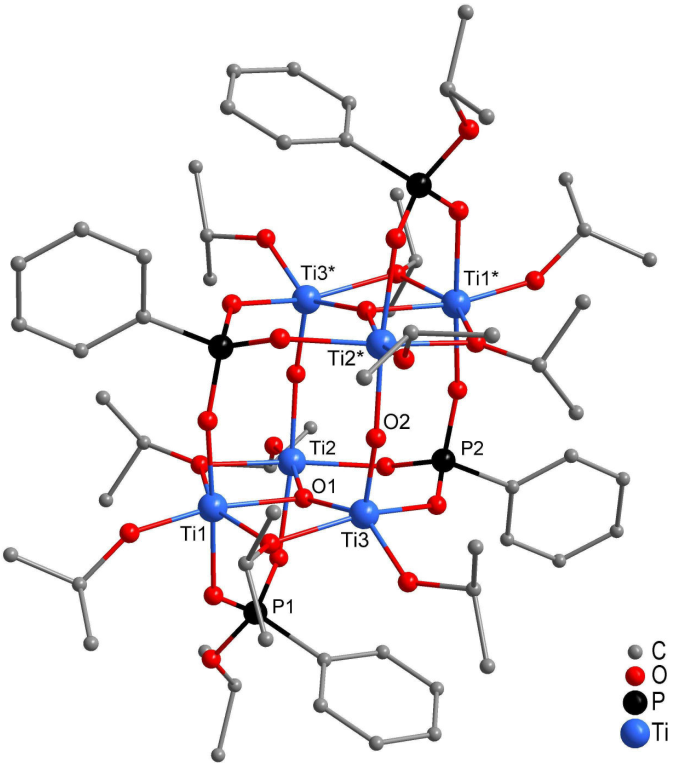


Figure 6.14: *Molecular structure of* $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O^iPr)_4(O^iPr)_6(\mu_3\text{-}O_3P{-}C_6H_5)_2\text{-}(\mu_2\text{-}O_2P(O^iPr)C_6H_5)_2$ *(**TiOPhPP**). Hydrogen atoms are omitted for clarity.*

The same unit cell as for **TiOPhPP** was found for crystals of the reaction of bis(trimethylsilyl) phenylphosphonate, bis(trimethylsilyl) allylphosphonate and $Ti(O^iPr)_4$(ratio 1:1:4). The structure was obtained without the direct addition of water. Since no other initial ratio of phosphonate to titanium isopropoxide was used, it is supposed that moisture was diffusing into the flask during the long reaction time. For the reaction of bis(trimethylsilyl) phenylphosphonate with $Ti(O^iPr)_4$ (ratio 1:2) no crystals were obtained. Therefore it seems possible that phenylphosphonic acid reacts differently and therefore (and not because of moisture) this structure was obtained upon reaction with $Ti(O^iPr)_4$.

The structure of **TiOPhPP** was obtained two times, this proves that the conclusion above (section 6.1.3) was correct and the $[Ti_6O_4(O^iPr)_{10}(OOR)_2(O_3PR)_2]$ clusters represent a rather robust structural entity. It also indicates (although not yet proven) that different carboxylic acids can be used in the formation of this Ti_6O_4 cluster core.

6.1.5 Phosphonate methacrylate titanium oxo clusters

In the last section (section 6.1.4) it was shown that the Ti_6O_4 cluster core can be obtained with monoisopropyl phosphonate coordinating instead of acetate, which was found to be a well reproducible reaction (section 6.1.3). The obvious question was if other carboxylic acids can be used in the same way as acetic acid. Methacrylic acid (McOH) is one of the most used carboxylic acids in oxo cluster chemistry due to its small rigid size and the polymerizable group (for class II hybrid materials). Several different crystal structures using different titanium alkoxides and methacrylic acid were so far reported[3,173,190,239] and some can be found in section 3.3. Therefore methacrylic acid is a versatile ligand for oxo clusters.

Methacrylic acid could produce water as well through *in situ* ester formation, but would additionally provide reactive ligands in the obtained clusters.[2,336] Especially the combination of 3-bromopropylphosphonate and methacrylate ligands in one cluster appeared attractive, because the presence of two different functionalities could allow two different networks to be linked.

When bis(trimethylsilyl) ethylphosphonate was reacted with methacrylic acid (McOH) and $Ti(O^iPr)_4$ in a 1:1:3 molar ratio the cluster $Ti_5(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_4(O^iPr)_7(OMc)(O_3PEt)_3$ (**TiOMcEtPP**, figure 6.15) was formed. This cluster type was previously obtained, as an exception from the above mentioned general outcome of the reactions with acetic acid, when bis(trimethylsilyl) 3-bromopropylphosphonate was reacted with acetic acid and $Ti(O^iPr)_4$ in a 1:1:2 ratio at room temperature. The asymmetric unit of crystalline **TiOMcEtPP** contains two independent molecules with very similar bond distances and angles.

The structure of **TiOMcEtPP** is related to that of the clusters $[Ti_4(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_5\text{-}(O_3PR)_3L]$ (L = neutral ligand)[227,228,233,320], which consist of a symmetrical $Ti_3(\mu_3\text{-}O)\text{-}(\mu_2\text{-}O^iPr)_3(O^iPr)_3$ unit to which a $Ti(O^iPr)_2L$ 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 **TiOMcEtPP**, the capping $Ti(O^iPr)_2L$ group is replaced by a $Ti_2(\mu_2\text{-}O^iPr)(O^iPr)_4(\mu_2\text{-}OMc)$ moiety. Two of the phosphonate ligands are coordinated to only one Ti atom of the Ti_2 unit and have a 3.111[74] binding mode, while the third bridges both of them and has a binding mode of 4.211.

NMR spectra of the solid residue of **TiOMcEtPP** in C_6D_6 showed numerous signals. In the ^{31}P NMR spectrum, for example, eight resonances were observed, while two signals are expected if the solid state structure of **TiOMcEtPP** was retained in solution. The ^1H NMR and ^{13}C NMR spectra also showed a too large number of signals as well. Therefore it is assumed that a mixture of different compounds was initially obtained and only **TiOMcEtPP** crystallized.

When a 1:2:3 mixture of bis(trimethylsilyl) allylphosphonate, methacrylic acid and $Ti(O^iPr)_4$ was heated to reflux, the complex $Ti_{10}(\mu_2\text{-}O^iPr)_2(O^iPr)_{14}(O_3PCH_2CH{=}CH_2)_{10}(OMc)_4$ (**TiOMcAllylPP**, figure 6.16) was obtained instead after crystallization from CH_2Cl_2. The outcome of this reaction contrasts that with that of acetic acid which resulted in the formation of $Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2CH{=}CH_2)_2$[315].

The structure of **TiOMcAllylPP** consists of two $Ti_5(\mu_2\text{-}O^iPr)(O^iPr)_7(O_3P{-}allyl)_5(OMc)_2$ units, which are bridged by two (3.111) phosphonate ligands. The Ti_5 units are composed of

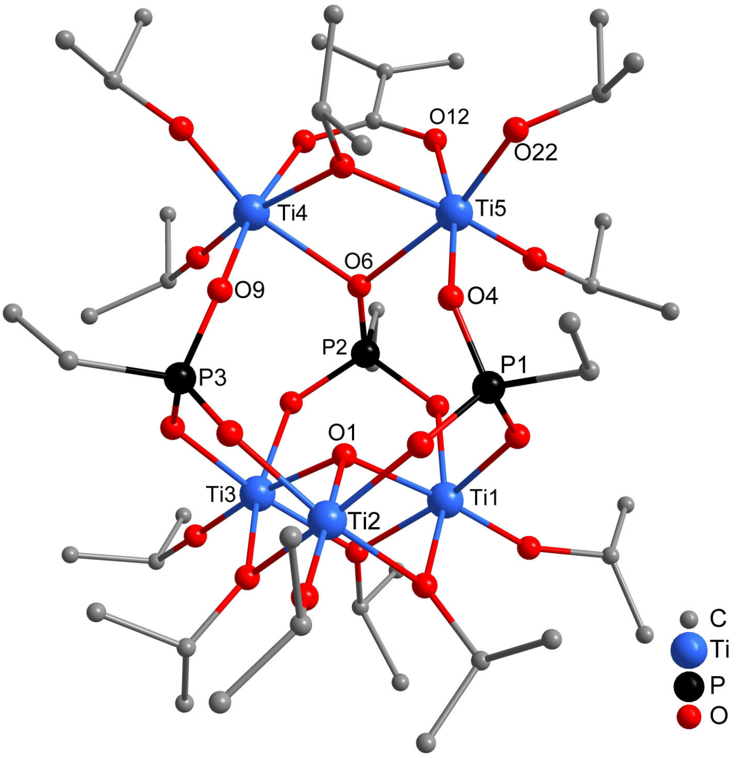


Figure 6.15: *Molecular structure of* $Ti_5(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_4(O^iPr)_7(OMc)(O_3PEt)_3$ *(**TiOMcEtPP**). Hydrogen atoms are omitted for clarity.*

methacrylate-bridged dimers $Ti_2(\mu_2\text{-}O^iPr)(O^iPr)_3(OMc)$ [Ti2, Ti5] and $Ti_2(O^iPr)_3(OMc)$ [Ti3, Ti4], respectively, which are connected through phosphonate ligands among each other as well as to the fifth titanium atom [Ti1]. Each of the octahedrally coordinated titanium atoms is at least bound to two different phosphonate ligands; Ti1 is coordinated by five different oxygen atoms of phosphonate ligands and one isopropoxo ligand. The complexity of the structure of **TiOMcAllylPP** is also reflected in the different binding modes of the phosphonate ligands, of which six are 3.111, two are 3.211 and two are 4.211 (see figure 6.17).

Reaction of $Ti(O^iPr)_4$ with various bis(trimethylsilyl) phosphonates resulted in oxo clusters with a relatively low degree of condensation (defined O:Ti ratio of the Ti/O core[141]) of 0.25 or 0.29[320]. This was attributed to the slow esterification of phosphonic acids (compared to carboxylic acids in related reactions[113]). The condensation degree was increased to 0.67, when acetic acid was added to the precursor mixture[315].

Replacement of acetic acid by methacrylic acid surprisingly had the reverse effect, i.e. the condensation degree was lower than in the absence of carboxylic acid. The condensation degree was 0.2 in **TiOMcEtPP**, and **TiOMcAllylPP** contained no oxo groups at all. There is no straightforward approach to an explanation because of the complexity of such reactions. The first step in such reactions is the substitution of an OR ligand of the metal alkoxide with an carboxylate or

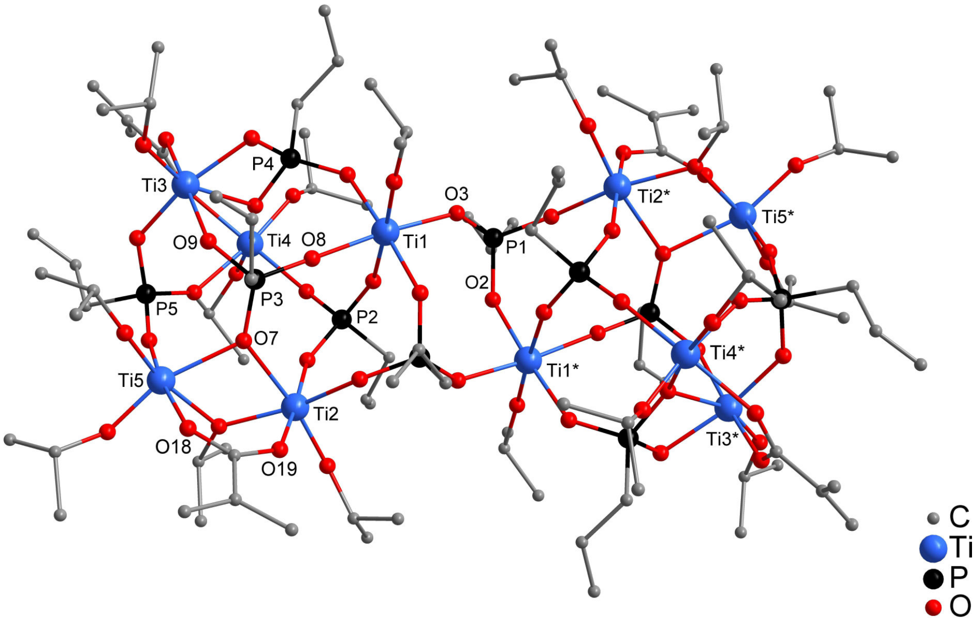


Figure 6.16: *Molecular structure of* $Ti_{10}(\mu_2\text{-}O^iPr)_2(O^iPr)_{14}(O_3PCH_2CH{=}CH_2)_{10}(OMc)_4$ *(**TiOMcAllylPP**). Hydrogen atoms are omitted for clarity.*

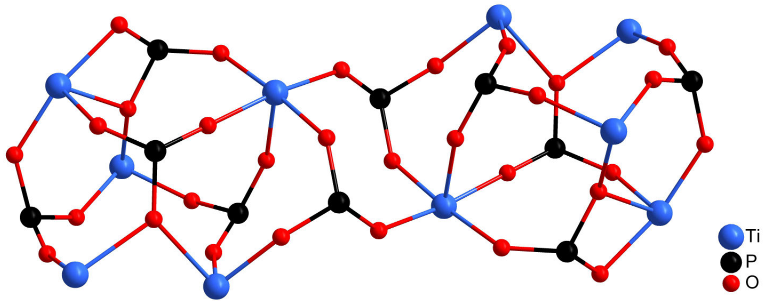


Figure 6.17: *Core of **TiOMcAllylPP** exhibiting the different binding modes of the phosphonates. Hydrogen and carbon atoms as well as methacrylates and isopropoxo ligands are omitted for clarity.*

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

The most likely possibility is that multiple substitution of $\mathrm{Ti(O^iPr)_4}$ by phosphonic and/or methacrylic acid results in derivatives which, for steric or electronic reasons, are less prone to hydrolysis and condensation reactions. It must be pointed out that **TiOMcAllylPP** was only obtained in low yields after recrystallization. Therefore it cannot be excluded that **TiOMcAllylPP** is a by-product which had the highest tendency for crystallization. Similarly, NMR spectra of the solid part of **TiOMcEtPP** showed a mixture of compounds.

Notwithstanding the results show that methacrylate ligands, i.e. carboxylate ligands with polymerizable groups, can be incorporated in phosphonate-substituted titanium oxo clusters. This widens the preparative options for cluster compounds with both reactive and non-reactive ligands.

Chapter 7

Summary

7.1 The reactivity of carboxylic acids

In the first part of this work, carboxylate-substituted titanium and zirconium oxo clusters were synthesized (an overview of obtained structures is given in table 7.1). The two new titanium oxo clusters, **TiCycloBu** and **TiBenzCl**, were obtained by the reaction of titanium isopropoxide with an excess of the corresponding carboxylic acid. The outcome of the reaction of titanium isopropoxide with triphenylacetic acid and acetic acid was **TiTPA**. This showed that a specific ligand arrangement cannot be obtained by mixing two differently sterically demanding carboxylic acids, but it was observed that acetic acid acts as *in situ* source of water. Additional reactions were done with adamantylcarboxylic acid, leading to **TiAda** and **ZrAda**. In the structure of **TiAda** a chelating carboxylate ligand was observed which is unusual in titanium oxo clusters.

Reacting equimolar portions of carboxylic acid with titanium isopropoxide led to the formation of a dimeric complex (**TiBenzMeCl**). The same reaction with zirconium butoxide resulted in the formation of an oxo cluster with a nuclearity of 10, **ZrBenzMeCl**. This cluster is interesting since only few zirconium clusters with a nuclearity higher than 6 are known. Therefore a similar reaction was performed with pentinoic acid and indeed a zirconium oxo cluster with a nuclearity of 9 was obtained, **ZrPentin**. This cluster was obtained in the presence of an equimolar portion of carboxylic acid, but water was added deliberately.

Reaction of titanium isopropoxide with 4-(imidazol-1-yl)-butyric acid did not lead to the formation of an oxo cluster but instead to a coordination polymer, **TiBuImid**. This coordination polymer is built by mononuclear titanium units and exhibits a chelating carboxylate.

The reaction system of methacrylic acid and titanium isopropoxide in different ratios was elucidated. With an increase of the portion of methacrylic acid, a decrease in the poisoning ratio and an increase of the degree of condensation was observed. The obtained clusters, **TiOMc1**, **TiOMc2**, **TiOMc6** and **TiOMc8**, show different structural features, thus a stepwise building of the larger clusters was not observed.

Table 7.1: *Carboxylate substituted titanium and zirconium oxo clusters and complexes presented in this work.*

Cluster	Formula	O/M	p
TiCycloBu	$Ti_6O_6(O^iPr)_2(OOCC_4H_7)_{10}$	1	0.056
TiBenzCl	$Ti_4O_2(O^iPr)_6(OOC{-}C_6H_4{-}Cl)_6)$	0.5	0.25
TiTPA	$Ti_3O_2(O^iPr)_3(OOCCPh_3)_5$	0.67	0.167
TiAda	$Ti_3O(O^iPr)_6(OOC{-}\text{adamantyl})_4$	0.33	0.389
ZrAda	$Zr_6O_4(OH)_4(OOC{-}\text{adamantyl})_{12}$	0.67	0.125
TiBenzMeCl	$Ti_2(O^iPr)_6(OOC{-}C_6H_4{-}CH_2Cl)_2(^iPrOH)$	0	0.5
ZrBenzMeCl	$Zr_{10}O_8(O^nBu)_{16}(OOC{-}C_6H_4{-}CH_2Cl)_8$	0.8	0.176
ZrPentin	$Zr_9O_6(O^nBu)_{18}(OOC{-}C \equiv C{-}CH_2CH_3)_6$	0.67	0.133
TiBuImid	$[Ti(O^iPr)_3(OOCCH_2CH_2CH_2C_3N_2H_3)]_n$	0	1
TiOMc1	$Ti_2(O^iPr)_6(OMc)_2{}^iPrOH$	0	0.5
TiOMc2	$Ti_6O_4(O^iPr)_8(OMc)_8$	0.67	0.167
TiOMc6	$Ti_9O_8(O^iPr)_4(OMc)_{16}$	0.89	0.074
TiOMc8	$Ti_8O_8(OMc)_{16}$	1	0

7.2 The reactivity of anhydrides

The reactions of titanium isopropoxide with cyclic anhydrides led to the formation of different compounds (an overview of the obtained structures is given in table 7.2). The addition of phthalic anhydride to titanium isopropoxide led to the formation of **Tiphthal1**, a dimeric complex with monoisopropylester units, while the same reaction in presence of acetic acid led to the formation of **Tiphthal2**, a hexanuclear titanium oxo cluster. As observed earlier, this proves the role of acetic acid as *in situ* source of water.

A similar reaction was conducted with maleic anhydride and titanium isopropoxide, without addition of acetic acid. This led to the formation of a titanium oxo cluster, **TiMal**, which has two coordinating maleates but no coordinating monoester.

Table 7.2: *Titanium oxo clusters and complexes obtained with anhydrides as starting compounds.*

Cluster	Formula	O/Ti	p
TiPhthal1	$Ti_2(O^iPr)_6(OOC{-}C_6H_4{-}COO^iPr)_2(^iPrOH)$	0	0.5
TiPhthal2	$Ti_6O_6(O^iPr)_6(OOC{-}C_6H_4{-}COO^iPr)_6$	1	0.167
TiMal	$Ti_6O_3(O^iPr)_{14}(OOC{-}CH{=}CH{-}COO)_2$	0.5	0.278

7.3 The reactivity of calix[4]arenes and oximes

It was shown that ^{t}butyl-calix[4]arene and cyclohexyldioxime are viable ligands for oxo clusters. An overview of the obtained clusters is given in table 7.3. The reaction of titanium butoxide with ^{t}butyl-calix[4]arene ($Calix^{tBu}(OH)_4$) led to the formation of a dimeric complex, **TiCalix**. The reaction with zirconium butoxide on the other hand led to a trimeric complex, **Zr3Calix**. When the same reaction was conducted in the presence of water or acetic acid an oxo cluster was obtained, **Zr4Calix2**. Two $Calix^{tBu}O_4$ ligands are coordinating to this tetranuclear cluster, which shows disordered central metal atom.

The reaction of 1,2-cyclohexanedioxime with zirconium butoxide in the presence of acetic acid led to the formation of a zirconium oxo cluster with a nuclearity of 10, **ZrHexOx**. In this reaction, acetic acid acted as *in situ* water source, but also to provide ligands, thus six acetates are found in the structure.

Table 7.3: *Calix[4]arene and oximate substituted titanium and zirconium oxo clusters and complexes presented in this work.*

Cluster	Formula	O/M	p
Zr3Calix	$Zr_3(O^nBu)_8(Calix^{tBu}O_4)$	0	0.211
TiCalix	$Ti_2(O^nBu)_2(Calix^{tBu}O_3(OH))_2$	0	0.667
Zr4Calix2	$Zr_4O(O^nBu)_6(Calix^{tBu}O_4)_2(^nBuOH)_2$	0.25	0.231
ZrHexOx	$Zr_{10}O_4(O^nBu)_{18}((ON)_2cyclohexan)_4(OAc)_6$	0.4	0.171

7.4 The reactivity of phosphonic acids and their derivatives

A large part of this work deals with the reactivity of phosphonic acids and their bis(trimethylsilyl)-esters towards oxo cluster formation. An overview of the obtained structures is given in table 7.4. Differently substituted oxo clusters built by two Ti_4O units were obtained by the reaction of different bis(trimethylsilyl) phosphonates with titanium isopropoxide. Two different modes of this "dimerization" of the Ti_4O units were found: a) with two bridging monoisopropylester b) with a shared titanium atom. In the presence of a neutral ligand, however, clusters consisting of one Ti_4O unit were obtained. The reaction of vinylphosphonate with titanium isopropoxide led to the formation of the cluster **TiVinylPP** with phosphate ligands in each Ti_4O unit. In the reactions with zirconium alkoxides crystals were only obtained for a phenylphosphonate derivative, **ZrPhPP**. The structure is built up by two $Zr_3O(OR)_6$ units which have also been found in the titanium derivatives.

Similar reactions were conducted in the presence of acetic acid since it was observed earlier that acetic acid often acts as *in situ* source of water. The reaction of different phosphonates, titanium isopropoxide and acetic acid led to the formation of a Ti_6O_4 cluster with two phosphonate and two acetate ligands. The same reaction with xylylphosphonate or 3-bromopropylphosphonate, on the other, resulted in the formation of different oxo cluster species.

For incorporation of a polymerizeable double bond into the clusters, further reactions were performed using methacrylic acid instead of acetic acid. This did not lead to the formation of the $\mathrm{Ti_6O_4}$ cluster but a $\mathrm{Ti_5O}$ cluster, **TiOMcEtPP**, or a phosphonate substituted complex with a nuclearity of 10, **TiOMcAllylPP**.

Table 7.4: Phosphonate substituted titanium and zirconium oxo clusters and complexes presented in this work.

Cluster	Formula	O/M	*p*
TiDMSOAllylPA	$\mathrm{Ti_4O(O^iPr)_8(O_3P{-}allyl)_3(DMSO)}$	0.25	0.25
TiAllylPP	$\mathrm{Ti_8O_2(O^iPr)_{14}(O_3P{-}allyl)_6(O_2P(O^iPr)allyl)_2}$	0.25	0.167
TiAllylPP2	$\mathrm{Ti_8O_2(O^iPr)_{14}(O_3P{-}allyl)_6(O_2P(O^iPr)allyl)_2}$	0.25	0.167
TiEtPP	$\mathrm{Ti_8O_2(O^iPr)_{14}(O_3P{-}ethyl)_6(O_2P(O^iPr)ethyl)_2}$	0.25	0.167
TiClPrPP	$\mathrm{Ti_7O_2(O^iPr)_{12}(O_3PCH_2CH_2CH_2Cl)_6}$	0.29	0.143
TiBzlPP	$\mathrm{Ti_7O_2(O^iPr)_{12}(O_3P{-}CH_2{-}C_6H_5)_6}$	0.29	0.143
TiBrPrPP	$\mathrm{Ti_7O_2(O^iPr)_{12}(O_3PCH_2CH_2CH_2Br)_6}$	0.29	0.143
TiXylPP	$\mathrm{Ti_4O(O^iPr)_8(O_3P{-}xyl)_3(^iPrOH)}$	0.25	0.25
TiNpMePP	$\mathrm{Ti_4(O^iPr)_8(O_3PMeNp)_4(^iPrOH)_2}$	0	0.375
TiCl3MePP	$\mathrm{Ti_4O(O^iPr)_8(O_3PCCl_3)_3(DMF)}$	0.25	0.25
TiVinylPP	$\mathrm{Ti_8O_2(O^iPr)_{14}(PO_4)_2(O_3P(vinyl))_4(^iPrOH)_2}$	0.25	0.208
ZrPhPP	$\mathrm{Zr_6O_2(O^nBu)_{12}(O_3P{-}Ph)_4}$	0.33	0.167
TiOAcEtPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PEt)_2}$	0.67	0.176
TiOAcNpMePP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2naphthyl)_2}$	0.67	0.176
TiOAcVinylPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3P{-}vinyl)_2}$	0.67	0.176
TiOAcAllylPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3P{-}allyl)_2}$	0.67	0.176
TiOAcClPrPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2CH_2CH_2Cl)_2}$	0.67	0.176
TiOAcBzlPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2C_6H_5)_2}$	0.67	0.176
TiOAcBrPrPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2CH_2CH_2Br)_2}$	0.67	0.176
TiOAcPhPA	$\mathrm{Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3P{-}C_6H_5)_2}$	0.67	0.176
TiOAcBrPrPP2	$\mathrm{Ti_5O(O^iPr)_{11}(OAc)(O_3PCH_2CH_2CH_2Br)_3}$	0.2	0.233
TiOAcXylPP	$\mathrm{Ti_5O_3(O^iPr)_6(OAc)_4(O_3P{-}xylyl)_2}$	0.6	0.133
TiOPhPP	$\mathrm{Ti_6O_4(O^iPr)_{10}(O_3P{-}C_6H_5)_2(O_2P(O^iPr)C_6H_5)_2}$	0.67	0.176
TiOMcEtPP	$\mathrm{Ti_5O(O^iPr)_{11}(OMc)(O_3PEt)_3}$	0.2	0.233
TiOMcAllylPP	$\mathrm{Ti_{10}(O^iPr)_{16}(O_3PCH_2CH{=}CH_2)_{10}(OMc)_4}$	0	0.233

Part III

Experimental

Chapter 8

Experimental

8.1 General methods and materials

All reactions involving metal alkoxides were performed using standard Schlenk techniques or glove box. Chemicals have been obtained from commercial suppliers (Sigma-Aldrich, ABCR, TCI, Alfa Aesar) and were used as received. Solvents (THF, CH_2Cl_2, 2-propanol, 1-butanol, pentane, hexane, toluene) and chemicals, if necessary, were dried prior to use according to standard techniques.[337] Anhydrous solvents were subsequently stored in argon gas over molecular sieve. Deuterated solvents were purchased from Eurisotop or Sigma-Aldrich, degassed using freeze-pump-thaw technique and stored over molecular sieve in argon atmosphere.

8.2 Analytical techniques

Infrared spectra were recorded on a Bruker Tensor 27 spectrometer under ambient conditions performing 32 scans at a resolution of 4 cm^{-1} on a diamond ATR unit.

^{1}H, ^{31}P and ^{13}C solution NMR spectra were mainly recorded on a Bruker AVANCE 250 (250.13 MHz ^{1}H, 62.86 MHz ^{13}C, 101.25 MHz ^{31}P). Part of the NMR measurements were conducted on a Bruker AVANCE 400 MHz (400.13 MHz ^{1}H, 100.56 MHz ^{13}C, 161.97 MHz ^{31}P) and Bruker AVANCE 200 MHz (200.13 MHz ^{1}H, 50.29 MHz ^{13}C, 81.01 MHz ^{31}P). Correlation spectra were recorded on a Bruker AVANCE DPX 300 (300.13 MHz ^{1}H, 75.42 MHz ^{13}C, 30.42 MHz ^{15}N). All devices were equipped with a 5 mm inverse-broadband probe head and a z-gradient unit. 2D experiments were measured with Bruker standard pulse sequences: HMBC (Heteronuclear Multiple Bond Correlation).

All single crystal X-ray measurements were performed using MoKα radiation ($\lambda = 71.073$ pm). Data were collected on a Bruker AXS SMART APEX II four-circle diffractometer with κ -geometry at 100 K (unless impossible due to phase transition) with φ and ω-scans and variable frame width. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections. SAINT PLUS software (Bruker Analytical X-ray Instruments, 2007) was used to integrate the frames. Symmetry was checked with the program PLATON. Structures were solved by the Patterson method (SHELXS97). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL97) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms on carbon atoms were inserted in calculated positions and refined riding with the corresponding atom.

8.3 Synthesis of precursors

4-(1H-Imidazol-1-yl)butanoic acid

The reaction was done according to Karachev *et al.*[338] and Alekseenko *et al.*[339]. 5 g (217 mmol) of sodium were solved in 80 ml of dry ethanol. 14.8 g (217 mmol) of imidazole were then added to the solution. After 1 hour of stirring at room temperature, the solution was evaporated to dryness to obtain sodium imidazolate as a white powder. 21 ml (275 mmol) of butyrolactate were then added, and the mixture was heated to 175 °C for 16 hours. After cooling to room temperature, 35 ml of a 6 molar hydrochloric acid were added. After 1 hour of stirring, the solution was evaporated to dryness to obtain a solid, which was recrystallized from 2-propanol. The obtained white powder was then dried at 150 °C and 1 mbar for further reactions. Yield 3 g (9 %).
^{1}H NMR (DMSO$-d_6$, 250 MHz) δ (ppm) = 1.89 (quin. (J = 7.15 Hz), 2H, CH_2), 2.13 (t (J = 7.29 Hz), 2H, CH_2-COO), 3.95 (t (J = 7.19 Hz), 2H, CH_2-N), 5.31 (s (broad), 1H, COOH), 6.87 (s, 1H, CH-*CH*-N), 7.14 (s, 1H, CH-*CH*-N), 7.60 (s, 1H, N-CH-N).
^{13}C NMR (DMSO$-d_6$, 62.90 MHz) δ (ppm) = 26.57 (CH_2), 31.03 ($\mathit{CH_2}$-COOH), 45.71 (CH_2-N), 119.72 (CH-*CH*-N), 128.70 (CH-*CH*-N), 137.64 (N-CH-N), 174.25 (COOH).

^{t}Butyl-calix[4]arene

^{t}Butyl-calix[4]arene was obtained as described by Gutsche *et al.*[287]. The outcome was verified using ^{1}H-NMR spectroscopy.
^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.21 (s, 36H, CH_3), 3.4 - 4.3 (m, 8H, CH_2), 7.05 (s, 8H, CH), 10.34 (s, 4H, OH). (Toluene adduct: 2.11 (s, 3H, CH_3), 7.15 - 7.30 (m, 5H, CH)).

Synthesis of diethyl allylphosphonate

The synthesis was done similarly to known precedures.[76,82,86,340–342] In round bottom flask equipped with a Dean-Stark apparatus, 7 ml (81 mmol) of allylbromide were mixed with 9.25 ml (54 mmol) of triethyl phosphite and heated to 150 °C oil bath temperature. Eliminated ethylbromide was collected in the trap. Excess allylbromide was removed *in vacuo* and the product was distilled (75 °C, 1 mbar) to obtain analytically pure diethyl allylphosphonate. Yield 4.6 g (48 %).
^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.20 (t (J = 7.07 Hz), 6H, CH_3), 2.50 (dd ($J_{H\text{-}H}$ = 7.31 Hz, $J_{P\text{-}H}$ = 21.94 Hz), 2H, CH_2-P), 3.99 (m (J = 7.25 Hz), 4H, CH_2-O), 5.04 - 5.16 (m, 2H,

CH_2), 5.58-5.79 (m, 1H, CH).
^{31}P NMR ($CDCl_3$, 62.90 MHz) δ (ppm) = 26.95.

Synthesis of diethyl naphtylmethylphosphonate

A mixture of 2 g (9 mmol) of 2-(bromomethyl)naphthalene and 3.1 ml (18.1 mmol) of triethylphosphite was heated to reflux for 16 h. Volatiles were removed *in vacuo* and the product was obtained by distillation (170 °C, 1 mbar). Yield 1.84 g (74 %).
^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.23 (t (J = 7.03 Hz), 6H, CH_3), 3.31 (d ($J_{P\text{-}H}$ = 21.69 Hz), 2H, CH_2-P), 4.01 (m, 4H, CH_2-O), 7.40 - 7.48 (m, 3H, CH), 7.72 - 7.83 (m, 4H, CH).
^{31}P NMR ($CDCl_3$, 62.90 MHz) δ (ppm) = 26.30.

Synthesis of diethyl 3,5-(dimethyl)phenylphosphonate

The synthesis proceeded similar to what has been reported by Deng *et al.*[343]. 1.36 ml (10 mmol) of 3,5-(dimethyl)bromobenzene were dissolved in 30 ml of THF under argon and cooled to -88 °C. 4.8 ml (12 mmol) of a 2.5 molar suspension of *n*-butyllithium in *n*-hexane was added slowly under stirring conditions. After 1 h of stirring at -88 °C the mixture was allowed to warm to room temperature. The mixture was then cooled again to -88 °C and 2.17 ml (15 mmol) of diethyl chlorophosphate was added. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. 33 ml of saturated aqueous NH_4Cl were added under air and extracted 3 times with 20 ml portions of ethylacetate. The organic phases were combined, dried with Na_2SO_4, filtered, concentrated *in vacuo* and purified using flash chromatography (1:1 EtOAc:hexane). Fractions were taken and analyzed using ^{31}P- and ^{1}H-NMR spectroscopy. Analytically pure diethyl xylylphosphonate was obtained after removing the solvent *in vacuo*. Yield 760 mg (30 %).
^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.32 (t (J = 7.03 Hz), 6H, CH_3), 2.35 (s, 6H, CH_3-Ph), 3.99 - 4.19 (m, 4H, CH_2-O), 7.14 (s, 1H, CH), 7.42 (d ($J_{P\text{-}H}$ = 14.13 Hz), 2H, CH).
^{31}P NMR ($CDCl_3$, 62.90 MHz) δ (ppm) = 19.81.

Synthesis of dimethyl 3-chloropropylphosphonate

10.9 g (97 mmol) of potassium *tert*-butoxide was suspended in 50 ml of dry THF under argon atmosphere and 9.8 ml (106.8 mmol) of dimethyl phosphite were added. The resulting mixture was added dropwise to 12.5 ml (126.4 mmol) of 1-bromo-3-chloropropane diluted in 40 ml of dry THF under stirring conditions. The obtained solution was refluxed for 1 h and stirred overnight at room temperature. The volatiles were removed in vacuo and the remaining liquid was distilled (110 °C, 1 mbar) to obtain the product as a clear liquid. Yield 8.9 g (45 %).
^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.78 - 2.09 (m, 4H, CH_2), 3.55 (t (J = 6.32 Hz), 2H, CH_2-Cl), 3.69 (d, 6H, CH_3-O). (an additional triplet can be found at 3.41 ppm for the bromo species (about 7 % according to integrals)).
^{31}P NMR ($CDCl_3$, 62.90 MHz) δ (ppm) = 33.47. (additional peak for the bromo species at 33.20 ppm).

Synthesis of bis(trimethylsilyl) phosphonates

In a typical experiment, one part (1 ml, 5.8 mmol) of diethyl allylphosphonate was diluted in 10 ml CH_2Cl_2 under argon atmosphere and three parts (2.3 ml, 17.4 mmol) of trimethylsilyl bromide were added slowly by a syringe. The obtained solution was stirred for 16 h. Afterwards the volatiles were removed *in vacuo*. Yield 1.5 g (97 %).
^{1}H NMR (D_2O, 250 MHz) δ (ppm) = 0.31 (s, 18H, CH_3-Si), 2.51 (dd ($J_{\text{H-H}}$ = 7.56 Hz, $J_{\text{P-H}}$ = 22.60 Hz), 2H, CH_2-P), 5.04 - 5.14 (m, 2H, CH_2), 5.82 - 6.02 (m, 1H, CH).
^{31}P NMR (D_2O, 62.90 MHz) δ (ppm) = 8.76.

Synthesis of allylphosphonic acid

Unlike for alkyl phosphonates[341], the hydrolysis of diethyl allylphosphonate cannot be done using HCl. The hydrolysis is done by means of transesterification using trimethylsilyl bromide to form the bis(trimethylsilyl)ester, followed by hydrolysis (water/THF) or methanolysis.[76–78]
First, bis(trimethylsilyl) allylphosphonate was synthesized from diethyl allylphosphonate (see section 8.3). 2 ml (8 mmol) of bis(trimethylsilyl) allylphosphonate was hydrolyzed by the addition of 10 ml of methanol and subsequent stirring for 48 h. After removal of the volatiles *in vacuo* the product was obtained as a white powder. Yield 0.95 g (97 %).
^{1}H NMR (D_2O, 250 MHz) δ (ppm) = 2.45 (dd ($J_{\text{H-H}}$ = 7.43 Hz, $J_{\text{P-H}}$ = 21.74 Hz), 2H, CH_2-P), 4.99 - 5.11 (m, 2H, CH_2), 5.52 - 5.72 (m, 1H, CH).
^{31}P NMR (D_2O, 62.90 MHz) δ (ppm) = 26.32.

8.4 Synthesis of complexes and oxo clusters

8.4.1 Synthesis using carboxylic acids

$Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_4(O^iPr)_2(\mu_2\text{-}OOCC_4H_7)_{10}$ (TiCycloBu).

0.31 ml (1 mmol) of $Ti(O^iPr)_4$ were slowly added to 0.38 ml (4 mmol) of cyclobutane carboxylic acid under stirring. A clear solution was obtained of which crystals of **TiCycloBu** were obtained after 3 weeks. Yield 80 mg (32 %).
^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.22 (d (J = 6.28 Hz), 6H, CH_3 (O^iPr)), 1.31 (d (J = 6.08 Hz), 6H, CH_3 (O^iPr)), 1.73 - 2.05 (m, 20H, CH_2-*CH_2*-CH_2), 2.06 - 2.50 (m, 40H, *CH_2*-CH), 2.95 - 3.11 (m, 5H, CH (cyclobutyl)), 3.14 - 3.33 (m, 5H, CH (cyclobutyl)), 4.82 (m (J = 6.16 Hz), 1H, CH (O^iPr)), 5.00 (m (J = 6.28 Hz), 1H, CH (O^iPr)).
^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm) = 18.24 (CH_2-*CH_2*-CH_2), 18.35 (CH_2-*CH_2*-CH_2), 18.52 (CH_2-*CH_2*-CH_2), 18.72 (CH_2-*CH_2*-CH_2), 21.79 (CH_3 (O^iPr)), 24.38 (CH_3 (O^iPr)), 25.14 (*CH_2*-CH), 25.24 (*CH_2*-CH), 25.29 (*CH_2*-CH), 25.40 (*CH_2*-CH), 25.46 (*CH_2*-CH), 25.57 (*CH_2*-CH), 25.61 (*CH_2*-CH), 25.70 (*CH_2*-CH), 37.74 (*CH*-COO), 38.37, 39.47 (*CH*-COO), 40.00 (*CH*-COO), 40.14 (*CH*-COO), 40.24 (*CH*-COO), 67.26 (*CH* (O^iPr)), 77.19 (*CH* (O^iPr)), 81.47 (*CH* (O^iPr)), 180.80 (COO), 182.88 (COO), 184.38 (COO), 185.18 (COO), 185.78 (COO), 186.80 (COO).

$\mathbf{Ti_4(\mu_3\text{-}O)_2(O^iPr)_6(\mu_2\text{-}OOC{-}C_6H_4{-}Cl)_6}$ (TiBenzCl).

0.31 ml (1 mmol) of $Ti(O^iPr)_4$ were added to a suspension of 0.63 g (4 mmol) of 4-chlorobenzoic acid in 3 ml of THF under stirring. A clear solution was obtained from which crystals of **TiBenzCl** were obtained after few days. Yield 60 mg (24 %).
^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.18 (d (J = 6.16 Hz), 12H, CH_3 (O^iPr)), 1.23 - 1.53 (m, 24H, CH_3 (O^iPr)), 4.00 (m (J = 6.08), 2H, CH (O^iPr)), 5.00 (m (J = 6.08), 1H, CH (O^iPr)), 5.32 - 5.52 (m, 2H, CH (O^iPr)), 5.65 - 5.80 (m, 1H, CH (O^iPr)), 6.52 - 6.67 (m, 2H, CH (arom)), 6.86 (d (J = 8.37 Hz), 1H, CH (arom)), 7.11 (d (J = 8.37 Hz), 1H, CH (arom)), 7.21 - 7.38 (m, 3H, CH (arom)), 7.41 - 7.59 (m, 7H, CH (arom)), 7.87 - 8.38 (m, 9H, CH (arom)).

$\mathbf{Ti_3O_2(O^iPr)_3(OOCCPh_3)_5}$ (TiTPA).

158.4 µl (0.55 mmol) of $Ti(O^iPr)_4$ were added to a suspension of 315 mg (1.09 mmol) of triphenylacetic acid in 3 ml of 2-propanol. 62.5 µl (1.09 mmol) of acetic acid were added to the obtained suspension. Since no clear solution was achieved after heating, 2 ml of CH_2Cl_2 were added. The then clear solution was stirred for 5 min at room temperature. After 4 months crystals of **TiTPA** suitable for single crystal XRD were obtained. Yield 270 mg (82 %).
^{1}H NMR (C_6D_6, 250 MHz) δ (ppm) = 0.74 (d (J = 6.09 Hz), 6H, CH_3 (O^iPr)), 0.90 (d (J = 6.09 Hz), 6H, CH_3 (O^iPr)), 0.92 (d (J = 5.94 Hz), 6H, CH_3 (O^iPr)), 3.82 (m (J = 6.12 Hz), 1H, CH (O^iPr)), 4.62 (m (J = 6.05 Hz), 2H, CH (O^iPr)), 7.09 - 7.33 (m, 57H, CH (arom)), 7.39 - 7.64 (m, 18H, CH (arom)).
^{13}C NMR (C_6D_6, 62.9 MHz) δ (ppm) = 23.58 (CH_3), 24.18 (CH_3), 24.25 (CH_3), 68.63 (C-Ph_3), 69.13 (C-Ph_3), 69.41 (C-Ph_3), 79.38 (CH (O^iPr)), 79.52 (CH (O^iPr)), 126.63 (CH (arom)), 127.50 (CH (arom)), 130.90 (CH (arom)), 131.10 (CH (arom)), 131.19 (CH (arom)), 143.29 (C-C (arom)), 144.19 (C-C (arom)), 144.41 (C-C (arom)), 181.08 (COO), 181.34 (COO), 185.44 (COO) (some signals of the aromatic region are overlapping with the solvent signals (C_6D_6)).

$\mathbf{[Ti_3O(O^iPr)_6(OOC{-}adamantyl)_4]_2{\cdot}THF}$ (TiAda).

678 mg (3.76 mmol) of adamantylcarboxylic acid were suspended in 2 ml of THF and 620 µl (2.14 mmol) of $Ti(O^iPr)_4$ were added. A clear solution was obtained after stirring from which crystals of **TiAda** were formed after 16 weeks. Yield 470 mg (52 %).
^{1}H NMR (CD_2Cl_2, 250 MHz) δ (ppm) = 1.17 - 1.44 (m, 36H, CH_3), 1.61 - 1.76 (broad, 24H, CH_2), 1.82 - 1.95 (broad m, 24H, CH_2), 1.95 - 2.05 (broad, 12H, CH), 4.75 (m, 1H, CH), 4.93 (m, 3H, CH), 5.08 (m, 1H, CH), 5.32 (m, 1H, CH).
^{13}C NMR (CD_2Cl_2, 62.9 MHz) δ (ppm) = 23.34 (CH_3), 24.41 (CH_3), 24.75 (CH_3), 24.87 (CH_3), 25.11 (CH_3), 25.16 (CH_3), 25.54 (CH_3), 27.86 (CH_2), 28.12 (CH_2), 28.22 (CH_2), 28.32 (CH_2), 28.51 (CH_2), 28.67 (CH_2), 36.38 (CH), 36.66 (CH), 36.81 (CH), 37.00 (CH_2), 37.81 (CH), 38.80 (CH_2), 38.96 (CH_2), 39.12 (CH_2), 39.16 (CH_2), 39.29 (CH_2), 39.36 (CH_2), 40.35 (C-COO), 40.98 (C-COO), 41.25 (C-COO), 41.45 (C-COO), 77.46 (CH (O^iPr)), 77.85 (CH (O^iPr)), 78.72 (CH (O^iPr)), 78.77 (CH (O^iPr)), 78.97 (CH (O^iPr)), 182.83 (COO), 183.35 (COO), 184.83 (COO), 185.29 (COO) (signals overlapping due to similar shift, therefore assignment is preliminary).

$\mathbf{Zr_6(\mu_3\text{- }O)_4(\mu_3\text{- }OH)_4(OOC{-}adamantyl)_{12}{\cdot}2(adamantoic\ acid)}$ (ZrAda).

320 µl (0.70 mmol) of $Zr(O^nBu)_4$ were added to 754 mg (4.18 mmol) of adamantylcarboxylic acid in 2 ml of THF. Out of the clear solution crystals of **ZrAda** formed after 18 weeks. Yield 290 mg (77 %).
^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.70 (broad, 82H, CH_2), 1.89 (broad, 82H, CH_2), 2.00 (broad, 42H, CH).
^{13}C NMR ($CDCl_3$, 62.9 MHz) δ (ppm) = 28.00 (broad, CH_2), 36.55 (broad, CH), 38.72 (broad, CH_2), 40.69 (broad, C), 182.99 (broad, COO).

$\mathbf{Ti_2(\mu_2\text{- }O^iPr)_2(O^iPr)_4(OOC{-}C_6H_4{-}CH_2Cl)_2(^iPrOH)}$ (TiBenzMeCl).

510 µl (1.76 mmol) of $Ti(O^iPr)_4$ were added to a suspension of 300 mg (1.76 mmol) of 4-(chloromethyl)benzoic acid in 5 ml of ^{i}PrOH. The suspension was heated to reflux and the solution put to crystallization at room temperature. After 4 weeks the solution was reduced *in vacuo* and a crystalline solid precipitated. Crystals suitable for single crystal XRD were obtained by recrystallization from mother liquid. Yield 200 mg (27 %).
^{1}H NMR (C_6D_6, 250 MHz) δ (ppm) = 1.04 - 1.24 (broad, 12H, CH_3), 1.47 (d (J = 6.16 Hz), 18H, CH_3), 1.37 - 1.63 (broad, 12H, CH_3), 3.84 - 4.11 (broad, 2H, CH (O^iPr)), 4.06 (s, 4H, CH_2-Cl), 5.21 (m (J = 6.14 Hz), 5H, CH (O^iPr)), 7.17 (d (J = 8.13 Hz), 4H, CH), 8.47 (d (J = 8.96 Hz), 4H, CH).
^{13}C NMR ($CDCl_3$, 62.90 MHz) δ (ppm) = 25.26 (CH_3), 25.58 (CH_3), 45.40 (CH_2), 78.44 (CH (O^iPr)), 128.29 (CH arom.), 130.81 (CH arom.), 134.45 (CH arom.), 141.69 (CH arom.), 172.62 (COO) (the peak at 25.58 ppm was unusually broad).

$\mathbf{Zr_{10}(\mu_4\text{- }O)_4(\mu_3\text{- }O)_4(O^nBu)_{16}(OOC{-}Ph{-}CH_2Cl)_8}$ (ZrBenzMeCl).

To a suspension of 240 mg (1.41 mmol) of 4-(chloromethyl)benzoic acid in 3 ml of ^{n}BuOH was added 643 µl (1.41 mmol) of $Zr(O^nBu)_4$ quickly. A clear solution was obtained which was heated to reflux for 10 seconds the solution was cooled to room temperature. After 2 weeks crystals of **ZrBenzMeCl** were grown. Yield 60 mg (12 %).
^{1}H NMR (CD_2Cl_2, 200 MHz) δ (ppm) = 0.14 - 2.27 (m, 112H, $CH_2{-}CH_2{-}CH_3$), 2.89 - 4.53 (m, 32H, $CH_2{-}O$), 4.54 - 4.89 (m, 16H, $CH_2{-}Cl$), 6.81 - 8.27 (m, 32H, CH (aromatic)) (integrals were almost perfect, but signals were overlapping due to multiplicity).

$\mathbf{Zr_9(\mu_4\text{- }O)_2(\mu_3\text{- }O)_4(O^nBu)_{18}(OOCCCCH_2CH_3)_6}$ (ZrPentin).

9.6 µl (0.53 mmol) of water in 1 ml of ^{n}BuOH were added to a mixture of 210 mg (2.14 mmol) of 2-pentinoic acid and 1 ml (2.18 mmol) of $Zr(O^nBu)_4$ in 2 ml ^{n}BuOH. After 34 weeks part of the solvent of the clear solution was removed *in vacuo*. After 8 additional weeks, crystals of **ZrPentin** were obtained. Yield 250 mg (37 %).
^{1}H NMR (C_6D_6, 200 MHz) δ (ppm) = 0.86 - 1.44 (m, 72H, CH_3), 1.45 - 2.20 (m, 72H, CH_2), 2.21 - 2.66 (m, 12H, CH_2 (pentynoate)), 4.18 - 5.35 (m, 36H, $CH_2{-}O$).
^{13}C NMR (C_6D_6, 50.3 MHz) δ (ppm) = 12.48 (CH_2 (pentynoate)), 12.66 (CH_2 (pentynoate)), 12.80 (CH_2 (pentynoate)), 12.89 (CH_2 (pentynoate)), 14.18 (CH_3), 14.51 (CH_3), 14.65 (CH_3), 14.94 (CH_3), 15.23 (CH_3), 19.45 ($\mathit{CH_2}$-CH_3 (butanoate)), 19.73 ($\mathit{CH_2}$-CH_3 (butanoate)), 20.04 ($\mathit{CH_2}$-CH_3 (butanoate)), 20.17 ($\mathit{CH_2}$-CH_3 (butanoate)), 35.14 ($\mathit{CH_2}$-CH_2-O (butanoate)), 35.72

($\mathit{CH_2}$-CH$_2$-O (butanoate)), 35.96 ($\mathit{CH_2}$-CH$_2$-O (butanoate)), 36.26 ($\mathit{CH_2}$-CH$_2$-O (butanoate)), 36.61 ($\mathit{CH_2}$-CH$_2$-O (butanoate)), 37.03 ($\mathit{CH_2}$-CH$_2$-O (butanoate)), 69.15 (CH$_2$-O), 69.62 (CH$_2$-O), 70.27 (CH$_2$-O), 70.45 (CH$_2$-O), 71.02 (CH$_2$-O), 71.72 (CH$_2$-O), 76.24 (C (pentynoate)), 78.08 (C (pentynoate)), 85.31 (*C*-COO), 88.84 (*C*-COO), 89.08 (*C*-COO), 159.94 (COO), 160.11 (COO), 160.86 (COO), 161.17 (COO).

Titanium tris(isopropoxo) 4-(imidazol−1−yl)butanate (TiBuImid).

Ti(O^{i}Pr)$_4$ (1.1 ml, 3.8 mmol) was added to a solution of 590 mg (3.8 mmol) of 4-(imidazol-1-yl)-butanoic acid in 3 ml of water-free isopropanol under argon. After 4 weeks crystals of **TiBuImid** were obtained. Yield 450 mg (31 %).
^{1}H NMR (CDCl$_3$, 250 MHz) δ (ppm) = 1.22 (d (J = 6.10 Hz), 18H, CH$_3$), 1.83 (m, 2H, CH$_2$), 2.05 (m, 2H, CH$_2$), 3.78 (t (J = 6.63 Hz), 2H, CH$_2$), 4.70 (m, 3H, CH (O^{i}Pr)), 6.74 (s, 1H, CH), 7.17 (s, 1H, CH), 7.59 (s, 1H, CH).
^{13}C NMR (CDCl$_3$, 62.90 MHz) δ (ppm) = 25.96 (CH$_3$), 26.69 (CH$_2$), 32.64 (CH$_2$), 46.67 (CH$_2$), 77.36 (CHMe$_2$), 118.29 (CH), 129.75 (CH), 138.07 (CH).
IR (cm^{-1}) = 3144 (vw), 2963 (w), 2927 (vw), 2860 (vw), 1724 (vvw), 1549 (m),1520 (w), 1462 (m), 1443 (w), 1373 (w), 1359 (w), 1328 (w), 1226 (w), 1161 (w), 1118 (m), 1103 (m), 1084 (m), 1020 (w), 980 (m), 942 (w), 845 (w), 733 (m), 665 (w).

8.4.2 Synthesis of titanium complexes and oxo clusters using different amounts of methacrylic acid

$Ti_2(\mu_2\text{-}O^iPr)_2(O^iPr)_4(\mu_2\text{-}OMc)(OMc)(^iPrOH)$ (TiOMc1).

291 µl (3.45 mmol) of methacrylic acid were added to 1 ml (3.45 mmol) of Ti(O^{i}Pr)$_4$ in 1 ml of ^{i}PrOH. After 1 minute stirring at room temperature the solution was put to crystallization at -9 °C. Crystals of **TiOMc1** were obtained after 4 days. Yield 500 mg (43 %).
^{1}H NMR (C$_6$D$_6$, 250 MHz) δ (ppm) = 0.94 - 1.82 (m, 42H, CH (O^{i}Pr)), 1.95 - 2.29 (m, 6H, $\mathit{CH_3}$-C), 4.51 (broad, 2H, CH (O^{i}Pr)), 4.88 - 5.33 (m, 5H, CH (O^{i}Pr)), 5.42 (broad, 2H, $\mathit{CH_2}$-C), 6.47 (broad, 2H, $\mathit{CH_2}$-C). (all peaks very broad).
^{13}C NMR (C$_6$D$_6$, 62.90 MHz) δ (ppm) = 18.22 (broad, $\mathit{CH_3}$-C), 24.98 (CH$_3$ (O^{i}Pr)), 25.37 (broad, CH$_3$ (O^{i}Pr)), 77.90 (CH (O^{i}Pr), 72.3 - 79.36 (broad peak, CH (O^{i}Pr)), 125.1 - 126.8 (broad, C-CH$_2$) (the peaks are broad which is unusual for ^{13}C NMR data, and some peaks are obviously missing for that reason).

$Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O^iPr)_2(O^iPr)_6(\mu_2\text{-}OMc)_8$ (TiOMc2).

582 µl (6.9 mmol) of methacrylic acid were added to 1 ml (3.45 mmol) of Ti(O^{i}Pr)$_4$. After 1 minute stirring the solution was put to crystallization at room temperature. Crystals of **TiOMc2** were obtained after 8 weeks. Yield 350 mg (40 %).
^{1}H NMR (CDCl$_3$, 200 MHz) δ (ppm) = 1.00 - 1.44 (m, 48H, CH$_3$ (O^{i}Pr)), 1.68 - 1.96 (m, 24H, CH$_3$ (OMc)), 3.97 (m (J = 6.16 Hz), 1H, CH), 4.30 (m (J = 6.06 Hz), 1H, CH), 4.58 - 4.85 (m, 4H, CH), 4.93 - 5.12 (m, 2H, CH), 5.24 - 5.56 (m, 8H, CH$_2$), 5.90 - 6.27 (m, 8H, CH$_2$).
^{13}C NMR (CDCl$_3$, 50.3 MHz) δ (ppm) = 18.17 (CH$_3$ (OMc)), 18.26 (CH$_3$ (OMc)), 18.48 (CH$_3$

(OMc)), 18.58 (CH_3 (OMc)), 18.64 (CH_3 (OMc)), 18.74 (CH_3 (OMc)), 18.81 (CH_3 (OMc)), 24.41 (CH_3 (O^{i}Pr)), 24.52 (CH_3 (O^{i}Pr)), 24.90 (CH_3 (OMc)), 25.25 (CH_3 (O^{i}Pr)), 25.33 (CH_3 (O^{i}Pr)), 25.40 (CH_3 (O^{i}Pr)), 25.47 (CH_3 (O^{i}Pr)), 77.20 (CH (O^{i}Pr)), 78.13 (CH (O^{i}Pr)), 78.40 (CH (O^{i}Pr)), 78.85 (CH (O^{i}Pr)), 80.27 (CH (O^{i}Pr)), 81.62 (CH (O^{i}Pr)), 81.75 (CH (O^{i}Pr)), 125.81 (CH_2), 126.96 (CH_2), 127.90 (CH_2), 137.45 (C (OMc)), 137.61 (C (OMc)), 138.12 (C (OMc)), 138.55 (C (OMc)), 138.75 (C (OMc)), 139.19 (C (OMc)), 139.29 (C (OMc)), 139.40 (C (OMc)), 172.77 (COO), 173.14 (COO), 174.31 (COO), 174.71 (COO), 175.12 (COO), 175.81 (COO).

$\mathbf{Ti_9(\mu_3\text{-}O)_2(\mu_2\text{-}O)_6(O^iPr)_4(\mu_2\text{-}OMc)_{16}\cdot {}^iPrOH \cdot (McOH)_2}$ (TiOMc6).

1.75 ml (20.7 mmol) of methacrylic acid were added to 1 ml (3.45 mmol) of Ti(O^{i}Pr)$_4$ under vigorous stirring. After 1 minute the stirring bar was removed and the solution was put to crystallization at room temperature. Crystals suitable for single crystal XRD measurements were obtained after 16 weeks. Yield 330 mg (39 %).
^{1}H NMR ($CDCl_3$, 200 MHz) δ (ppm) = 0.88 - 1.11 (m, 3H, CH_3 (O^{i}Pr)), 1.14 (d (J = 6.12 Hz), 6H, CH_3 (O^{i}Pr)), 1.17 - 1.60 (m, 15H, CH_3 (O^{i}Pr)), 1.64 - 1.96 (m, 48H, CH_3 (OMc)), 3.97 (m (J = 6.11 Hz), 1H, CH), 4.93 - 5.04 (m, 1H, CH), 5.20 - 5.58 (m, 16H, CH_2), 5.61 (m, 3H, CH), 5.95 - 6.31 (m, 16H, CH_2).

$\mathbf{Ti_8O_8(OMc)_{16}}$ (TiOMc8).

2.3 ml (27.6 mmol) of methacrylic acid were added to 1 ml (3.45 mmol) of Ti(O^{i}Pr)$_4$. The solution was stirred for 5 min. After several months, the crystals of **TiOMc8** were obtained from mother liquor. Yield 80 mg (12 %).
^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.85 - 1.93 (m, 48H, CH_3), 5.29 - 5.69 (m, 16H, CH_2), 6.17 - 6.22 (m, 16H, CH_2).
^{13}C NMR ($CDCl_3$, 250 MHz) δ (ppm) = 17.9 - 18.4 (CH_3), 126.0 - 128.3 (CH_2), 136.2 - 138.4 (C), 176.7 (COO).
IR (cm^{-1}): 2972 (w), 1641 (w), 1535 (s), 1479 (m), 1453 (m), 1422(s),1389 (m), 1242 (s), 1008(m), 942(m), 825(w), 719(s), 654 (w).

8.4.3 Synthesis using anhydrides

$\mathbf{Ti_2(O^iPr)_6(\mu_2\text{-}OOC{-}C_6H_4{-}COO^iPr)(\eta_1\text{-}OOC{-}C_6H_4{-}COO^iPr)({}^iPrOH)}$ (TiPhthal1).

An amount of 1.08 g (3.8 mmol) of Ti(O^{i}Pr)$_4$ was added to a suspension of 560 mg (3.8 mmol) of phthalic anhydride in 291 µl (3.8 mmol) of iso-propanol. The mixture was heated until a clear solution was obtained. Crystals of **TiPhthal1** were obtained within 24 h at room temperature. Yield 1.86 g (100 %).
^{1}H NMR (CD_2Cl_2, 300 MHz) δ (ppm) = 1.29 (d (J = 6.1 Hz), 42H, CH_3), 1.39 (d (J = 6.0 Hz), 12H, CH_3 (isopropyl ester)), 4.60 - 5.20 (m, 7H, CH (O^{i}Pr)), 5.25 (m, 2H, CH (isopropyl ester)), 7.3 - 7.7 (m, 6H, CH (Ph)), 8.12 (broad, 2H, CH-C-COOTi).
^{13}C NMR (CD_2Cl_2, 75 MHz) δ (ppm) = 21.4 (CH_3 (ester)), 24.71 (CH_3 (^{i}PrOH, H-bond)),

25.55 (CH_3 (O^iPr)), 68.4 (CH (ester, H-bonded)), 69.3 (CH (ester)), 76.2 - 78.2 (CH (O^iPr, terminal)), 79 - 81 (CH (O^iPr, bridging)), 127 - 136 (CH (aryl)), 166.6 (COO (ester)), 167.8 (COO (ester, H-bonded)), 182.5 (COO-Ti).
IR (cm^{-1}): 2972 (w, C-H), 1723 (m, C=O, ester), 1550 (m, C=O, acetate), 1493 (w), 1403 (m), 1290(m), 1109(s), 1076(m), 1011(m), 851(w), 822(w).

$\mathbf{Ti_6O_6(O^iPr)_6(OOC{-}C_6H_4{-}COO^iPr)_6}$ (TiPhthal2).

An amount of 1.2 g (4.25 mmol) of $Ti(O^iPr)_4$ was added to a suspension of 630 mg (4.25 mmol) of phthalic anhydride in a mixture of 255 mg (4.25 mmol) of acetic acid and 1 ml of iso-propanol (17 mmol). The suspension was heated until a clear solution was obtained. Colorless crystals of **TiPhthal2** were obtained after 10 weeks at room temperature. Yield 600 mg (43 %).
^{1}H NMR (CD_2Cl_2, 250 MHz) δ (ppm) = 0.8 - 1.7 (m, 72H, CH_3), 4.5 - 5.3 (m, 12H, CH), 7.1 - 8.1 (m, 24H, aryl).
^{13}C NMR (CD_2Cl_2, 63 MHz) δ (ppm) = 21 - 25 (CH_3 (O^iPr)), 68.5 - 69.5 (CH (ester)), 79 - 80 (CH (O^iPr)), 128 - 135 (C (aryl)), 166 - 168 (COO^iPr) 174 - 180 (COO (acetate)).
IR (cm^{-1}): 2972 (w, C-H), 1726 (m, C=O, ester), 1555 (m, C=O, acetate), 1400 (s), 1275 (m), 1108 (m), 1075 (m), 1008 (m), 950 (m), 840 (m).

$\mathbf{Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)(\mu_2\text{-}O^iPr)_4(O^iPr)_{10}(OOC{-}CH{=}CH{-}COO)_2}$ (TiMal).

8.8 ml (30.3 mmol) of $Ti(O^iPr)_4$ were added to 2.96 g (30.1 mmol) of maleic anhydride in 9.3 ml of ^{i}PrOH. After 16 weeks at room temperature crystals of **TiMal** were obtained. Yield 200 mg (3 %).
^{1}H NMR (C_6D_6, 200 MHz) δ (ppm) = 1.34 - 1.54 (m, 60H, CH_3), 1.63 (d (J = 6.22 Hz), 6H, CH_3), 1.73 (d (J = 6.26 Hz), 6H, CH_3), 1.92 (d (J = 6.26 Hz), 6H, CH_3), 1.94 (d (J = 6.22 Hz), 6H, CH_3), 5.00 (m (J = 6.21 Hz), 2H, CH), 5.07 - 5.31 (m, 10H, CH), 5.40 (m (J = 6.11 Hz), 2H, CH), 6.06 (s, 4H, CH (maleate)).
^{13}C NMR (C_6D_6, 50.3 MHz) δ (ppm) = 24.47 (CH_3), 24.84 (CH_3), 24.90 (CH_3), 25.10 (CH_3), 25.44 (CH_3), 25.60 (CH_3), 25.71 (CH_3), 25.80 (CH_3), 25.90 (CH_3), 26.04 (CH_3), 26.11 (CH_3), 76.58 (CH (O^iPr)), 77.25 (CH (O^iPr)), 77.86 (CH (O^iPr)), 78.40 (CH (O^iPr)), 78.81 (CH (O^iPr)), 79.28 (CH (O^iPr)), 79.35 (CH (O^iPr)), 134.41 (CH (maleate)), 171.45 (COO), 173.21 (COO).

8.4.4 Synthesis of ^{t}butyl-calix[4]arene derivatives.

$\mathbf{Zr_3(O^nBu)_8}$(^{t}butyl-calix[4]arene) (Zr3calix).

$Zr(O^nBu)_4$ (0.98 ml, 2.14 mmol) was added quickly to a suspension of 347 mg (0.54 mmol) of ^{t}butyl-calix[4]arene in 2 ml of ^{n}BuOH under argon. The suspension was heated until a clear solution was obtained and then immediately cooled to room temperature. Crystals of **Zr3calix** were obtained after 4 days. Yield 660 mg (82 %).
^{1}H NMR (C_6D_6, 250 MHz) δ (ppm) = 0.89 (t (J = 7.30 Hz), 6H, CH_3 (O^nBu)), 0.93 (s, 9H, CH_3 (calix)), 0.95 (t (J = 7.18 Hz), 6H, CH_3 (O^nBu)), 1.02 (s, 9H, CH_3 (calix)), 1.05 (t (J = 7.15 Hz), 6H, CH_3 (O^nBu)), 1.12 (t (J = 7.30 Hz), 6H, CH_3 (O^nBu)), 1.17 - 1.33 (m, 3H,

CH₂-CH$_3$), 1.34 - 1.58 (m, 9H, *CH₂*-CH$_3$), 1.59 (s, 18H, CH$_3$ (calix)), 1.6 - 1.81 (m, 12H, CH$_2$ (O^{n}Bu)), 1.87 - 2.01 (m, 2H, *CH₂*-CH$_2$-O), 2.24 (quin. (J = 7.38 Hz), 2H, *CH₂*-CH$_2$-O), 2.39 - 2.58 (m, 4H, CH$_2$), 3.59 (d (J = 11.88 Hz), 2H, CH$_2$ (calix)), 3.64 (d (J = 11.87 Hz), 2H, CH$_2$ (calix)), 4.17 (t (J = 6.17 Hz), 4H, CH$_2$-O (term. O^{n}Bu)), 4.24 (t (J = 5.78 Hz), 4H, CH$_2$-O (term. O^{n}Bu)), 4.39 - 4.49 (m, 2H, CH$_2$-O (μ_2-O^{n}Bu)), 4.50 - 4.62 (m, 2H, CH$_2$-O (μ_3-O^{n}Bu)), 4.80 - 4.92 (m, 2H, CH$_2$-O (μ_3-O^{n}Bu)), 5.02 (t (J = 7.24 Hz), 2H, CH$_2$-O (μ_2-O^{n}Bu)), 5.23 (d (J = 12.18 Hz), 2H, CH$_2$ (calix)), 5.32 (d (J = 12.13 Hz), 2H, CH$_2$ (calix)), 7.08 (m, 4H, CH (arom.)), 7.49 (m, 4H, CH (arom.)).

^{13}C NMR (C$_6$D$_6$, 62.9 MHz) δ (ppm) = 13.52 (CH$_3$ (O^{n}Bu)), 13.76 (CH$_3$ (O^{n}Bu)), 14.15 (CH$_3$ (O^{n}Bu)), 19.10 (*CH₂*-CH$_3$), 19.25 (*CH₂*-CH$_3$), 19.34 (*CH₂*-CH$_3$), 30.74 (CH$_3$ (calix)), 31.08 (CH$_3$ (calix)), 31.96 (CH$_3$ (calix)), 33.15 (*C*-CH$_3$ (calix)), 34.07 (*C*-CH$_3$ (calix)), 34.22 (*C*-CH$_3$ (calix)), 34.72 (*CH₂*-CH$_2$-O), 36.01 (*CH₂*-CH$_2$-O), 36.34 (*CH₂*-CH$_2$-O), 36.50 (*CH₂*-CH$_2$-O), 70.09 (CH$_2$-O), 70.82 (CH$_2$-O), 71.30 (CH$_2$-O), 72.04 (CH$_2$-O), 123.83 (CH (arom)), 124.48 (CH (arom)), 125.30 (CH (arom)), 126.02 (CH (arom)), 129.39 (*C*-CO (arom)), 132.28 (*C*-CO (arom)), 134.16 (*C*-CO (arom)), 140.16 (*C*-C(CH$_3$)$_3$), 141.76 (*C*-C(CH$_3$)$_3$), 143.00 (*C*-C(CH$_3$)$_3$), 153.22 (C-O (arom)), 157.00 (C-O (arom)), 157.42 (C-O (arom)).

Ti_2(O^{n}Bu)$_2$(^{t}butyl-calix[4]arene)$_2$ (TiCalix).

To a suspension of 630 mg (0.97 mmol) of ^{t}butyl-calix[4]arene in 4 ml ^{n}BuOH was added 1.32 ml (3.88 mmol) of Ti(O^{n}Bu)$_4$quickly. After an immediate change from colorless to yellow, a suspension was obtained. After heating and addition of 4 ml toluene, a red solution was received. Crystals of **TiCalix** were grown after 2 weeks. Yield 480 mg (66 %).

^{1}H NMR (C$_6$D$_6$, 250 MHz) δ (ppm) = 0.77 - 0.99 (m, 14H, CH$_3$), 1.04 - 1.75 (m, 64H, CH$_3$), 2.32 (s, 3H, CH$_3$ (toluene)), 3.18 - 5.08 (m, 22H, CH$_2$), 6.86 - 7.25 (m, 16H, CH (arom)).

^{13}C NMR (C$_6$D$_6$, 62.9 MHz) δ (ppm) = 13.82CH$_3$ (O^{n}Bu), 13.92CH$_3$ (O^{n}Bu), 18.86 (*CH₂*-CH$_3$), 21.43 (*CH₂*-CH$_3$), 31.40 (CH$_3$ (^{t}butyl-calix[4]arene)), 31.55 (CH$_3$ (^{t}butyl-calix[4]arene)), 31.65 (CH$_3$ (^{t}butyl-calix[4]arene)), 32.61 (CH$_3$ (^{t}butyl-calix[4]arene)), 34.01 (*C*-(CH$_3$)$_3$), 34.76 (*C*-(CH$_3$)$_3$), 62.89 (CH$_2$-O), 77.22 (CH$_2$-O), 124.53 (*C*-CH$_2$), 125.78 (*C*-CH$_2$), 125.93 (*C*-CH$_2$), 126.16 (*C*-CH$_2$), 127.69 (CH (arom)), 129.43 (CH (arom)), 129.65 (CH (arom)), 132.27 (CH (arom)), 132.53 (CH (arom)), 133.00 (CH (arom)), 137.85 (*C*-C-(CH$_3$)$_3$), 142.88 (*C*-C-(CH$_3$)$_3$), 143.13 (*C*-C-(CH$_3$)$_3$), 144.36 (*C*-C-(CH$_3$)$_3$), 145.65 (*C*-C-(CH$_3$)$_3$), 146.67 (*C*-C-(CH$_3$)$_3$), 155.99 (C-O (arom)), 157.64 (C-O (arom)), 160.54 (C-O (arom)).

Zr_4(μ_3- O)(O^{n}Bu)$_6$(^{t}butyl-calix[4]arene)$_2$(^{n}BuOH)$_2$ (Zr4Calix2).

815 µl (1.78 mmol) of Zr(O^{n}Bu)$_4$ were added to a mixture of 330 mg (0.45 mmol) of ^{t}butyl-calix[4]arene and 25.5 µl (1.78 mmol) of acetic acid in 2 ml ^{n}BuOH. The suspension was heated under stirring until a clear solution was obtained. After cooling to room temperature, crystals of **Zr4Calix2** formed after 18 weeks from mother liquor. Yield 360 mg (70 %).

The same unit cell was found for a reaction without acetic acid, and water was added instead. In this reaction, 754 mg (1.16 mmol) of ^{t}butyl-calix[4]arene were suspended in 3 ml 1-butanol. To this suspension, 4.25 ml (9.3 mmol) of Zr(O^{n}Bu)$_4$ were added quickly. The mixture was heated until a clear solution was obtained. After cooling to room temperature, 1.16 ml (4.64

mmol) of a 4 molar solution of water in THF was added. Crystals of **Zr4Calix2** suitable for single crystal XRD were obtained after 16 weeks. Yield 800 mg (60 %).
^{1}H NMR (C$_6$D$_6$, 250 MHz) δ (ppm) = 0.56 (t (J = 7.5 Hz), 3H, CH$_3$ (O^{n}Bu)), 0.83 - 0.90 (m, 9H, CH$_3$ (O^{n}Bu)), 0.91 (s, 18H, CH$_3$ (^{t}butyl-calix[4]arene)), 0.93 - 0.96 (m, 12H, CH$_3$ (O^{n}Bu)), 0.97 (s, 18H, CH$_3$ (^{t}butyl-calix[4]arene)), 1.15 - 1.38 (m, 16H, CH_2-CH$_3$), 1.44 - 1.65 (m, 16H, CH_2-CH$_2$-O), 1.54 (s, 18H, CH$_3$ (^{t}butyl-calix[4]arene)), 1.56 (s, 18H, CH$_3$ (^{t}butyl-calix[4]arene)), 2.76 - 2.92 (broad, 2H, OH), 3.51 (d (J = 12.2 Hz), 2H, CH$_2$−Ph), 3.63 (d (J = 12.5 Hz), 2H, CH$_2$−Ph), 3.66 (d (J = 12.5 Hz), 2H, CH$_2$−Ph), 3.71 (d (J = 13.1 Hz), 2H, CH$_2$−Ph), 4.00 (t (J = 6.7 Hz), 10H, CH$_2$-O (O^{n}Bu)), 4.22 (t (J = 6.2 Hz), 2H, CH$_2$-O (O^{n}Bu)), 4.35 (t (J = 6.3 Hz), 2H, CH$_2$-O (O^{n}Bu)), 5.19 (d (J = 12.0 Hz), 2H, CH$_2$−Ph), 5.21 (d (J = 12.0 Hz), 2H, CH$_2$−Ph), 5.26 - 5.34 (m, 2H, CH$_2$-O (O^{n}Bu)), 5.42 (d (J = 12.3 Hz), 2H, CH$_2$−Ph), 5.53 (d (J = 12.5 Hz), 2H, CH$_2$−Ph), 7.02 - 7.13 (m, 8H, CH (arom)), 7.44 - 7.52 (m, 8H, CH (arom)).
^{13}C NMR (C$_6$D$_6$, 62.9 MHz) δ (ppm) = 12.56 (CH$_3$ (O^{n}Bu)), 13.85 (CH$_3$ (O^{n}Bu)), 14.05 (CH$_3$ (O^{n}Bu)), 14.11 (CH$_3$ (O^{n}Bu)), 18.92 (CH_2-CH$_3$), 19.06 (CH_2-CH$_3$), 19.13 (CH_2-CH$_3$), 19.72 (CH_2-CH$_3$), 30.77 (CH$_3$ (^{t}butyl-calix[4]arene)), 30.83 (CH$_3$ (^{t}butyl-calix[4]arene)), 31.90 (CH$_3$ (^{t}butyl-calix[4]arene)), 33.25 (CH$_2$), 33.29 (CH$_2$), 34.07 (C-(CH$_3$)$_3$), 34.36 (C-(CH$_3$)$_3$), 34.98 (C-(CH$_3$)$_3$), 35.22 (C-(CH$_3$)$_3$), 36.21 (CH_2-Ph), 36.29 (CH_2-Ph), 67.29 (CH$_2$-O), 71.67 (CH$_2$-O), 71.92 (CH$_2$-O), 72.06 (CH$_2$-O), 73.52 (CH$_2$-O), 74.70 (CH$_2$-O), 123.93 (C-CH$_2$), 124.18 (C-CH$_2$), 124.52 (C-CH$_2$), 124.99 (C-CH$_2$), 125.40 (C-CH$_2$), 125.62 (C-CH$_2$), 126.00 (C-CH$_2$), 129.64 (CH (arom)), 129.71 (CH (arom)), 129.86 (CH (arom)), 130.30 (CH (arom)), 130.45 (CH (arom)), 131.05 (CH (arom)), 131.79 (CH (arom)), 132.17 (CH (arom)), 132.89 (CH (arom)), 133.45 (CH (arom)), 142.13 (C-C−(CH$_3$)$_3$), 142.27 (C-C−(CH$_3$)$_3$), 142.36 (C-C−(CH$_3$)$_3$), 143.70 (C-C−(CH$_3$)$_3$), 143.96 (C-C−(CH$_3$)$_3$), 151.69 (C-O (arom)), 152.44 (C-O (arom)), 156.75 (C-O (arom)), 157.28 (C-O (arom)), 157.44 (C-O (arom)) (assignment of ^{13}C NMR signal in the region of 30 - 36 ppm is uncertain).

8.4.5 Synthesis of the dioximate zirconium oxo cluster

Zr$_{10}$(μ$_4$- O)$_2$(μ$_3$- O)$_2$(μ$_2$- O^{n}Bu)$_{10}$(O^{n}Bu)$_8$(1,2-cyclohexanedioxime)$_4$(μ$_2$- OAc)$_2$-(OAc)$_2$ (ZrHexOx).

3.2 ml (7 mmol) of Zr(O^{n}Bu)$_4$were added to 500 mg (3.5 mmol) of 1,2-cyclohexanedioxime in 2 ml of ^{n}BuOH. Immediately afterwards, 400 µl (7 mmol) of acetic acid were added. Crystals of **ZrHexOx** were obtained after 3 weeks of crystallization. Yield 30 mg (1.4 %).
^{1}H NMR (C$_6$D$_6$, 250 MHz) δ (ppm) = 0.85 - 1.91 (m, 130H, CH$_3$−CH$_2$−CH$_2$), 1.92 - 2.01 (m, 6H, CH$_3$ (OAc)), 2.01 - 2.18 (m, 12H, CH$_3$ (OAc)), 2.19 - 3.32 (m, 30H, CH$_2$ (cyclohexyl)), 3.36 - 3.52 (broad, 2H, CH$_2$ (cyclohexyl)), 3.90 - 4.26 (m, 8H, CH$_2$-O), 4.27 - 4.56 (m, 8H, CH$_2$-O), 4.57 -5.07 (m, 16H, CH$_2$-O).
^{13}C NMR (C$_6$D$_6$, 62.9 MHz) δ (ppm) = 13.80 - 14.82 (m, CH$_3$), 19.01 - 19.96 (m, CH_2-CH$_3$), 21.31 - 21.87 (m, CH$_2$ (cyclohexyl)), 22.93 (CH$_2$ (cyclohexyl)), 24.30 - 25.62 (m, CH_2-C (cyclohexyl)), 26.53 (broad, CH$_3$ (OAc)), 34.29 - 37.51 (m, CH_2-CH$_2$-O), 69.41 - 71.60 (m, CH$_2$-O), 141.39 (C (cyclohexyl)), 141.58 (C (cyclohexyl)), 142.33 (C (cyclohexyl)), 142.54 (C (cyclohexyl)), 149.32 (C (cyclohexyl)), 149.84 (C (cyclohexyl)), 154.29 (C (cyclohexyl)), 154.47 (C (cyclohexyl)), 177.49 (COO), 177.73 (COO), 179.42 (COO), 180.21 (COO), 190.19 (COO), 190.57 (COO).

8.4.6 Synthesis of phosphonate titanium oxo clusters

Ti$_4$O(O^{i}Pr)$_8$(O$_3$P(allyl))$_3$(DMSO) (TiDMSOAllylPA).

Allylphosphonic acid (315 mg, 2.6 mmol) was dissolved in 3 ml of water-free DMSO under inert atmosphere and 1.5 ml (5.2 mmol) of Ti(O^{i}Pr)$_4$were added slowly under vigorous stirring. The formed suspension was stirred until a clear solution was obtained. Crystalline **TiDMSOAllylPA** was obtained after 4 weeks. Yield 600 mg (62 %).
^{1}H NMR (C$_6$D$_6$, 250 MHz) δ (ppm) = 1.48 (d (J = 6.15 Hz), 12H, CH$_3$ (O^{i}Pr)), 1.49 (d (J = 6.18 Hz), 12H, CH$_3$ (O^{i}Pr)), 1.68 (d (J = 6.35 Hz), 12H, CH$_3$ (O^{i}Pr)), 1.73 (d (J = 6.28 Hz), 12H, CH$_3$ (O^{i}Pr)), 1.94 (s, 6H, SCH$_3$), 2.76 (dd (J$_{\text{H-H}}$ = 7.30 Hz, J$_{\text{P-H}}$ = 21.6 Hz), 4H, PCH$_2$), 2.87 (dd (J$_{\text{H-H}}$ = 7.40 Hz, J$_{\text{P-H}}$ = 22.0 Hz), 2H, PCH$_2$), 4.74 (m, 6H, CH$_2$ (allyl)), 5.22 (m, 11H, CH (O^{i}Pr)), 6.31 (m, 3H, CH (allyl)).
^{31}P NMR (C$_6$D$_6$, 101.2 MHz) δ (ppm) = 14.48, 16.01.
^{13}C NMR (C$_6$D$_6$, 62.9 MHz) δ (ppm) = 24.90 (s, CH$_3$ (O^{i}Pr)), 24.97 (s, CH$_3$ (O^{i}Pr)), 25.13 (s, CH$_3$ (O^{i}Pr)), 25.19 (s, CH$_3$ (O^{i}Pr)), 34.16 (d, J = 150.3 Hz, PCH$_2$), 34.85 (d, J = 151.4 Hz, PCH$_2$), 39.34 (s, SCH$_3$), 77.80 (s, CH (O^{i}Pr)), 78.02 (s, CH (O^{i}Pr)), 78.96 (s, CH (O^{i}Pr)), 79.53 (s, CH (O^{i}Pr)), 116.76 (d (J = 14.7 Hz), CH$_2$ (allyl)), 117.49 (d (J = 15.1 Hz), CH$_2$ (allyl)), 131.86 (d (J = 11.3 Hz), CH (allyl)), 132.65 (d (J = 10.9 Hz), CH (allyl)).

Ti$_8$O$_2$(O^{i}Pr)$_{12}$(O$_3$P(allyl))$_6$(O$_2$(O^{i}Pr)P(allyl))$_2$ (TiAllylPP & TiAllylPP2).

Bis(trimethylsilyl) allylphosphonate (200 mg, 0.8 mmol) was added in a ratio of 1:2 to 464 µl (1.6 mmol) of Ti(O^{i}Pr)$_4$ in 1 ml of isopropyl alcohol. Crystals of the cluster **TiAllylPP** or **TiAllylPP2** were obtained after 6 weeks. Yield 70 mg (30 %).
^{1}H NMR (C$_6$D$_6$, 250 MHz) δ (ppm) = 1.36 - 1.50 (m, 48H, CH$_3$ (O^{i}Pr), 1.62 - 1.80 (m, 48H, CH$_3$ (O^{i}Pr), 2.65 - 2.94 (m, 8H, PCH$_2$), 3.05 - 3.34 (m, 6H, PCH$_2$), 3.62 - 3.88 (m, 2H, PCH$_2$), 4.61 - 4.79 (m, 6H, CH (O^{i}Pr)), 5.11 - 538 (m, 24H, CH$_2$ (allyl) and CH (O^{i}Pr)), 5.50 - 5.65 (d, 2H, CH$_2$ (allyl)), 6.16 - 6.50 (m, 8H, CH (allyl)).
^{31}P NMR (C$_6$D$_6$, 101.2 MHz) δ (ppm) = 13.77, 13.99, 15.50, 15.69, 16.57.
^{13}C NMR (C$_6$D$_6$, 62.9 MHz) δ (ppm) = 23.89 (s, CH$_3$ (O^{i}Pr)), 24.06 (s, CH$_3$ (O^{i}Pr)), 24.73 (s, CH$_3$ (O^{i}Pr)), 24.84 (s, CH$_3$ (O^{i}Pr)), 25.11 (s, CH$_3$ (O^{i}Pr)), 25.28 (s, CH$_3$ (O^{i}Pr)), 25.34 (s, CH$_3$ (O^{i}Pr)), 32.84 (d (J = 145.5 Hz), PCH$_2$), 34.31 (d (J = 154.3 Hz), PCH$_2$), 34.86 (d (J = 149.9 Hz), PCH$_2$), 69.34 (s, CH (O^{i}Pr)), 69.45 (s, CH (O^{i}Pr)), 77.50 (s, CH (O^{i}Pr)), 77.72 (s, CH (O^{i}Pr)), 77.79 (s, CH (O^{i}Pr)), 78.07 (s, CH (O^{i}Pr)), 78.53 (s, CH (O^{i}Pr)), 78.69 (s, CH (O^{i}Pr)), 79.03 (s, CH (O^{i}Pr)), 79.26 (s, CH (O^{i}Pr)), 82.34 (s, CH (O^{i}Pr)), 82.67 (s, CH (O^{i}Pr)), 116.35 (d (J = 14.6 Hz), CH$_2$ (allyl)), 116.68 (d (J = 15.3 Hz), CH$_2$ (allyl)), 116.88 (d (J = 15.3 Hz), CH$_2$ (allyl)), 116.99 (d (J = 15.3 Hz), CH$_2$ (allyl)), 117.34 (d (J = 14.2 Hz), CH$_2$ (allyl)), 131.78 (d (J = 11.2 Hz), CH (allyl)), 131.90 (d (J = 10.6 Hz), CH (allyl)), 132.16 (d (J = 10.7 Hz), CH (allyl)), 132.70 (d (J = 11.6 Hz), CH (allyl)), 133.39 (d (J = 11.0 Hz), CH (allyl)).

Ti$_8$(μ_3- O)$_2$(μ_2- O^{i}Pr)$_6$(O^{i}Pr)$_8$(O$_3$PCH$_2$CH$_3$)$_6$(O$_2$(O^{i}Pr)PCH$_2$CH$_3$)$_2$ (TiEtPP).

Ti(O^{i}Pr)$_4$ (420 µl, 1.45 mmol) was diluted with 3 ml of ^{i}PrOH and 200 µl (0.72 mmol) of bis(trimethylsilyl) ethylphosphonate were added quickly. The mixture was stirred for 5 min. Crystals of **TiEtPP** were obtained after 4 weeks. Yield 40 mg (45 %).

^{1}H NMR (CDCl$_3$, 250 MHz) δ (ppm) = 1.02 - 1.48 (m, 120H, CH$_3$), 1.48 - 2.18 (m, 16H, CH$_2$), 4.42 - 4.70 (m, 6H, CH), 4.74 - 5.02 (m, 10H, CH).
^{31}P NMR (CDCl$_3$, 101.2 MHz) δ (ppm) = 18.91, 19.01, 19.22, 19.58, 20.11, 20.37, 20.61, 24.12.
^{13}C NMR (CD$_2$Cl$_2$, 62.90 MHz) δ (ppm) = 7.11 (d (J = 52.86), $\mathrm{PCH_2}\mathit{CH_3}$), 7.67 (d (J = 51.43 Hz), $\mathrm{PCH_2}\mathit{CH_3}$), 19.98 (d (J = 155.2 Hz), PCH$_2$), 23.97 (s, CH$_3$), 24.26 (s, CH$_3$ (O^{i}Pr)), 24.52 (s, CH$_3$ (O^{i}Pr)), 24.69 (s, CH$_3$ (O^{i}Pr)), 25.10 (s, CH$_3$ (O^{i}Pr)), 64.16 (s, CH (O^{i}Pr)), 68.45 (s, CH (O^{i}Pr)), 77.91 (s, CH (O^{i}Pr)), 79.02 (s, CH (O^{i}Pr)), 79.54 (s, CH (O^{i}Pr)).

$\mathbf{Ti_7(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_6(O^iPr)_6(O_3PCH_2CH_2CH_2Cl)_6}$ (TiClPrPP).

Bis(trimethylsilyl) 3-chloropropylphosphonate (300 µl, 1.11 mmol) was diluted with 2 ml of ^{i}PrOH and 576 µl (2 mmol) of Ti(O^{i}Pr)$_4$ were added quickly under inert atmosphere. After 14 weeks small crystals were obtained; for further growth 0.5 ml volatiles were removed *in vacuo* to obtain crystals suitable for single crystal XRD after additional 2 weeks. Yield 100 mg (17 %).
^{1}H NMR (CDCl$_3$, 250 MHz) δ (ppm) = 1.45 (d (J = 6.16 Hz), 36H, CH$_3$ (O^{i}Pr)), 1.62 (d (J = 6.32 Hz), 36H, CH$_3$ (μ_2- O^{i}Pr)), 1.91 (dt (J$_{\text{P-H}}$ = 18.96 Hz, J$_{\text{H-H}}$ = 7.11 Hz), 12H, PCH$_2$), 2.38 (m, 12H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2}$), 3.84 (t (J = 6.32 Hz), 12H, CH$_2$Cl), 4.68 (m, 6H, CH (O^{i}Pr)), 5.16 (m, 6H, CH (μ_2-O^{i}Pr)).
^{31}P NMR (CDCl$_3$, 101.2 MHz) δ (ppm) = 18.76.
^{13}C NMR (C$_6$D$_6$, 62.90 MHz) δ (ppm) = 24.33 (d (J = 148 Hz), PCH$_2$), 24.47 (s, CH$_3$ (O^{i}Pr), 24.74 (s, CH$_3$ (O^{i}Pr), 26.74 (d (J = 5 Hz), CH$_2$), 46.33 (d (J = 13 Hz), CH$_2$Cl), 78.46 (s, CH (O^{i}Pr)), 79.78 (s, CH (O^{i}Pr).
The ^{1}H-NMR spectrum shows a small triplet at 3.72, and the ^{31}P spectrum a small signal at 18.50 ppm for the bromo species.

$\mathbf{Ti_7(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_6(O^iPr)_6(O_3PCH_2C_6H_5)_6}$ (TiBzlPP).

Bis(trimethylsilyl) benzylphosphonate (200 µl, 0.64 mmol) was diluted with 1 ml of ^{i}PrOH and 370 µl (1.28 mmol) of Ti(O^{i}Pr)$_4$ were 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 (ppm) = 1.12 - 1.49 (m, 72H, CH$_3$ (O^{i}Pr)), 3.13 - 3.96 (m, 12H, PCH$_2$)), 4.45 - 5.41 (m, 12H, CH (O^{i}Pr)), 7.21 - 8.08 (m, 30H, CH (Ph)).
^{31}P NMR (CD$_2$Cl$_2$, 101.2 MHz) δ (ppm) = 13.13, 13.57, 15.39, 15.73, 23.63, 24.28.

$\mathbf{Ti_7(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_6(O^iPr)_6(O_3PCH_2CH_2CH_2Br)_6}$ (TiBrPrPP).

388 µl (1.34 mmol) of Ti(O^{i}Pr)$_4$ were added to 200 µl (0.67 mmol) of bis(trimethylsilyl) 3-bromopropylphosphonate in 2 ml of 2-propanol. Crystals suitable for single crystal XRD were obtained after 18 weeks. Yield 100 mg (39 %).
^{1}H NMR (C$_6$D$_6$, 250 MHz) δ (ppm) = 1.39 - 1.49 (m, 36H, CH$_3$ (O^{i}Pr)), 1.57 - 1.70 (m, 36H, CH$_3$ (O^{i}Pr)), 1.72 - 2.10 (m, 12H, PCH$_2$), 2.23 - 2.59 (m, 12H, CH$_2$), 3.42 - 3.76 (m, 10H, CH$_2$−Br), 3.90 - 3.98 (m, 2H, CH$_2$−Br), 4.59 - 4.75 (m, 5H, CH (O^{i}Pr)), 5.07 - 5.22 (m, 6H, CH (O^{i}Pr)), 5.29 - 5.40 (m, 5H, CH (O^{i}Pr)).
^{31}P NMR (C$_6$D$_6$, 101.2 MHz) δ (ppm) = 27.20, 27.71, 29.43, 29.62, 29.81, 30.12, 30.33.
^{13}C NMR (C$_6$D$_6$, 62.9 MHz) δ (ppm) = 24.29, 24.48, 24.75, 24.80, 24.96, 25.10, 26.54, 26.89, 27.20, 27.27, 27.41, 27.97, 34.48 (CH$_2$−Br), 34.56 (CH$_2$−Br), 34.71 (CH$_2$−Br), 34.81 (CH$_2$−Br),

35.70 ($CH_2{-}Br$), 35.94 ($CH_2{-}Br$), 78.03 (CH), 78.48 (CH), 79.09 (CH), 79.20 (CH), 79.36 (CH), 79.49 (CH), 79.81 (CH), 82.75 (CH) (signals in the range 24.29 - 27.97 result from PCH_2- and CH_3 groups).

$\mathbf{Ti_4O(O^iPr)_8(O_3P{-}xyl)_3(^iPrOH)}$ (TiXylPP).

Bis(trimethylsilyl) 3,5-dimethylphenylphosphonate (100 mg, 0.3 mmol) was diluted with 1 ml of ^{i}PrOH, and 176 µl (0.6 mmol) of $Ti(O^iPr)_4$ were added quickly. Crystals suitable for single crystal XRD were obtained after 3 weeks. Yield 100 mg (72 %).
^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.17 (d (J = 6.1 Hz), 18H, CH_3 (O^iPr)), 1.40 (d (J = 6.2 Hz), 18H, CH_3 (O^iPr)), 1.46 (d (J = 6.3 Hz), 18H, CH_3 (O^iPr)), 2.34 (s, 18H, CCH_3), 4.71 (m, 5H, CH (O^iPr)), 5.06 (m, 4H, CH (O^iPr)), 7.11 (s, 3H, CCH), 7.53 (d (J = 13.9 Hz), CCH).
^{31}P NMR ($CDCl_3$, 101.2 MHz) δ (ppm) = 10.18.
^{13}C NMR (C_6D_6, 62.90 MHz) δ (ppm) = 21.10 (s, CH_3 (O^iPr)), 24.79 (s, CH_3 (O^iPr)), 24.93 (s, CH_3 (O^iPr)), 78.12 (s, CH (O^iPr)), 78.33 (s, CH (O^iPr)), 79.33 (s, CH (O^iPr)), 129.47 (d (J = 10.7 Hz), *C*CH), 131.38 (d (J = 197 Hz), PC), 131.77 (s, C*CH*), 136.76 (d (J = 16 Hz), C (xyl)).

$\mathbf{Ti_4(\mu_2\text{-}O^iPr)(O^iPr)_7(O_3PMeNp)_4(^iPrOH)_2 \cdot 2\,^iPrOH}$ (TiNpMePP).

Bis(trimethylsilyl) 2-naphthylmethylphosphonate (420 mg, 1.15 mmol) was dissolved in 2 ml of ^{i}PrOH, and 665 µl (2.3 mmol) of $Ti(O^iPr)_4$ were added quickly. Crystals suitable for single crystal XRD were obtained after one day. Yield 200 mg (40 %).
^{1}H NMR (C_6D_6, 250 MHz) δ = 1.00 - 1.65 (m, 60H, CH_3), 3.20 - 3.90 (m, 8H, CH_2), 4.00 - 4.60 (m, 6H, CH), 5.00 - 5.60 (m, 6H, CH), 7.20 - 8.20 (m, 28H, CH (naphthyl)).
^{31}P NMR (C_6D_6, 101.2 MHz) δ (ppm) = 12.82, 13.24, 17.43, 21.62.
^{13}C NMR (C_6D_6, 62.90 MHz) δ (ppm) = 22.87 (s, CH_3), 23.60 (s, CH_3), 23.90 (s, CH_3), 24.05 (s, CH_3), 24.29 (s, CH_3), 24.56 (s, CH_3), 24.79 (s, CH_3), 24.93 (s, CH_3), 25.47 (s, CH_3), 25.81 (s, CH_3), 26.17 (s, CH_3), 26.34 (s, CH_3), 35.77 (d (J = 143 Hz), CH_2), 36.61 (d (J = 140 Hz), CH_2), 37.01 (d (J = 143 Hz), CH_2), 71.77 (s, CH (O^iPr)), 78.38 (s, CH (O^iPr)), 78.74 (s, CH (O^iPr)), 81.09 (s, CH (O^iPr)), 81.84 (s, CH (O^iPr)), 82.68 (s, CH (O^iPr)), 84.57 (s, CH (O^iPr)), 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).

$\mathbf{Ti_4(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_5(O_3PCCl_3)_3(DMF)}$ (TiCl3MePP).

250 µl (0.87 mmol) of bis(trimethylsilyl) trichloromethylphosphonate were added to a solution of 500 µl (1.75 mmol) of $Ti(O^iPr)_4$ in 1 ml of 2-propanol and 1 ml of dimethylformamide. Crystals of **TiCl3MePP** were obtained after 8 weeks. Yield 50 mg (9 %).
^{1}H NMR (C_6D_6, 250 MHz) δ = 1.21 - 1.50 (m, 30H, CH_3 (O^iPr)), 1.68 (broad d (J = 6.24), 18H, CH_3 (O^iPr)), 2.28 (s, 3H, CH_3-N), 2.38 (s, 3H, CH_3-N), 4.51 - 4.75 (m, 5H, CH (O^iPr)), 5.12 - 5.27 (m, 3H, CH (O^iPr)), 8.66 (s, 1H, CH (DMF)). ^{31}P NMR (C_6D_6, 101.2 MHz) δ (ppm) = 13.17, 13.07.
^{13}C NMR (C_6D_6, 62.90 MHz) δ (ppm) = 24.31 (CH_3 (O^iPr)), 24.91 (CH_3 (O^iPr)), 25.07 (CH_3 (O^iPr)), 25.66 (CH_3 (O^iPr)), 26.48 (CH_3 (O^iPr)), 31.67 (CH_3-N), 36.90 (CH_3-N), 76.06 (CH (O^iPr)), 76.22 (CH (O^iPr)), 79.20 (CH (O^iPr)), 81.79 (CH (O^iPr)), 81.91 (CH (O^iPr)), 169.4 (CH (DMF)) (the doublet for the C-Cl_3 group was not found).

$Ti_8(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_6(O^iPr)_{10}(PO_4)_2(O_3P{-}vinyl)_4 \cdot 2\,CH_2Cl_2$ (TiVinylPP).
261 µl (0.9 mmol) of $Ti(O^iPr)_4$ were added to 2 ml of a 0.45 molar solution of bis(trimethylsilyl) vinylphosphonate in CH_2Cl_2. 2 ml of 2-propanol were added afterwards and stirred for 5 min. Part of the solvent was removed *in vacuo* after 16 weeks and after further 3 weeks crystals of **TiVinylPP** were obtained in a solid non-crystalline matrix. Only a few crystals for single crystal XRD were obtained as yield.

8.4.7 Synthesis of phosphonate zirconium oxo cluster

$Zr_6(\mu_3\text{-}O)_2(\mu_2\text{-}O^nBu)_6(O^nBu)_6(O_3P{-}Ph)_4$ (ZrPhPP).
100 µl (0.33 mmol) of bis(trimethylsilyl) phenylphosphonate were added to 302 µl (0.66 mmol) of $Zr(O^nBu)_4$ in 2 ml of ^nBuOH. After 16 weeks at room temperature part of the solvent was removed from the clear solution. Crystals of **ZrPhPP** were obtained after 5 additional weeks at -20 °C. Yield 50 mg (22 %).
^1H NMR (CD_2Cl_2, 250 MHz) δ = 0.61 - 1.07 (m, 36H, CH_3), 1.08 - 1.86 (m, 48H, CH_2), 3.50 - 4.38 (m, 24H, CH_2-O), 7.30 - 7.53 (m, 12H, CH), 7.68 - 8.05 (m, 8H, CH).
^{31}P NMR (CD_2Cl_2, 101.2 MHz) δ (ppm) = 6.57.
^{13}C NMR (CD_2Cl_2, 62.9 MHz) δ (ppm) = 13.65 (CH_3), 13.93 (CH_3), 18.88 (*CH_2*-CH_3), 19.10 (*CH_2*-CH_3), 34.98 (*CH_2*-CH_2-O), 35.60 (*CH_2*-CH_2-O), 36.08 (*CH_2*-CH_2-O), 69.66 (*CH_2*-O), 69.92 (*CH_2*-O), 70.12 (*CH_2*-O), 127.58 (CH), 127.82 (CH), 130.87 (CH), 131.02 (CH) (some signals are obviously missing due to low concentration of the sample (10000 scans measured)).

8.4.8 Synthesis of phosphonate acetate titanium oxo cluster

$Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PEt)_2$ (TiOAcEtPP).
184 mg (0.72 mmol) of bis(trimethylsilyl) ethylphosphonate were added in a ratio of 1:4 to 840 µl (2.9 mmol) of $Ti(O^iPr)_4$ in 3 ml of isopropanol. 83 µl (1.4 mmol) of CH_3COOH were quickly added afterwards. After 8 weeks, the cluster (**TiOAcEtPP**) was obtained in good crystal quality. Yield 200 mg (43 %).
^1H NMR (C_6D_6, 250 MHz) δ (ppm) = 1.30 - 1.48 (m, 4H, CH_3 (ethyl)), 1.37 (d (J = 5.98 Hz), 12H, CH_3 (O^iPr)), 1.40 (d (J = 6.05 Hz), 12H, CH_3 (O^iPr)), 1.52 (d (J = 6.08 Hz), 12H, CH_3 (O^iPr)), 1.63 - 1.79 (m, 4H, CH_2), 1.78 (d (J = 6.28 Hz), 12H, CH_3 (O^iPr)), 1.84 (d (J = 6.30 Hz), 12H, CH_3 (O^iPr)), 2.00 (s, 6H, CH_3 (Ac)), 4.84 (m (J = 6.20 Hz), 2H, CH (O^iPr)), 5.03 (m (J = 6.12 Hz), 4H, CH (O^iPr)), 5.36 (m (J= 6.28 Hz), 4H, CH (O^iPr))
^{31}P NMR (C_6D_6, 101.2 MHz) δ (ppm) = 18.0.
^{13}C NMR (C_6D_6, 62.9 MHz) δ (ppm) = 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).

$Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2C_{10}H_7)_2$ (TiOAcNpMePP).

627 µl (2.16 mmol) of $Ti(O^iPr)_4$ were added to a solution of 62 µl (1.08 mmol) of CH_3COOH and 396 mg (1.08 mmol) of bis(trimethylsilyl) naphthylmethylphosphonate in 2 ml of isopropyl alcohol. After 5 min of stirring, the stirring bar was removed and the flask put for crystallization. After 3 months, crystals of **TiOAcNpMePP** were obtained in good quality. Yield 200 mg (25 %).

^{1}H NMR (C_6D_6, 400 MHz) δ (ppm) = 1.30 (d (J = 5.68 Hz), 12H, CH_3 (O^iPr)), 1.41 (d (J = 6.16 Hz), 12H, CH_3 (O^iPr)), 1.44 (d (J = 5.32 Hz), 12H, CH_3 (O^iPr)), 1.61 (d (J = 6.04 Hz), 12H, CH_3 (O^iPr)), 1.67 (d (J = 5.32 Hz), 12H, CH_3 (O^iPr)), 1.89 (s, 6H, CH_3 (Ac)), 3.32 (d ($J_{P\text{-}H}$ = 22.65 Hz), 4H, $P-CH_2$), 4.85 (m (J = 6.16 Hz), 2H, CH (O^iPr)), 4.95 (m, 4H, CH (O^iPr)), 5.23 (m (J = 6.06), 4H, CH (O^iPr)), 7.33 (t (J = 7.43 Hz), 2H, CH ($C_{10}H_7$)), 7.39 (t (J = 7.63 Hz), 2H, CH ($C_{10}H_7$)), 7.76 (d (J = 8.00 Hz), 2H, CH ($C_{10}H_7$)), 7.84 (d (J = 9.04 Hz), 2H, CH ($C_{10}H_7$)), 7.85 (d (J = 6.61 Hz), 2H, CH ($C_{10}H_7$)), 7.89 (d (J = 7.72 Hz), 4H, CH ($C_{10}H_7$)).

^{31}P NMR (C_6D_6, 162 MHz) δ (ppm) = 11.58.

^{13}C NMR (C_6D_6, 100.6 MHz) δ (ppm) = 23.49 (s, CH_3 (O^iPr)), 23.81 (s, CH_3 (O^iPr)), 24.16 (s, CH_3 (O^iPr)), 24.87 (s, CH_3 (O^iPr)), 25.31 (s, CH_3 (Ac)), 35.23 (d (J = 151.8 Hz), CH_2-P), 77.75 (s, CH (O^iPr)), 78.71 (s, CH (O^iPr)), 79.27 (s, CH (O^iPr)), 125.10 (s, CH ($C_{10}H_7$)), 125.54 (s, CH ($C_{10}H_7$)), 127.25 (s, CH ($C_{10}H_7$)), 128.74 (d (J = 8.78), CH ($C_{10}H_7$)), 129.32 (d (J = 4.61 Hz), *C*-CH_2 ($C_{10}H_7$)), 132.48 (s, CH ($C_{10}H_7$)), 132.56 (s, CH ($C_{10}H_7$)), 132.64 (d (J = 9.67 Hz), CH ($C_{10}H_7$)), 133.87 (s, C ($C_{10}H_7$)), 133.92 (s, C ($C_{10}H_7$)), 177.95 (s, COO).

$Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3P-vinyl)_2$ (TiOAcVinylPP).

2 ml of a 0.45 molar solution of (0.9 mmol) of bis(trimethylsilyl) vinylphosphonate in CH_2Cl_2 were added in a ratio of 1:2 to 522 µl (1.8 mmol) of $Ti(O^iPr)_4$ in 1 ml of isopropanol. 51.5 µl (0.9 mmol) of CH_3COOH were quickly added afterwards. After 5 months, the CH_2Cl_2 was removed and after additional 2 weeks crystals of **TiOAcVinylPP** in satisfactory quality were obtained. Yield 80 mg (21 %).

^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.38 (d (J = 6.16 Hz), 12H, CH_3 (O^iPr)), 1.39 (d (J = 6.16 Hz), 12H, CH_3 (O^iPr)), 1.52 (d (J = 6.10 Hz), 12H, CH_3 (O^iPr)), 1.80 (d (J = 6.32 Hz), 12H, CH_3 (O^iPr)), 1.84 (d (J = 6.32 Hz), 12H, CH_3 (O^iPr)), 1.99 (s, 6H, CH_3 (Ac)), 4.85 (m (J = 6.20 Hz), 2H, CH (O^iPr)), 5.05 (m (J = 6.12 Hz), 4H, CH (O^iPr)), 5.38 (m (J = 6.28 Hz), 4H, CH (O^iPr)), 5.72 (ddd ($J_{P\text{-}H}$ = 49.52 Hz, J_{trans} = 12.00 Hz, J_{cis} = 3.48), 4H, CH (vinyl)), 6.21 - 6.56 (m, 4H, CH_2 (vinyl)).

^{31}P NMR (C_6D_6, 101.2 MHz) δ (ppm) = 15.80.

^{13}C NMR (C_6D_6, 62.9 MHz) δ (ppm) = 23.61 (s, CH_3 (O^iPr)), 23.97 (s, CH_3 (O^iPr)), 24.28 (s, CH_3 (O^iPr)), 24.72 (s, CH_3 (O^iPr)), 25.26 (s, CH_3 (O^iPr)), 25.32 (s, CH_3 (Ac)), 77.78 (s, CH (O^iPr)), 78.66 (s, CH (O^iPr)), 79.49 (s, CH (O^iPr)), 128.95 (s, CH_2), 130.69 (d (J = 203.96 Hz), CH (vinyl)), 177.98 (C, COO).

$Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3P{-}allyl)_2$ (TiOAcAllylPP & TiOAcAllylPP2).

400 mg (1.6 mmol) of bis(trimethylsilyl) allylphosphonate were added in a ratio of 1:2 to 930 µl (3.2 mmol) of $Ti(O^iPr)_4$ in 2 ml of isopropanol. 91 µl (1.6 mmol) of CH_3COOH were quickly added afterwards. After 3 weeks, the cluster (**TiOAcAllylPP**) was obtained in good crystal quality. Yield 500 mg (48 %).

The cluster **TiOAcAllylPP2** was obtained when 12 ml (40.77 mmol) of $Ti(O^iPr)_4$ were quickly added to a mixture of 3.4 ml (13.6 mmol) of bis(trimethylsilyl) allylphosphonate and 1.55 ml (27.2 mmol) of acetic acid in 15 ml of 2-propanol. The solution was refluxed for 16 h. After cooling to room temperature a white powder precipitated. For higher yield, part of the 2-propanol was removed *in vacuo*. The resulting suspension was filtered and the powder washed twice with small portions of isopropanol and once with 0 °C hexane. After drying *in vacuo*, part of the powder was recrystallized from CH_2Cl_2 for single crystal XRD. Yield 6.92 g (80 %).

^{1}H NMR (CD_2Cl_2, 250 MHz) δ (ppm) = 1.11 (d (J = 6.13 Hz), 12H, CH_3 (O^iPr)), 1.20 (d (J = 6.10 Hz), 12H, CH_3 (O^iPr)), 1.34 (d (J = 6.23 Hz), 12H, CH_3 (O^iPr)), 1.43 (d (J = 6.33 Hz), 12H, CH_3 (O^iPr)), 1.47 (d (J = 6.48 Hz), 12H, CH_3 (O^iPr)), 1.90 (s, 6H, CH_3 (Ac)), 2.43 (dd ($J_{H\text{-}H}$ = 7.4 Hz; $J_{P\text{-}H}$ = 23.0 Hz), 4H, CH_2 (allyl)), 4.73 (m, 6H, CH (O^iPr)), 4.97 (m, 4H, CH (O^iPr)), 5.09 (m, 4H, CH_2 (allyl)), 5.90 (m, 2H, CH (allyl)).

^{31}P NMR (CD_2Cl_2, 101.2 MHz) δ (ppm) = 11.9.

^{13}C NMR (CD_2Cl_2, 62.9 MHz) δ (ppm) = 23.38 (s, CH_3), 23.61 (s, CH_3), 23.76 (s, CH_3), 24.38 (s, CH_3), 24.77 (s, CH_3), 24.89 (s, CH_3), 32.85 (d (J = 154.13 Hz), CH_2P), 77.21 (s, CH), 78.52 (s, CH), 80.05 (s, CH), 117.12 (d (J = 14.96 Hz), CH_2), 130.66 (d (J = 11.47 Hz), CH), 177.70 (s, COO).

$Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2CH_2CH_2Cl)_2$ (TiOAcClPrPP).

224 mg (0.74 mmol) of bis(trimethylsilyl) chloropropylphosphonate were added in a ratio of 1:4 to 860 µl (3.0 mmol) of $Ti(O^iPr)_4$ in 3 ml of isopropanol. 85 µl (1.5 mmol) of CH_3COOH were quickly added afterwards. After 3 weeks, the cluster (**TiOAcClPrPP**) was obtained in good crystal quality. Yield 100 mg (20 %).

^{1}H NMR (CD_2Cl_2, 250 MHz) δ (ppm) = 1.13 (d (J = 6.00 Hz), 12H, CH_3 (O^iPr)), 1.21 (d (J = 5.95 Hz), 12H, CH_3 (O^iPr)), 1.35 (d (J = 6.05 Hz), 12H, CH_3 (O^iPr)), 1.45 (d (J = 5.80 Hz), 12H, CH_3 (O^iPr)), 1.47 (d (J = 5.33 Hz), 12H, CH_3 (O^iPr)), 1.71 (m ($J_{H\text{-}H}$ = 7.30 Hz, $J_{P\text{-}H}$ = 18.72 Hz), 4H, $CH_2{-}P$), 1.92 (s, 6H, CH_3 (Ac)), 2.15 (m, 4H, CH_2), 3.75 (t (J = 6.71 Hz), 4H, $CH_2{-}Cl$), 4.76 (m (J = 6.58 Hz), 6H, CH (O^iPr)), 4.98 (m (J = 6.16 Hz), 4H, CH (O^iPr)).

^{31}P NMR (CD_2Cl_2, 101.2 MHz) δ (ppm) = 15.44.

^{13}C NMR (CD_2Cl_2, 62.9 MHz) δ (ppm) = 23.59 (s, CH_3), 23.91 (s, CH_3), 24.25 (s, CH_3), 24.37 (d (J = 157.3 Hz), $CH_2{-}P$), 24.71 (s, CH_3), 25.28 (s, CH_3), 27.57 (d (J = 4.94 Hz), CH_2), 44.94 (d (J = 12.97 Hz), $CH_2{-}Cl$), 77.82 (s, CH), 78.70 (s, CH), 79.54 (s, CH), 178.13 (s, COO).

$Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2Ph)_2$ (TiOAcBzlPP).

2.8 ml (9.5 mmol) of $Ti(O^iPr)_4$ and 365 µl (6.4 mmol) of CH_3COOH were added to a solution of 1 g (3.2 mmol) of bis(trimethylsilyl) benzylphosphonate in 20 ml of ^{i}PrOH. After refluxing for 16 h and cooling to room temperature, a cloudy mixture was obtained. The suspension was concentrated under vacuum conditions and filtered. After washing two times with small por-

tions of ^{i}PrOH and drying, a white powder of **TiOAcBzlPP** was obtained. For single crystal measurements, part of the powder was crystallized from CH_2Cl_2 to obtain crystals in very high quality. Yield 1 g (45 %).
^{1}H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.34 (d (J = 6.13 Hz), 12H, CH_3 (O^{i}Pr)), 1.42 (d (J = 6.20 Hz), 12H, CH_3 (O^{i}Pr)), 1.47 (d (J = 6.10 Hz), 12H, CH_3 (O^{i}Pr)), 1.67 (d (J = 6.25 Hz), 12H, CH_3 (O^{i}Pr)), 1.73 (d (J = 6.23 Hz), 12H, CH_3 (O^{i}Pr)), 1.98 (s, 6H, CH_3 (Ac)), 3.19 (d ($J_{P\text{-}H}$ = 22.54 Hz), 4H, P$-$$CH_2$), 4.87 (m (J = 6.21 Hz), 2H, CH (O^{i}Pr)), 4.97 (m (J = 6.04 Hz), 4H, CH (O^{i}Pr)), 5.25 (m (J = 6.24), 4H, CH (O^{i}Pr)), 7.2 (m, 2H, CH (C_6H_5)), 7.33 (t (J = 7.66 Hz), 4H, CH (C_6H_5)), 7.64 (d (J = 7.49 Hz), 4H, CH (C_6H_5)).
^{31}P NMR ($CDCl_3$, 101.2 MHz) δ (ppm) = 23.6.
^{13}C NMR (C_6D_6, 62.9 MHz) δ (ppm) = 23.62 (s, CH_3 (O^{i}Pr)), 23.84 (s, CH_3 (O^{i}Pr)), 24.20 (s, CH_3 (O^{i}Pr)), 24.86 (s, CH_3 (O^{i}Pr)), 25.35 (s, CH_3 (Ac)), 34.94 (d (J = 152.2 Hz), $CH_2$$-$P), 77.73 (s, CH (O^{i}Pr)), 78.69 (s, CH (O^{i}Pr)), 79.16 (s, CH (O^{i}Pr)), 125.83 (d (J = 2.96), CH (C_6H_5)), 130.51 (d (J = 6.82 Hz), CH (C_6H_5)), 134.91 (d (J = 9.07 Hz), *C*-CH_2, C_6H_5), 177.88 (s, COO).

$Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PCH_2CH_2CH_2Br)_2$ (TiOAcBrPrPP).

29 ml (100 mmol) of Ti(O^{i}Pr)$_4$ and 3.83 ml (67 mmol) of CH_3COOH were added to a solution of 11.63 g (33.4 mmol) of bis(trimethylsilyl) 3-bromopropylphosphonate in 50 ml of ^{i}PrOH. After refluxing for 16 h and cooling to room temperature, a cloudy mixture was obtained. The suspension was concentrated under vacuum conditions and filtered. After washing two times with n-hexane and drying, a white powder of **TiOAcBrPrPP** was obtained. For single crystal measurements, part of the powder was crystallized from CH_2Cl_2 to obtain crystals in very high quality. Yield 8 g (33 %).
TiOAcBrPrPP was also obtained when 777 µl (2.68 mmol) of Ti(O^{i}Pr)$_4$ were added to a solution of 200 µl (0.67 mmol) of bis(trimethylsilyl) 3-bromopropylphosphonate and 77 µl (1.34 mmol) of acetic acid in 2 ml of 2-propanol. Crystals of **TiOAcBrPrPP** were obtained after 6 weeks at room temperature. Yield 120 mg (24 %).
^{1}H NMR (C_6D_6, 250 MHz) δ (ppm) = 1.37 (d (J = 6.15 Hz), 12H, CH_3 (O^{i}Pr)), 1.41 (d (J = 6.40 Hz), 12H, CH_3 (O^{i}Pr)), 1.51 (d (J = 6.08 Hz), 12H, CH_3 (O^{i}Pr)), 1.71 (m, 4H, $CH_2$$-$P), 1.76 (d (J = 6.16 Hz), 12H, CH_3 (O^{i}Pr)), 1.82 (d (J = 5.90 Hz), 12H, CH_3 (O^{i}Pr)), 2.04 (s, 6H, CH_3 (Ac)), 2.35 (m ($J_{H\text{-}H}$ = 7.23 Hz, $J_{P\text{-}H}$ = 17.30 Hz), 4H, CH_2), 3.52 (t (J = 7.35 Hz), 4H, $CH_2$$-$Br), 4.85 (m (J = 6.20 Hz), 2H, CH (O^{i}Pr)), 5.00 (m (J = 6.00 Hz), 4H, CH (O^{i}Pr)), 5.33 (m (J = 6.28 Hz), 4H, CH (O^{i}Pr)).
^{31}P NMR (C_6D_6, 101.2 MHz) δ (ppm) = 15.5.
^{13}C NMR (C_6D_6, 62.9 MHz) δ (ppm) = 23.64 (s, CH_3), 23.91 (s, CH_3), 24.25 (s, CH_3), 24.74 (s, CH_3), 25.29 (s, CH_3), 25.33 (s, CH_3), 25.71 (d (J = 157.2 Hz), $CH_2$$-$P), 27.85 (d (J = 4.49 Hz), CH_2), 33.71 (d (J = 12.98 Hz), $CH_2$$-$Br), 77.83 (s, CH), 78.70 (s, CH), 79.54 (s, CH), 178.14 (s, COO).

$Ti_6O_4(O^iPr)_{10}(OAc)_2(O_3PC_6H_5)_2$ (TiOAcPhPA).

534 mg (3.38 mmol) of phenylphosphonic acid were dissolved (by heating) in 10 ml of 2-propanol, and 386 µl (6.76 mmol) of acetic acid were added. When the solution was cooled to room temperature, 3 ml (10.1 mmol) of $Ti(O^iPr)_4$ were added, resulting in a cloudy suspension. The suspension was heated to reflux (a clear solution was obtained after heating) and after reflux for 16 h a suspension was obtained. After filtration, the solid residue was recrystallized from CH_2Cl_2. Crystals of **TiOAcPhPA** were grown for single crystal XRD, so the structure contains two solvent CH_2Cl_2. Yield 300 mg (12 %).
^1H NMR ($CDCl_3$, 250 MHz) δ (ppm) = 1.32 (d (J = 6.13 Hz), 12H, CH_3 (O^iPr)), 1.37 (d (J = 6.20 Hz), 12H, CH_3 (O^iPr)), 1.46 (d (J = 6.10 Hz), 12H, CH_3 (O^iPr)), 1.82 (d (J = 6.00 Hz), 12H, CH_3 (O^iPr)), 1.85 (d (J = 6.00 Hz), 12H, CH_3 (O^iPr)), 2.02 (s, 6H, CH_3 (Ac)), 4.38 (s, 2H, CH_2Cl_2), 4.83 (m (J = 6.20 Hz), 2H, CH (O^iPr)), 5.03 (m (J = 6.12 Hz), 4H, CH (O^iPr)), 5.41 (m (J = 6.28), 4H, CH (O^iPr)), 7.22 (m, 2H, CH (C_6H_5)), 7.36 (m (J = 3.79 Hz), 4H, CH (C_6H_5)), 8.37 (dd ($J_{\text{P-H}}$ = 13.76 Hz, $J_{\text{H-H}}$ = 6.93 Hz), 4H, CH (C_6H_5)).
^{31}P NMR (C_6D_6, 101.2 MHz) δ (ppm) = 16.06.
^{13}C NMR (C_6D_6, 50.32 MHz) δ (ppm) = 23.87 (s, CH_3 (O^iPr)), 24.30 (s, CH_3 (O^iPr)), 24.52 (s, CH_3 (O^iPr)), 24.79 (s, CH_3 (O^iPr)), 24.92 (s, CH_3 (O^iPr)), 25.50 (s, CH_3 (Ac)), 78.08 (s, CH (O^iPr)), 79.02 (s, CH (O^iPr)), 79.86 (s, CH (O^iPr)), 128.275 (s, CH C_6H_5), 130.52 (d (J = 2.95 Hz), CH C_6H_5), 131.21 (d (J = 9.49 Hz), CH C_6H_5), 134.68 (d (J = 208.20 Hz), CH C_6H_5), 178.38 (s, COO).

$Ti_5O(O^iPr)_{11}(OAc)(O_3PCH_2CH_2CH_2Br)_3$ (TiOAcBrPrPP2).

233 mg (0.67 mmol) of bis(trimethylsilyl) 3-bromopropylphosphonate were added in a ratio of 1:2 to 388 µl (2.9 mmol) of $Ti(O^iPr)_4$ in 2 ml of isopropanol. 38.3 µl (0.67 mmol) of CH_3COOH were added quickly afterwards. After 12 weeks, the cluster (**TiOAcBrPrPP2**) was obtained in satisfactory crystal quality. Yield 200 mg (57 %).
^1H NMR (C_6D_6, 250 MHz) δ (ppm) = 1.38 (d (J = 7.90 Hz), 6H, CH_3 (O^iPr)), 1.41 (d (J = 6.40 Hz), 6H, CH_3 (O^iPr)), 1.45 (d (J = 6.15 Hz), 18H, CH_3 (O^iPr)), 1.51 (d (J = 6.05 Hz), 6H, CH_3 (O^iPr)), 1.63 (d (J = 6.30 Hz), 12H, CH_3 (O^iPr)), 1.79 (m, 18H, CH_3 (O^iPr)), 1.85 - 2.01 (m, 6H, CH_2-P), 2.04 (s, 3H, CH_3 (Ac)), 2.29 - 2.54 (m, 6H, CH_2), 3.52 (t (J = 7.23 Hz), 2H, CH_2-Br), 3.71 (t (J = 6.40 Hz), 4H, CH_2-Br), 4.69 (m (J = 6.20 Hz), 2H, CH (O^iPr)), 4.84 (m (J = 6.28 Hz), 1H, CH (O^iPr)), 5.00 (m (J = 6.16 Hz), 2H, CH (O^iPr)), 5.16 (m (J = 6.44 Hz), 3H, CH (O^iPr)), 5.33 (m (J = 6.24 Hz), 3H, CH (O^iPr)).
^{31}P NMR (C_6D_6, 101.2 MHz) δ (ppm) = 27.44 (1P), 30.34 (2P).
^{13}C NMR (C_6D_6, 62.9 MHz) δ (ppm) = 23.65 (s, CH_3), 23.96 (s, CH_3), 24.26 (s, CH_3), 24.49 (s, CH_3), 24.74 (s, CH_3), 24.81 (s, CH_3), 25.22 (s, CH_3), 25.31 (s, CH_3), 26.95 (d (J = 4.52 Hz), CH_2), 27.86 (d (J = 4.99 Hz), CH_2), 33.73 (d (J = 12.59 Hz), CH_2-Br), 35.82 (d (J = 15.06 Hz), CH_2-Br), 77.84 (s, CH), 78.49 (s, CH), 78.73 (s, CH), 79.57 (s, CH), 79.82 (s, CH), 178.17 (s, COO).

$Ti_5O_3(O^iPr)_6(OAc)_4(O_3P{-}xylyl)_2$ (TiOAcXylPP).

100 mg (0.30 mmol) of bis(trimethylsilyl) xylylphosphonate were added to a solution of 176 µl (0.61 mmol) of $Ti(O^iPr)_4$ in 1 ml of isopropanol. 35 µl (0.61 mmol) of CH_3COOH were added afterwards. After 15 weeks, the cluster (**TiOAcXylPP**) was obtained in good crystal quality. Yield 200 mg (48 %).
^{1}H NMR (C_6D_6, 250MHz) δ (ppm) = 1.46 (d (J = 6.15 Hz), 6H, CH_3 (O^iPr)), 1.51 (d (J = 6.78 Hz), 6H, CH_3 (O^iPr)), 1.54 (d (J = 6.33 Hz), 12H, CH_3 (O^iPr)), 1.90 (d (J = 6.20 Hz), 6H, CH_3 (O^iPr)), 1.91 (d (J = 6.32 Hz), 6H, CH_3 (O^iPr)), 1.95 (s, 6H, CH_3 (Ac)), 1.98 (s, 6H, CH_3 (Ac)), 2.18 (s, 12H, CH_3 (Xyl)), 5.07 (m (J = 6.20 Hz), 2H, CH (O^iPr)), 5.22 (m (J = 6.12 Hz), 2H, CH (O^iPr)), 5.66 (m (J = 6.32 Hz), 2H, CH (O^iPr)), 6.91 (s, 2H, CH (Xyl)), 8.03 (s, 2H, CH (Xyl)), 8.08 (s, 2H, CH (Xyl)).
^{31}P NMR (C_6D_6, 101.2 MHz) δ (ppm) = 15.92.
^{13}C NMR (C_6D_6, 62.9 MHz) δ (ppm) = 20.92 (s, CH_3), 22.90 (s, CH_3), 23.30 (s, CH_3), 23.93 (s, CH_3), 24.05 (s, CH_3), 24.11 (s, CH_3), 24.16 (s, CH_3), 24.60 (s, CH_3), 24.77 (s, CH_3), 25.19 (s, CH_3), 80.57 (s, CH (O^iPr)), 81.41 (s, CH (O^iPr)), 82.27 (s, CH (O^iPr)), 129.80 (d (J = 10.0 Hz), CH), 131.44 (d (J = 201.0 Hz), C-P), 132.53 (d (J = 2.8 Hz), CH), 137.24 (d (J = 16.3 Hz), C), 177.87 (s, COO), 180.11 (s, COO).

8.4.9 Synthesis of phosphonate titanium oxo cluster under the presence of water

$Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(O^iPr)_{10}(O_3P{-}Ph)_2(O_2(O^iPr)P{-}Ph)_2$ (TiOPhPP).

3 µl (0.17 mmol) of water in 400 µl of ^{i}PrOH were added to 192 µl (0.66 mmol) of $Ti(O^iPr)_4$. To this solution were added 100 µl (0.33 mmol) of bis(trimethylsilyl) phenylphosphonate and stirred for 5 minutes. Crystals of **TiOPhPP** were obtained after 32 weeks. Yield 33 mg (36 %).
The same unit cell was found for the product of another reaction. In this reaction, a mixture of 200 µl (0.66 mmol) of bis(trimethylsilyl) phenylphosphonate and 166 µl (0.66 mmol) of bis(trimethylsilyl) allylphosphonate were added to a solution of 770 µl (2.65 mmol) of $Ti(O^iPr)_4$ in 3 ml of 2-propanol. A crystalline solid was obtained after 4 months which was recrystallized from CH_2Cl_2 to obtain crystals of **TiOPhPP** in satisfactory quality. Yield 50 mg (28 %).

8.4.10 Synthesis of phosphonate methacrylate titanium oxo cluster

$Ti_5O(O^iPr)_{11}(OMc)(O_3PCH_2CH_3)_3$ (TiOMcEtPP).

1.6 ml (5.42 mmol) of $Ti(O^iPr)_4$ were added to a solution of 500 µl (1.81 mmol) of bis(trimethylsilyl) ethylphosphonate and 153 µl (1.81 mmol) of methacrylic acid in 2 ml of isopropanol. After 5 min of stirring, the solution was put for crystallization. After 8 weeks, crystals of **TiOMcEtPP** were obtained in good quality. Yield 410 mg (35 %).
The obtained powder was washed with isopropyl alcohol and hexane. NMR measurements were carried out in C_6D_6, but the spectrum showed numerous signals which will not be listed here.

It is assumed that a mixture of different compounds was obtained initially and only the well crystallizing **TiOMcEtPP** was characterized by single crystal XRD. In the ^{31}P NMR spectrum, 2 peaks of different intensity were expected, while 8 were found. ^{1}H NMR and ^{13}C NMR data were not interpretable due to the high number of signals. Due to these circumstances, no NMR data of **TiOMcEtPP** will be listed here.

$Ti_{10}(O^iPr)_{16}(OMc)_4(O_3PCH_2CHCH_2)_{10}$ (TiOMcAllylPP).

7.1 ml (5.42 mmol) of $Ti(O^iPr)_4$ were added to a solution of 2 ml (1.81 mmol) of bis(trimethylsilyl) allylphosphonate and 1.35 ml (1.81 mmol) of methacrylic acid in 12 ml of isopropanol. The solution was heated to reflux for 16 h to obtain a suspension. After filtration, the residue was crystallized from CH_2Cl_2. Crystals of **TiOMcAllylPP** were grown in satisfactory quality. Yield 120 mg (5 %).

Unexpectedly, the crystals were insoluble in CD_2Cl_2 and any other non coordinating organic solvent after recrystallization and therefore no NMR measurements were conducted.

Part IV

Appendix

Appendix A

Distances and Angles

Table A.1: *Selected bond lengths and atom distances [pm] of* ***TiCycloBu*** *and* ***TiBenzCl****.*

TiCycloBu		**TiBenzCl**	
Metal-metal distances			
Ti(1)-Ti(2)	285.05(14)	Ti(1)-Ti(2)	359.2(3)
Ti(1)-Ti(3)	363.00(15)	Ti(1)-Ti(2)*	360.7(3)
Ti(2)-Ti(3)	347.07(14)	Ti(2)-Ti(2)*	287.8(3)
Ti(3)-Ti(2)*	340.22(14)		
Selected bond lengths			
Ti-O bond lengths of the oxo-bridges			
Ti(1)-O(1)	209.0(3)	Ti(1)-O(1)	206.5(5)
Ti(2)-O(1)	186.4(3)	Ti(2)-O(1)	191.4(5)
Ti(3)-O(1)	192.1(3)	O(1)-Ti(2)*	192.3(5)
Ti(1)-O(2)	183.6(4)		
Ti(2)-O(2)	180.8(4)		
Ti(2)-O(3)	200.4(4)		
Ti(3)-O(3)	172.2(4)		
Ti-O bond lengths of the terminal alkoxo groups			
Ti(1)-O(4)	176.5(4)	Ti(1)-O(8)	178.5(6)
		Ti(1)-O(9)	176.9(6)
		Ti(2)-O(10)	175.8(6)
Ti-O bond lengths of the bridging carboxylates			
Ti(1)-O(5)	204.0(4)	Ti(1)-O(2)	206.1(6)
Ti(1)-O(7)	200.9(4)	Ti(1)-O(4)	208.1(6)
Ti(1)-O(9)	201.0(4)	Ti(1)-O(6)	202.8(6)
Ti(2)-O(6)	203.5(4)	Ti(2)-O(3)	203.9(6)
Ti(2)-O(11)	203.2(4)	Ti(2)-O(5)	205.9(6)
Ti(2)-O(13)	201.0(4)	Ti(2)-O(7)	206.9(6)
Ti(3)-O(8)	215.3(4)		
Ti(3)-O(10)	201.0(4)		
Ti(3)-O(12)	206.3(4)		
Ti(3)-O(14)	201.3(4)		

Table A.2: *Selected bond angles [°] of* ***TiCycloBu*** *and* ***TiBenzCl****.*

TiCycloBu		**TiBenzVinyl**.	
Ti(2)-O(1)-Ti(3)	132.93(19)	Ti(1)-O(1)-Ti(2)	129.0(3)
Ti(2)-O(1)-Ti(1)	92.06(14)	Ti(1)-O(1)-Ti(2)*	129.5(3)
Ti(3)-O(1)-Ti(1)	129.56(17)	Ti(2)-O(1)-Ti(2)*	97.2(2)
Ti(2)-O(2)-Ti(1)	102.92(18)		
Ti(3)-O(3)-Ti(2)	131.7(2)		
Oxygen atoms in trans position on the octahedrally coordinated Ti atom			
O(2)-Ti(1)-O(7)	164.06(16)	O(1)-Ti(1)-O(8)	170.6(3)
O(4)-Ti(1)-O(1)	177.83(18)	O(2)-Ti(1)-O(6)	174.2(2)
O(9)-Ti(1)-O(5)	167.47(15)	O(4)-Ti(1)-O(9)	173.5(3)
O(1)-Ti(2)-O(11)	177.31(16)	O(1)-Ti(2)-O(7)*	174.6(2)
O(2)-Ti(2)-O(3)	178.48(16)	O(3)-Ti(2)-O(1)*	165.3(2)
O(13)-Ti(2)-O(6)	176.58(16)	O(5)-Ti(2)-O(10)	166.7(3)
O(1)-Ti(3)-O(12)	169.54(16)		
O(3)-Ti(3)-O(8)	168.37(17)		
O(10)-Ti(3)-O(14)	165.55(16)		
Oxygen atoms in cis position on the octahedrally coordinated Ti atom			
O-Ti(1)-O	84.81(17) - 101.04(17)	O-Ti(1)-O	170.6(3) - 174.2(2)
O-Ti(2)-O	84.82(15) - 96.33(15)	O-Ti(2)-O	165.3(2) - 174.6(2)
O-Ti(3)-O	79.51(15) - 100.29(17)		

Table A.3: *Bond lengths and atom distances [pm] for* ***TiTPA****,* ***TiAda*** *and* ***ZrAda***

TiTPA		**TiAda**		**ZrAda**	
Metal-metal distances					
Ti(1)-Ti(2)	289.19(7)	Ti(1)-Ti(2)	317.55(4)	Zr(1)-Zr(2)	349.37(6)
Ti(1)-Ti(3)	354.35(8)	Ti(1)-Ti(3)	357.31(4)	Zr(1)-Zr(3)	352.81(7)
Ti(2)-Ti(3)	352.11(8)	Ti(2)-Ti(3)	350.54(4)	Zr(1)-Zr(4)	350.03(6)
		Ti(4)-Ti(5)	317.59(4)	Zr(1)-Zr(5)	348.98(6)
		Ti(4)-Ti(6)	3.5708(4)	Zr(2)-Zr(3)	349.35(6)
		Ti(5)-Ti(6)	3.5017(4)	Zr(2)-Zr(5)	353.10(6)
				Zr(2)-Zr(6)	352.99(6)
				Zr(3)-Zr(4)	350.15(6)
				Zr(3)-Zr(6)	348.98(6)
				Zr(4)-Zr(5)	348.64(6)
				Zr(4)-Zr(6)	348.61(6)
				Zr(5)-Zr(6)	351.32(6)
Selected bond lengths					
Metal to oxygen distances for oxo bridges					
Ti(1)-O(1)	200.11(17)	Ti(1)-O(1)	210.07(11)	Zr(1)-O(2)	210.3(3)
Ti(2)-O(1)	197.86(16)	Ti(2)-O(1)	208.59(12)	Zr(3)-O(2)	210.5(3)
Ti(3)-O(1)	189.58(17)	Ti(3)-O(1)	180.01(12)	Zr(4)-O(2)	208.9(3)
Ti(1)-O(2)	184.54(18)	Ti(4)-O(16)	210.01(11)	Zr(1)-O(4)	204.9(3)
Ti(2)-O(2)	183.68(18)	Ti(5)-O(16)	208.79(12)	Zr(2)-O(4)	205.8(3)
		Ti(6)-O(16)	179.63(12)	Zr(5)-O(4)	205.5(3)
Ti-O distances for alkoxo ligands				Zr(2)-O(5)	206.3(3)
Terminal alkoxo ligands				Zr(3)-O(5)	204.2(3)
Ti(1)-O(14)	176.34(18)	Ti(1)-O(11)	177.55(12)	Zr(6)-O(5)	205.4(3)
Ti(2)-O(13)	176.82(17)	Ti(1)-O(12)	179.14(12)	Zr(4)-O(7)	203.5(3)
Ti(3)-O(15)	177.65(18)	Ti(2)-O(13)	179.15(12)	Zr(5)-O(7)	205.5(3)
		Ti(2)-O(14)	178.29(12)	Zr(6)-O(7)	205.1(3)
		Ti(3)-O(15)	178.05(12)	Zr-O distances for hydroxo-bridges	
		Ti(4)-O(26)	178.28(12)	*Zr(1)-O(1)*	221.8(3)
		Ti(4)-O(27)	178.83(12)	Zr(2)-O(1)	235.9(3)
		Ti(5)-O(28)	179.03(12)	Zr(3)-O(1)	221.8(3)
		Ti(5)-O(29)	179.08(12)	Zr(1)-O(3)	219.1(3)
		Ti(6)-O(30)	177.88(12)	Zr(4)-O(3)	219.0(3)
Bridging alkoxo ligands				Zr(5)-O(3)	239.6(3)
		Ti(1)-O(10)	200.65(12)	Zr(3)-O(6)	219.1(3)
		Ti(2)-O(10)	197.26(12)	Zr(4)-O(6)	219.0(3)
		Ti(4)-O(25)	201.43(12)	Zr(6)-O(6)	239.6(3)
		Ti(5)-O(25)	196.40(12)	Zr(2)-O(8)	226.9(3)
				Zr(5)-O(8)	226.4(3)
				Zr(6)-O(8)	226.0(3)

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TiTPA		**TiAda**		**ZrAda**	
Metal-oxygen distances for carboxylate ligands					
Ti(1)-O(3)	204.05(18)	Ti(1)-O(2)	209.12(12)	Zr(1)-O(9)	224.1(3)
Ti(1)-O(5)	213.81(18)	Ti(1)-O(4)	204.40(13)	Zr(1)-O(10)	228.1(3)
Ti(1)-O(7)	203.27(17)	Ti(2)-O(3)	209.46(12)	Zr(1)-O(11)	221.4(3)
Ti(2)-O(4)	205.13(17)	Ti(2)-O(9)	207.16(12)	Zr(1)-O(13)	222.4(3)
Ti(2)-O(9)	204.41(17)	Ti(3)-O(5)	200.15(14)	Zr(2)-O(14)	219.7(3)
Ti(2)-O(11)	213.22(18)	Ti(3)-O(6)	219.59(12)	Zr(2)-O(15)	219.9(3)
Ti(3)-O(6)	199.37(17)	Ti(3)-O(7)	209.84(13)	Zr(2)-O(17)	221.1(3)
Ti(3)-O(8)	203.15(17)	Ti(3)-O(8)	199.82(12)	Zr(2)-O(19)	221.2(3)
Ti(3)-O(10)	202.17(17)	Ti(4)-O(17)	207.99(12)	Zr(3)-O(16)	222.4(3)
Ti(3)-O(12)	201.27(17)	Ti(4)-O(19)	204.87(13)	Zr(3)-O(21)	224.3(3)
		Ti(5)-O(18)	209.89(12)	Zr(3)-O(22)	228.2(3)
		Ti(5)-O(21)	206.24(12)	Zr(3)-O(23)	221.3(3)
		Ti(6)-O(20)	199.60(15)	Zr(4)-O(25)	230.3(3)
		Ti(6)-O(22)	200.57(13)	Zr(4)-O(26)	230.5(3)
		Ti(6)-O(23)	210.24(14)	Zr(4)-O(27)	221.2(3)
		Ti(6)-O(24)	218.28(13)	Zr(4)-O(29)	221.0(3)
				Zr(5)-O(12)	216.3(3)
				Zr(5)-O(20)	221.5(3)
				Zr(5)-O(28)	218.3(3)
				Zr(5)-O(31)	221.7(3)
				Zr(6)-O(18)	221.6(3)
				Zr(6)-O(24)	216.0(3)
				Zr(6)-O(30)	218.5(3)
				Zr(6)-O(32)	221.7(3)

*Table A.4: Selected bond angles [°] of **TiTPA**, **TiAda** and **ZrAda**.*

TiTPA		**TiAda**		**ZrAda**	
Ti(1)-O(1)-Ti(2)	93.22(7)	Ti(1)-O(1)-Ti(2)	98.66(5)	Zr(1)-O(2)-Zr(3)	113.92(12)
Ti(1)-O(1)-Ti(3)	130.80(9)	Ti(1)-O(1)-Ti(3)	132.54(6)	Zr(1)-O(2)-Zr(4)	113.24(13)
Ti(2)-O(1)-Ti(3)	130.66(9)	Ti(2)-O(1)-Ti(3)	128.71(6)	Zr(3)-O(2)-Zr(4)	113.20(13)
Ti(1)-O(2)-Ti(2)	103.51(9)	Ti(4)-O(16)-Ti(5)	98.63(5)	Zr(1)-O(4)-Zr(2)	116.60(13)
		Ti(4)-O(16)-Ti(6)	132.67(6)	Zr(1)-O(4)-Zr(5)	116.52(14)
		Ti(5)-O(16)-Ti(6)	128.56(6)	Zr(2)-O(4)-Zr(5)	118.30(14)
Oxygen atoms in trans position on the octahedrally coordinated Ti atom				Zr(2)-O(5)-Zr(3)	116.66(13)
O(1)-Ti(1)-O(14)	176.56(8)	O(1)-Ti(1)-O(12)	167.09(5)	Zr(2)-O(5)-Zr(6)	118.06(13)
O(2)-Ti(1)-O(5)	164.28(8)	O(2)-Ti(1)-O(11)	173.28(6)	Zr(3)-O(5)-Zr(6)	116.85(14)
O(3)-Ti(1)-O(7)	168.36(8)	O(4)-Ti(1)-O(10)	164.93(5)	Zr(4)-O(7)-Zr(5)	116.95(13)
O(13)-Ti(2)-O(1)	175.60(8)	O(1)-Ti(2)-O(13)	167.24(5)	Zr(4)-O(7)-Zr(6)	117.12(13)
O(2)-Ti(2)-O(11)	162.45(7)	O(3)-Ti(2)-O(14)	171.33(6)	Zr(5)-O(7)-Zr(6)	117.66(13)
O(9)-Ti(2)-O(4)	168.33(8)	O(9)-Ti(2)-O(10)	165.91(5)	Zr(1)-O(1)-Zr(2)	99.48(11)
O(1)-Ti(3)-O(15)	173.54(8)	O(1)-Ti(3)-O(6)	160.02(5)	Zr(1)-O(1)-Zr(3)	105.37(11)
O(6)-Ti(3)-O(10)	173.95(8)	O(5)-Ti(3)-O(8)	164.45(6)	Zr(2)-O(1)-Zr(4)	99.47(11)
O(8)-Ti(3)-O(12)	174.94(7)	O(7)-Ti(3)-O(15)	152.61(5)	Zr(1)-O(3)-Zr(4)	106.04(11)
		O(16)-Ti(4)-O(27)	166.87(5)	Zr(1)-O(3)-Zr(5)	98.96(11)
		O(17)-Ti(4)-O(26)	172.84(6)	Zr(4)-O(3)-Zr(5)	98.86(10)
		O(19)-Ti(4)-O(25)	165.20(5)	Zr(3)-O(6)-Zr(6)	98.98(11)
		O(16)-Ti(5)-O(28)	167.38(5)	Zr(3)-O(6)-Zr(4)	106.12(12)
		O(18)-Ti(5)-O(29)	168.34(6)	Zr(4)-O(6)-Zr(6)	98.85(10)
		O(21)-Ti(5)-O(25)	166.41(5)	Zr(2)-O(8)-Zr(5)	102.33(12)
		O(16)-Ti(6)-O(24)	160.29(5)	Zr(2)-O(8)-Zr(6)	102.40(12)
		O(20)-Ti(6)-O(22)	163.53(6)	Zr(5)-O(8)-Zr(6)	101.89(11)
		O(23)-Ti(6)-O(30)	152.92(6)		
Oxygen atoms in cis position on the octahedrally coordinated Ti atom					
O-Ti(1)-O	79.68(7) - 103.53(9)	O-Ti(1)-O	76.30(5) - 98.98(6)		
O-Ti(2)-O	80.48(7) - 103.76(8)	O-Ti(2)-O	77.37(5) - 98.95(6)		
O-Ti(3)-O	85.64(7) - 95.99(7)	O-Ti(3)-O	60.81(5) - 108.08(5)		
		O-Ti(4)-O	76.08(5) - 99.15(6)		
		O-Ti(5)-O	80.88(5) - 99.95(6)		
		O-Ti(6)-O	60.99(5) - 107.59(5)		

Table A.5: *Selected bond lengths and atom distances [pm] of* ***TiBuImid*** *and* ***TiBenzMeCl****.*

TiBuImid		**TiBenzMeCl**	
	Metal-metal distances		
		Ti(1)-Ti(2)	324.38(7)
	Selected bond lengths		
Ti(1)-O(1)	183.42(11)	Ti(1)-O(1)	208.73(19)
Ti(1)-O(2)	217.34(11)	Ti(1)-O(3)	200.6(2)
Ti(1)-O(3)	217.82(11)	Ti(1)-O(5)	204.05(19)
Ti(1)-O(4)	177.80(11)	Ti(1)-O(6)	205.27(19)
Ti(1)-O(5)	181.40(11)	Ti(1)-O(7)	179.6(2)
Ti(1)-N(2)	223.79(13)	Ti(1)-O(8)	178.1(2)
		Ti(2)-O(2)	204.4(2)
		Ti(2)-O(5)	203.63(18)
		Ti(2)-O(6)	204.26(19)
		Ti(2)-O(9)	180.0(2)
		Ti(2)-O(10)	178.1(2)
		Ti(2)-O(11)	203.8(2)
		C(1)-O(1)	125.1(3)
		C(1)-O(2)	126.3(3)
		C(9)-O(3)	126.6(3)
		C(9)-O(4)	124.1(4)
		O(4)-O(11)	253.26(28)

Table A.6: *Selected bond angles [°] of* ***TiBuImid*** *and* ***TiBenzMeCl****.*

TiBuImid		**TiBenzMeCl**	
O(2)-C(6)-O(3)	118.58(13)	Ti(1)-O(5)-Ti(2)	105.44(8)
O(1)-Ti(1)-N(2)	168.91(5)	Ti(1)-O(6)-Ti(2)	104.76(8)
O(2)-Ti(1)-O(4)	154.72(5)	O(1)-C(1)-O(2)	126.1(3)
O(3)-Ti(1)-O(5)	153.08(5)	O(3)-C(9)-O(4)	126.4(3)
O(2)-Ti(1)-O(3)	60.24(4)	Ti(2)-O(11)-C(35)	130.83(18)
O(3)-Ti(1)-O(4)	95.60(5)	O(4)-H(1)-O(11)	171.272(4246)
O(4)-Ti(1)-O(5)	108.21(5)	*Trans oxygen atoms*	
O(2)-Ti(1)-O(5)	94.14(5)	O(1)-Ti(1)-O(3)	176.31(9)
O(2)-Ti(1)-N(2)	81.97(4)	O(5)-Ti(1)-O(7)	163.95(9)
O(3)-Ti(1)-N(2)	80.56(4)	O(6)-Ti(1)-O(8)	166.91(9)
		O(2)-Ti(2)-O(11)	170.90(9)
		O(5)-Ti(2)-O(10)	170.75(9)
		O(6)-Ti(2)-O(9)	164.26(9)
		Cis oxygen atoms	
		O-Ti(1)-O	72.70(7) - 99.20(11)
		O-Ti(2)-O	73.00(7) - 97.93(10)

Table A.7: *Bond lengths and atom distances [pm] for **ZrBenzMeCl** and **ZrPentin***

ZrBenzMeCl		**ZrPentin**	
Metal-metal distances			
Zr(1)-Zr(2)	347.35(8)	Zr(1)-Zr(2)	340.08(4)
Zr(1)-Zr(6)	399.58(8)	Zr(1)-Zr(4)	341.30(4)
Zr(1)-Zr(7)	357.31(8)	Zr(2)-Zr(3)	398.25(4)
Zr(2)-Zr(3)	347.96(7)	Zr(2)-Zr(4)	329.91(4)
Zr(2)-Zr(4)	340.02(7)	Zr(2)-Zr(5)	342.68(4)
Zr(2)-Zr(5)	341.51(8)	Zr(2)-Zr(8)	348.55(4)
Zr(2)-Zr(6)	339.60(8)	Zr(3)-Zr(5)	355.18(4)
Zr(2)-Zr(7)	349.73(8)	Zr(3)-Zr(8)	347.11(4)
Zr(3)-Zr(4)	349.53(8)	Zr(4)-Zr(5)	352.30(4)
Zr(3)-Zr(5)	407.82(10)	Zr(4)-Zr(6)	347.75(4)
Zr(4)-Zr(5)	346.25(8)	Zr(4)-Zr(7)	348.90(4)
Zr(4)-Zr(7)	343.57(7)	Zr(5)-Zr(6)	355.06(4)
Zr(4)-Zr(9)	337.19(8)	Zr(5)-Zr(7)	342.92(4)
Zr(4)-Zr(10)	401.98(8)	Zr(5)-Zr(8)	351.03(4)
Zr(5)-Zr(6)	343.88(9)	Zr(6)-Zr(7)	396.77(4)
Zr(5)-Zr(8)	407.79(10)	Zr(7)-Zr(8)	328.39(4)
Zr(5)-Zr(9)	342.91(8)	Zr(7)-Zr(9)	339.83(4)
Zr(6)-Zr(7)	342.52(8)	Zr(8)-Zr(9)	340.96(4)
Zr(6)-Zr(8)	348.90(9)		
Zr(6)-Zr(9)	338.88(8)		
Zr(7)-Zr(9)	351.06(8)		
Zr(7)-Zr(10)	357.06(9)		
Zr(8)-Zr(9)	346.59(9)		
Zr(9)-Zr(10)	345.59(8)		
Selected bond lengths			
Zr(2)-O(1)	223.0(4)	Zr(6)-O(1)	213.63(19)
Zr(3)-O(1)	215.2(4)	Zr(7)-O(1)	216.69(19)
Zr(4)-O(1)	227.9(4)	Zr(4)-O(1)	222.7(2)
Zr(5)-O(1)	219.0(4)	Zr(5)-O(1)	231.4(2)
Zr(5)-O(2)	217.6(4)	Zr(3)-O(2)	214.8(2)
Zr(6)-O(2)	227.0(4)	Zr(2)-O(2)	216.4(2)
Zr(8)-O(2)	215.4(4)	Zr(8)-O(2)	222.6(2)
Zr(9)-O(2)	224.4(4)	Zr(5)-O(2)	230.4(2)
Zr(1)-O(3)	212.5(4)	Zr(1)-O(3)	210.2(2)
Zr(2)-O(3)	221.8(4)	Zr(2)-O(3)	211.6(2)
Zr(6)-O(3)	218.6(4)	Zr(4)-O(3)	211.7(2)
Zr(7)-O(3)	229.4(4)	Zr(2)-O(4)	202.8(2)
Zr(4)-O(4)	218.1(4)	Zr(4)-O(4)	204.50(19)
Zr(7)-O(4)	232.0(4)	Zr(5)-O(4)	207.2(2)
Zr(9)-O(4)	220.8(4)	Zr(5)-O(5)	206.5(2)
Zr(10)-O(4)	212.6(4)	Zr(7)-O(5)	202.6(2)

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ZrBenzMeCl		**ZrPentin**	
Zr(2)-O(5)	205.5(4)	Zr(8)-O(5)	203.6(2)
Zr(5)-O(5)	208.6(4)	Zr(8)-O(6)	210.2(2)
Zr(6)-O(5)	205.9(4)	Zr(9)-O(6)	210.8(2)
Zr(2)-O(6)	204.2(4)	Zr(7)-O(6)	211.8(2)
Zr(4)-O(6)	202.3(4)		
Zr(7)-O(6)	207.7(4)		
Zr(4)-O(7)	204.7(4)		
Zr(5)-O(7)	210.6(4)		
Zr(9)-O(7)	205.1(4)		
Zr(6)-O(8)	202.5(4)		
Zr(7)-O(8)	207.7(4)		
Zr(9)-O(8)	204.0(4)		

Table A.8: *Selected bond angles [°] of **ZrBenzMeCl** and **ZrPentin**.*

ZrBenzMeCl		**ZrPentin**	
Zr(2)-O(1)-Zr(3)	105.14(16)	Zr(4)-O(1)-Zr(5)	101.74(8)
Zr(2)-O(1)-Zr(4)	97.88(15)	Zr(4)-O(1)-Zr(6)	105.66(8)
Zr(2)-O(1)-Zr(5)	101.20(15)	Zr(4)-O(1)-Zr(7)	105.12(8)
Zr(3)-O(1)-Zr(4)	104.12(16)	Zr(5)-O(1)-Zr(6)	105.79(8)
Zr(3)-O(1)-Zr(5)	139.91(19)	Zr(5)-O(1)-Zr(7)	99.83(8)
Zr(4)-O(1)-Zr(5)	101.56(16)	Zr(6)-O(1)-Zr(7)	134.45(10)
Zr(5)-O(2)-Zr(6)	101.33(18)	Zr(2)-O(2)-Zr(3)	134.90(10)
Zr(5)-O(2)-Zr(8)	140.8(2)	Zr(2)-O(2)-Zr(5)	100.11(8)
Zr(5)-O(2)-Zr(9)	101.77(16)	Zr(2)-O(2)-Zr(8)	105.10(8)
Zr(6)-O(2)-Zr(8)	104.11(16)	Zr(3)-O(2)-Zr(5)	105.78(9)
Zr(6)-O(2)-Zr(9)	97.32(17)	Zr(3)-O(2)-Zr(8)	105.02(8)
Zr(8)-O(2)-Zr(9)	104.02(18)	Zr(5)-O(2)-Zr(8)	101.57(8)
Zr(1)-O(3)-Zr(2)	106.23(17)	Zr(1)-O(3)-Zr(2)	107.49(9)
Zr(1)-O(3)-Zr(6)	135.90(19)	Zr(1)-O(3)-Zr(4)	108.01(9)
Zr(1)-O(3)-Zr(7)	107.88(17)	Zr(2)-O(3)-Zr(4)	102.42(9)
Zr(2)-O(3)-Zr(6)	100.90(16)	Zr(2)-O(4)-Zr(4)	108.20(9)
Zr(2)-O(3)-Zr(7)	101.64(15)	Zr(2)-O(4)-Zr(5)	113.42(9)
Zr(6)-O(3)-Zr(7)	99.70(16)	Zr(4)-O(4)-Zr(5)	117.69(9)
Zr(4)-O(4)-Zr(7)	99.45(15)	Zr(5)-O(5)-Zr(7)	113.91(9)
Zr(4)-O(4)-Zr(9)	100.37(16)	Zr(5)-O(5)-Zr(8)	117.73(9)
Zr(4)-O(4)-Zr(10)	137.9(2)	Zr(7)-O(5)-Zr(8)	107.91(9)
Zr(7)-O(4)-Zr(9)	101.62(16)	Zr(7)-O(6)-Zr(8)	102.18(9)
Zr(7)-O(4)-Zr(10)	106.78(16)	Zr(7)-O(6)-Zr(9)	107.03(9)
Zr(9)-O(4)-Zr(10)	105.74(17)	Zr(8)-O(6)-Zr(9)	108.17(9)
Zr(2)-O(5)-Zr(5)	111.09(18)		
Zr(2)-O(5)-Zr(6)	111.27(18)		
Zr(5)-O(5)-Zr(6)	112.12(19)		
Zr(2)-O(6)-Zr(4)	113.55(17)		
Zr(2)-O(6)-Zr(7)	116.24(18)		
Zr(4)-O(6)-Zr(7)	113.86(18)		
Zr(4)-O(7)-Zr(5)	112.96(18)		
Zr(4)-O(7)-Zr(9)	110.75(18)		
Zr(5)-O(7)-Zr(9)	111.13(17)		
Zr(6)-O(8)-Zr(7)	113.25(19)		
Zr(6)-O(8)-Zr(9)	112.94(19)		
Zr(7)-O(8)-Zr(9)	117.00(19)		

Table A.9: *Selected bond lengths and atom distances [pm] of* ***TiOMc1*** *and* ***TiOMc2****.*

TiOMc1		**TiOMc2**	
	Metal-metal distances		
Ti(1)-Ti(2)	323.45(3)	Ti(1)-Ti(2)	310.62(3)
		Ti(1)-Ti(3)	337.83(3)
	Selected bond lengths		
Ti(1)-O(2)	204.43(7)	Ti(1)-O(1)	190.47(9)
Ti(1)-O(5)	203.56(7)	Ti(2)-O(1)	207.22(9)
Ti(1)-O(6)	202.06(7)	Ti(3)-O(1)	190.61(9)
Ti(1)-O(9)	181.08(7)	Ti(1)-O(2)	174.97(9)
Ti(1)-O(10)	178.47(7)	Ti(3)-O(2)	188.93(9)
Ti(1)-O(11)	206.36(7)	Ti(1)-O(3)	204.65(10)
Ti(2)-O(1)	208.29(8)	Ti(3)-O(4)	208.92(10)
Ti(2)-O(3)	198.70(8)	Ti(1)-O(5)	200.24(10)
Ti(2)-O(5)	205.03(7)	Ti(3)-O(6)	210.19(10)
Ti(2)-O(6)	206.20(7)	Ti(1)-O(7)	200.51(10)
Ti(2)-O(7)	179.83(9)	Ti(2)-O(8)	216.27(11)
Ti(2)-O(8)	178.22(8)	Ti(2)-O(9)	204.82(10)
C(1)-O(1)	125.83(13)	Ti(3)-O(10)	203.00(10)
C(1)-O(2)	126.96(13)	Ti(1)-O(11)	208.74(9)
C(5)-O(3)	126.93(14)	Ti(2)-O(11)	195.72(10)
C(5)-O(4)	123.81(14)	Ti(2)-O(12)	179.95(10)
O(4)-O(11)	256.42(13)	Ti(2)-O(13)	179.03(11)
		Ti(3)-O(14)	175.98(11)

Table A.10: *Selected bond angles [°] of* ***TiOMc1*** *and* ***TiOMc2****.*

TiOMc1		**TiOMc2**	
Ti(1)-O(5)-Ti(2)	104.67(3)	Ti(1)-O(1)-Ti(2)	102.63(4)
Ti(1)-O(6)-Ti(2)	104.79(3)	Ti(1)-O(1)-Ti(3)	128.00(5)
O(1)-C(1)-O(2)	125.62(9)	Ti(3)-O(1)-Ti(2)	128.65(5)
O(3)-C(5)-O(4)	125.90(9)	Ti(1)-O(2)-Ti(3)	136.33(5)
Ti(1)-O(11)-C(27)	128.775(61)	Ti(2)-O(11)-Ti(1)	100.30(4)
O(4)-H(11)-O(11)	171.556(2343)		
Oxygen atoms in trans position on the octahedrally coordinated Ti atom			
O(2)-Ti(1)-O(11)	170.07(3)	O(1)-Ti(1)-O(3)	162.39(4)
O(5)-Ti(1)-O(9)	164.62(3)	O(2)-Ti(1)-O(11)	174.29(4)
O(6)-Ti(1)-O(10)	172.12(3)	O(5)-Ti(1)-O(7)	169.43(4)
O(1)-Ti(2)-O(3)	176.05(3)	O(1)-Ti(2)-O(12)	166.24(5)
O(6)-Ti(2)-O(7)	161.87(4)	O(8)-Ti(2)-O(13)	172.85(5)
O(5)-Ti(2)-O(8)	168.37(4)	O(9)-Ti(2)-O(11)	161.74(4)
		O(1)-Ti(3)-O(4)	168.11(5)
		O(2)-Ti(3)-O(10)	164.60(4)
		O(6)-Ti(3)-O(14)	172.82(5)
Oxygen atoms in cis position on the octahedrally coordinated Ti atom			
O-Ti(1)-O	73.87(3) - 98.31(3)	O-Ti(1)-O	77.53(4) - 104.91(4)
O-Ti(2)-O	72.70(3) - 100.21(4)	O-Ti(2)-O	76.77(4) - 100.86(5)
		O-Ti(3)-O	82.41(4) - 99.48(4)

Table A.11: *Bond lengths and atom distances [pm] for* ***TiOMc6*** *and* ***TiOMc8***

TiOMc6		**TiOMc8**	
Metal-metal distances			
Ti(1)-Ti(2)	297.6(4)	Ti(1)-Ti(2)	334.4(2)
Ti(1)-Ti(3)	345.6(3)	Ti(1)-Ti(4)*	331.5(2)
Ti(1)-Ti(9)	348.4(3)	Ti(2)-Ti(3)	336.6(2)
Ti(2)-Ti(3)	353.6(3)	Ti(3)-Ti(4)	335.0(2)
Ti(2)-Ti(9)	352.2(3)		
Ti(3)-Ti(4)	334.3(3)		
Ti(4)-Ti(5)	335.2(3)		
Ti(5)-Ti(6)	336.4(3)		
Ti(6)-Ti(7)	337.7(4)		
Ti(7)-Ti(8)	340.7(3)		
Ti(8)-Ti(9)	337.8(3)		
Selected bond lengths			
Metal to oxygen distances for μ_3-oxo bridges			
Ti(1)-O(1)	190.8(9)		
Ti(2)-O(1)	194.9(8)		
Ti(9)-O(1)	194.6(8)		
Ti(1)-O(2)	193.8(8)		
Ti(2)-O(2)	195.4(8)		
Ti(3)-O(2)	191.2(7)		
Metal to oxygen distances for μ_2-oxo bridges			
Ti(3)-O(3)	173.1(8)	Ti(1)-O(1)	175.3(6)
Ti(4)-O(3)	190.4(7)	Ti(1)-O(2)	185.7(6)
Ti(4)-O(4)	172.3(8)	Ti(2)-O(2)	177.5(6)
Ti(5)-O(4)	190.1(8)	Ti(2)-O(3)	186.6(6)
Ti(5)-O(5)	171.9(8)	Ti(3)-O(3)	178.3(6)
Ti(6)-O(5)	192.0(8)	Ti(3)-O(4)	185.5(6)
Ti(6)-O(6)	170.3(8)	Ti(4)-O(1)	185.2(6)
Ti(7)-O(6)	194.2(8)	Ti(4)-O(4)	178.7(6)
Ti(7)-O(7)	180.2(8)		
Ti(8)-O(7)	180.2(8)		
Ti(8)-O(8)	194.0(8)		
Ti(9)-O(8)	170.4(8)		
Metal to oxygen distances for methacrylates			
Ti(1)-O(9)	210.5(9)	Ti(1)-O(5)	204.7(6)
Ti(2)-O(10)	211.6(10)	Ti(1)-O(7)	199.6(7)
Ti(1)-O(11)	200.2(9)	Ti(1)-O(9)	202.9(6)
Ti(9)-O(12)	203.3(11)	Ti(1)-O(11)	209.0(7)
Ti(1)-O(13)	203.9(9)	Ti(2)-O(10)	201.7(7)
Ti(3)-O(14)	199.6(9)	Ti(2)-O(12)	206.3(7)
Ti(2)-O(15)	194.4(10)	Ti(2)-O(13)	208.4(6)

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TiOMc6		**TiOMc8**	
Ti(9)-O(16)	216.2(10)	Ti(2)-O(15)	201.3(6)
Ti(2)-O(17)	197.3(9)	Ti(3)-O(14)	202.8(6)
Ti(3)-O(18)	211.6(10)	Ti(3)-O(16)	203.0(6)
Ti(3)-O(19)	202.0(8)	Ti(3)-O(17)	209.2(6)
Ti(4)-O(20)	213.9(8)	Ti(3)-O(19)	198.2(6)
Ti(3)-O(21)	202.8(9)	Ti(4)-O(6)	209.3(7)
Ti(4)-O(22)	200.7(9)	Ti(4)-O(8)	202.3(7)
Ti(4)-O(23)	199.8(9)	Ti(4)-O(18)	202.8(6)
Ti(5)-O(24)	199.7(10)	Ti(4)-O(20)	199.9(7)
Ti(4)-O(25)	199.9(8)		
Ti(5)-O(26)	212.0(9)		
Ti(5)-O(27)	198.5(9)		
Ti(6)-O(28)	213.3(11)		
Ti(5)-O(29)	199.7(10)		
Ti(6)-O(30)	203.3(10)		
Ti(6)-O(31)	197.0(10)		
Ti(7)-O(32)	208.4(12)		
Ti(6)-O(33)	202.0(10)		
Ti(7)-O(34)	209.5(10)		
Ti(7)-O(35)	203.6(10)		
Ti(8)-O(36)	201.6(9)		
Ti(8)-O(37)	210.6(9)		
Ti(9)-O(38)	202.6(9)		
Ti(8)-O(39)	208.5(11)		
Ti(9)-O(40)	198.3(12)		
Metal to oxygen distances for terminal isopropoxo ligands			
Ti(1)-O(41)	172.2(8)		
Ti(2)-O(42)	175.0(8)		
Ti(7)-O(43)	172.8(13)		
Ti(8)-O(44)	177.2(10)		

Table A.12: *Selected angles [°] of* ***TiOMc6*** *and* ***TiOMc8****.*

TiOMc6		**TiOMc8**	
Ti(1)-O(1)-Ti(9)	129.4(4)	Ti(2)-Ti(1)-Ti(4)*	132.68(7)
Ti(1)-O(1)-Ti(2)	101.0(4)	Ti(1)-Ti(2)-Ti(3)	132.82(7)
Ti(9)-O(1)-Ti(2)	129.4(5)	Ti(2)-Ti(3)-Ti(4)	136.67(6)
Ti(3)-O(2)-Ti(1)	127.7(4)	Ti(1)*-Ti(4)-Ti(3)	135.98(6)
Ti(3)-O(2)-Ti(2)	132.3(4)	Ti(1)-O(1)-Ti(4)	133.8(3)
Ti(1)-O(2)-Ti(2)	99.7(3)	Ti(2)-O(2)-Ti(1)	134.1(3)
Ti(3)-O(3)-Ti(4)	133.7(4)	Ti(3)-O(3)-Ti(2)	134.6(3)
Ti(4)-O(4)-Ti(5)	135.3(5)	Ti(4)-O(4)-Ti(3)	133.8(3)
Ti(5)-O(5)-Ti(6)	135.1(4)	*Trans oxygen atoms*	
Ti(6)-O(6)-Ti(7)	135.6(5)	O(1)-Ti(1)-O(11)	173.2(3)
Ti(7)-O(7)-Ti(8)	142.0(5)	O(2)-Ti(1)-O(5)	169.5(3)
Ti(9)-O(8)-Ti(8)	135.8(5)	O(7)-Ti(1)-O(9)	172.9(3)
		O(2)-Ti(2)-O(13)	173.2(3)
		O(3)-Ti(2)-O(12)	170.1(3)
		O(10)-Ti(2)-O(15)	173.9(3)
		O(3)-Ti(3)-O(17)	172.0(3)
		O(4)-Ti(3)-O(14)	167.9(3)
		O(16)-Ti(3)-O(19)	172.8(3)
		O(1)-Ti(4)-O(18)	168.9(3)
		O(4)-Ti(4)-O(6)	170.0(2)
		O(8)-Ti(4)-O(20)	171.4(3)
		Cis oxygen atoms	
		O-Ti(1)-O	80.6(3) - 97.8(3)
		O-Ti(2)-O	81.8(3) - 98.5(3)
		O-Ti(3)-O	81.9(3) - 100.6(3)
		O-Ti(4)-O	80.7(3) - 100.3(3)

Table A.13: *Selected bond lengths and atom distances [pm] of* ***TiPhthal1*** *and* ***TiPhthal2****.*

TiPhthal1		**TiPhthal2**	
Metal-metal distances			
Ti(1)-Ti(2)	322.73(6)	Ti(1)-Ti(2)	309.99(18)
		Ti(1)-Ti(3)	311.54(16)
		Ti(1)-Ti(2)*	348.63(14)
		Ti(1)-Ti(3)*	349.88(18)
		Ti(2)-Ti(3)	349.72(17)
		Ti(2)-Ti(3)*	311.40(16)
Selected bond lengths			
Ti(1)-O(1)	177.82(15)	Ti(1)-O(1)	189.8(4)
Ti(1)-O(2)	181.02(15)	Ti(1)-O(2)	187.0(4)
Ti(1)-O(7)	204.92(13)	Ti(1)-O(3)	213.8(4)
Ti(1)-O(6)	205.35(13)	Ti(1)-O(4)	175.6(5)
Ti(1)-O(8)	210.41(13)	Ti(1)-O(7)	206.4(4)
Ti(1)-O(12)	198.09(13)	Ti(1)-O(11)	205.5(5)
Ti(2)-O(3)	181.94(14)	Ti(2)-O(1)	215.3(4)
Ti(2)-O(4)	177.39(13)	Ti(2)-O(2)	192.0(4)
Ti(2)-O(5)	207.53(13)	Ti(2)-O(3)	187.3(4)
Ti(2)-O(6)	202.86(13)	Ti(2)-O(5)	174.4(5)
Ti(2)-O(7)	202.86(13)	Ti(2)-O(8)	205.1(4)
Ti(2)-O(9)	206.15(13)	Ti(2)-O(15)	208.2(4)
C(22)-O(8)	125.4(2)	Ti(3)-O(1)	188.6(4)
C(22)-O(9)	126.4(2)	Ti(3)-O(2)	216.4(4)
C(33)-O(12)	128.1(2)	Ti(3)-O(3)	192.2(4)
C(33)-O(13)	124.3(2)	Ti(3)-O(6)	176.2(4)
O(5)-O(13)	260.29(21)	Ti(3)-O(12)	206.2(5)
		Ti(3)-O(16)	208.5(4)

Table A.14: *Selected bond angles [°] of **TiPhthal1** and **TiPhthal2**.*

TiPhthal1		**TiPhthal2**	
Ti(1)-O(6)-Ti(2)	104.48(6)	Ti(2)-Ti(1)-Ti(3)	68.48(4)
Ti(1)-O(7)-Ti(2)	104.64(6)	Ti(1)-Ti(2)-Ti(3)	55.97(3)
O(8)-C(22)-O(9)	126.60(16)	Ti(1)-Ti(3)-Ti(2)	55.55(3)
O(12)-C(33)-O(13)	125.86(18)	Ti(2)-Ti(1)*-Ti(3)	60.09(4)
Ti(2)O(5)-C(13)	127.53(13)	Ti(1)*-Ti(2)-Ti(3)	60.13(3)
O(5)-H(5D)-O(13)	174.63(26)	Ti(1)*-Ti(3)-Ti(2)	59.78(3)
		Ti(2)*-Ti(1)-Ti(3)	55.95(4)
		Ti(1)-Ti(2)*-Ti(3)	55.99(4)
		Ti(1)-Ti(3)-Ti(2)*	68.06(4)
		Ti(2)-Ti(1)-Ti(3)*	55.92(4)
		Ti(1)-Ti(2)-Ti(3)*	68.53(4)
		Ti(1)-Ti(3)*-Ti(2)	55.54(4)
		Ti(1)-O(1)-Ti(2)	99.66(18)
		Ti(1)-O(1)-Ti(3)	135.3(2)
		Ti(2)-O(1)-Ti(3)	100.67(19)
		Ti(1)-O(2)-Ti(2)	133.8(2)
		Ti(1)-O(2)-Ti(3)	100.85(18)
		Ti(2)-O(2)-Ti(3)	99.19(19)
		Ti(1)-O(3)-Ti(2)	101.00(19)
		Ti(1)-O(3)-Ti(3)	100.10(18)
		Ti(2)-O(3)-Ti(3)	134.3(2)
Oxygen atoms in trans position on the octahedrally coordinated Ti atom			
O(1)-Ti(1)-O(6)	167.33(6)	O(1)-Ti(1)-O(11)	158.74(19)
O(2)-Ti(1)-O(7)	163.22(6)	O(2)-Ti(1)-O(7)	162.90(19)
O(8)-Ti(1)-O(12)	175.48(5)	O(3)-Ti(1)-O(4)	177.21(19)
O(3)-Ti(2)-O(7)	166.28(6)	O(1)-Ti(2)-O(5)	177.67(19)
O(4)-Ti(2)-O(6)	168.57(6)	O(2)*-Ti(2)-O(8)	160.27(19)
O(5)-Ti(2)-O(9)	171.39(5)	O(3)-Ti(2)-O(15)	160.18(19)
		O(1)*-Ti(3)-O(12)	158.16(19)
		O(2)-Ti(3)-O(6)	173.44(17)
		O(3)-Ti(3)-O(16)	162.83(19)
Oxygen atoms in cis position on the octahedrally coordinated Ti atom			
O-Ti(1)-O	84.55(5) - 99.33(7)	O-Ti(1)-O	77.48(17) - 102.56(19)
O-Ti(2)-O	73.78(5) - 97.93(7)	O-Ti(2)-O	77.60(17) - 103.2(2)
		O-Ti(3)-O	76.60(17) - 105.6(2)

Table A.15: *Bond lengths and atom distances [pm] for* ***TiMal*** *and* ***ZrHexOx***

TiMal		**ZrHexOx**	
Metal-metal distances			
Ti(1)-Ti(2)	314.84(8)	Zr(1)-Zr(2)	384.07(11)
Ti(1)-Ti(3)	365.74(10)	Zr(1)-Zr(3)	339.34(10)
Ti(2)-Ti(3)	309.62(9)	Zr(2)-Zr(3)	345.20(12)
Ti(3)-Ti(4)	355.37(8)	Zr(2)-Zr(4)	358.68(12)
Ti(4)-Ti(5)	314.87(9)	Zr(2)-Zr(5)	353.06(12)
Ti(4)-Ti(6)	363.95(10)	Zr(3)-Zr(4)	390.52(11)
Ti(5)-Ti(6)	309.49(11)	Zr(3)-Zr(5)	343.00(11)
		Zr(4)-Zr(5)	345.81(12)
Selected bond lengths			
Metal to oxygen distances of oxo bridges			
Ti(1)-O(1)	197.9(2)	Zr(2)-O(1)	231.6(5)
Ti(2)-O(1)	198.1(2)	Zr(3)-O(1)	214.7(5)
Ti(3)-O(1)	186.0(2)	Zr(4)-O(1)	217.2(5)
Ti(4)-O(2)	198.1(2)	Zr(5)-O(1)	213.9(5)
Ti(5)-O(2)	200.5(3)	Zr(1)-O(2)	204.6(5)
Ti(6)-O(2)	184.4(3)	Zr(2)-O(2)	210.8(5)
Ti(3)-O(3)	178.0(2)	Zr(3)-O(2)	204.6(5)
Ti(4)-O(3)	184.9(2)		
Metal to oxygen/nitrogen distances of oximate ligands			
		Zr(1)-N(1)	236.2(7)
		Zr(1)-N(2)	232.8(6)
		Zr(1)-O(4)	209.8(5)
		Zr(2)-O(3)	215.9(6)
		Zr(4)-N(3)	222.9(9)
		Zr(4)-O(5)	213.7(7)
		Zr(3)-N(4)	220.6(6)
		Zr(3)-O(6)	213.1(7)
Metal to oxygen distances of carboxylates			
Ti(1)-O(5)	215.6(2)	Zr(1)-O(7)	224.1(6)
Ti(1)-O(9)	204.2(2)	Zr(2)-O(8)	219.3(6)
Ti(2)-O(4)	217.0(2)	Zr(3)-O(9)	215.4(6)
Ti(3)-O(8)	205.4(2)	Zr(4)-O(10)	218.9(7)
Ti(4)-O(6)	202.8(2)	Zr(5)-O(11)	224.6(6)
Ti(4)-O(10)	210.5(2)	Zr(5)-O(12)	225.2(6)
Ti(5)-O(11)	213.5(3)		
Ti(6)-O(7)	205.9(3)		
Metal to oxygen distances of bridging alkoxo ligands			
Ti(1)-O(12)	202.1(2)	Zr(1)-O(13)	223.6(5)
Ti(2)-O(12)	201.8(2)	Zr(3)-O(13)	209.5(5)

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TiMal		**ZrHexOx**	
Ti(2)-O(13)	201.4(2)	Zr(2)-O(14)	216.7(6)
Ti(3)-O(13)	200.6(2)	Zr(5)-O(14)	214.8(6)
Ti(4)-O(14)	201.0(2)	Zr(3)-O(15)	210.1(5)
Ti(5)-O(14)	202.0(3)	Zr(5)-O(15)	217.8(5)
Ti(5)-O(15)	202.7(3)	Zr(4)-O(16)	210.6(6)
Ti(6)-O(15)	199.0(3)	Zr(5)-O(16)	218.4(6)
		Zr(2)-O(17)	218.4(6)
		Zr(4)-O(17)	212.9(6)
Metal to oxygen distances of terminal alkoxo ligands			
Ti(1)-O(16)	178.7(2)	Zr(1)-O(18)	193.8(5)
Ti(1)-O(17)	179.3(2)	Zr(2)-O(19)	193.5(6)
Ti(2)-O(18)	179.8(2)	Zr(4)-O(20)	194.6(7)
Ti(2)-O(19)	179.1(2)	Zr(5)-O(21)	191.8(6)
Ti(3)-O(20)	177.1(2)		
Ti(4)-O(21)	177.0(2)		
Ti(5)-O(22)	179.3(3)		
Ti(5)-O(23)	179.9(3)		
Ti(6)-O(24)	175.7(3)		
Ti(6)-O(25)	174.5(4)		

Table A.16: *Selected angles [°] of* ***TiMal*** *and* ***ZrHexOx****.*

TiMal		**ZrHexOx**	
Ti(2)-Ti(1)-Ti(3)	53.490(17)	Zr(2)-Zr(1)-Zr(3)	56.598(21)
Ti(1)-Ti(2)-Ti(3)	71.697(19)	Zr(1)-Zr(2)-Zr(3)	55.149(21)
Ti(1)-Ti(3)-Ti(2)	54.814(18)	Zr(1)-Zr(2)-Zr(4)	119.582(28)
Ti(1)-Ti(3)-Ti(4)	105.117(19)	Zr(1)-Zr(2)-Zr(5)	101.161(27)
Ti(2)-Ti(3)-Ti(4)	116.653(24)	Zr(3)-Zr(2)-Zr(4)	67.36(3)
Ti(3)-Ti(4)-Ti(5)	137.001(26)	Zr(3)-Zr(2)-Zr(5)	58.83(2)
Ti(3)-Ti(4)-Ti(6)	145.698(25)	Zr(4)-Zr(2)-Zr(5)	58.13(2)
Ti(5)-Ti(4)-Ti(6)	53.659(22)	Zr(1)-Zr(3)-Zr(2)	68.25(2)
Ti(4)-Ti(5)-Ti(6)	71.31(2)	Zr(1)-Zr(3)-Zr(4)	123.048(25)
Ti(4)-Ti(6)-Ti(5)	55.037(22)	Zr(1)-Zr(3)-Zr(5)	113.24(3)
Ti(1)-O(1)-Ti(3)	144.54(12)	Zr(2)-Zr(3)-Zr(4)	57.967(22)
Ti(2)-O(1)-Ti(3)	107.39(10)	Zr(2)-Zr(3)-Zr(5)	61.73(2)
Ti(1)-O(1)-Ti(2)	105.31(10)	Zr(4)-Zr(3)-Zr(5)	55.805(22)
Ti(4)-O(2)-Ti(6)	144.11(14)	Zr(2)-Zr(4)-Zr(3)	54.672(21)
Ti(5)-O(2)-Ti(6)	106.95(12)	Zr(2)-Zr(4)-Zr(5)	60.12(2)
Ti(4)-O(2)-Ti(5)	104.33(11)	Zr(3)-Zr(4)-Zr(5)	55.125(22)
Ti(3)-O(3)-Ti(4)	156.58(13)	Zr(2)-Zr(5)-Zr(3)	59.44(2)
Ti(1)-O(12)-Ti(2)	102.43(10)	Zr(2)-Zr(5)-Zr(4)	61.75(2)
Ti(2)-O(13)-Ti(3)	100.76(10)	Zr(3)-Zr(5)-Zr(4)	69.07(3)
Ti(4)-O(14)-Ti(5)	102.75(11)	Zr(2)-O(1)-Zr(3)	101.3(2)
Ti(5)-O(15)-Ti(6)	100.82(11)	Zr(2)-O(1)-Zr(4)	106.0(2)
Trans oxygens		Zr(2)-O(1)-Zr(5)	104.8(2)
O(1)-Ti(1)-O(16)	169.53(10)	Zr(3)-O(1)-Zr(4)	129.4(3)
O(5)-Ti(1)-O(17)	177.10(10)	Zr(3)-O(1)-Zr(5)	106.3(2)
O(9)-Ti(1)-O(12)	157.88(9)	Zr(4)-O(1)-Zr(5)	106.7(2)
O(1)-Ti(2)-O(19)	167.81(11)	Zr(1)-O(2)-Zr(2)	135.2(3)
O(4)-Ti(2)-O(18)	177.95(12)	Zr(1)-O(2)-Zr(3)	112.1(2)
O(12)-Ti(2)-O(13)	148.89(10)	Zr(3)-O(2)-Zr(2)	112.4(2)
O(2)-Ti(4)-O(3)	168.25(10)	Zr(1)-O(13)-Zr(3)	103.1(2)
O(6)-Ti(4)-O(14)	160.02(11)	Zr(2)-O(14)-Zr(5)	109.8(2)
O(10)-Ti(4)-O(21)	176.81(11)	Zr(3)-O(15)-Zr(5)	106.5(2)
O(2)-Ti(5)-O(23)	167.04(13)	Zr(4)-O(16)-Zr(5)	107.4(3)
O(11)-Ti(5)-O(22)	176.84(14)	Zr(2)-O(17)-Zr(4)	112.5(3)
O(14)-Ti(5)-O(15)	148.15(11)		
Cis oxygens			
O-Ti(1)-O	75.74(9) - 103.47(11)		
O-Ti(2)-O	74.47(9) - 103.64(12)		
O-Ti(4)-O	76.40(10) - 101.57(10)		
O-Ti(5)-O	73.89(11) - 106.04(13)		

Table A.17: *Bond lengths and atom distances [pm] for **Zr3Calix**, **TiCalix** and **Zr4Calix2***

Zr3Calix		**TiCalix**		**Zr4Calix2**	
Metal-metal distances					
Zr(1)-Zr(2)	341.38(3)	Ti(1)-Ti(1)*	331.98(13)	Zr(1)-Zr(2)	338.88(9)
Zr(1)-Zr(3)	340.77(3)			Zr(1)-Zr(3)	338.53(9)
Zr(2)-Zr(3)	331.71(3)			Zr(2)-Zr(3)	333.39(9)
				Zr(2)-Zr(4B)	338.44(19)
				Zr(3)-Zr(4A)	341.77(14)
Selected bond lengths					
Metal to oxygen distances for oxo bridges					
				Zr(2)-O(1)	213.3(5)
				Zr(3)-O(1)	212.2(5)
				Zr(4A)-O(1)	214.2(5)
				Zr(4B)-O(1)	212.1(5)
Metal to oxygen distances for calix[4]arenes					
Zr(1)-O(1)	242.05(15)	Ti(1)-O(1)	179.4(3)	Zr(1)-O(2)	212.1(4)
Zr(1)-O(2)	195.86(15)	Ti(1)-O(2)	180.7(3)	Zr(1)-O(6)	210.0(5)
Zr(1)-O(3)	202.73(15)	Ti(1)-O(3)	193.9(3)	Zr(2)-O(6)	233.7(4)
Zr(1)-O(4)	195.08(15)	Ti(1)-O(4)	224.0(3)	Zr(2)-O(7)	196.1(5)
Zr(2)-O(1)	206.65(15)			Zr(2)-O(8)	220.4(5)
				Zr(2)-O(9)	194.4(5)
				Zr(3)-O(2)	227.0(4)
				Zr(3)-O(3)	195.1(6)
				Zr(3)-O(4)	220.4(5)
				Zr(3)-O(5)	194.9(5)
				Zr(4A)-O(4)	212.7(5)
				Zr(4B)-O(8)	212.3(5)
Metal to oxygen distances for μ_3- ^{n}butoxo ligands					
Zr(1)-O(5)	234.05(14)			Zr(1)-O(12)	230.6(5)
Zr(1)-O(6)	232.80(15)			Zr(1)-O(13)	226.5(5)
Zr(2)-O(5)	229.73(15)			Zr(2)-O(12)	229.2(4)
Zr(2)-O(6)	227.53(15)			Zr(2)-O(13)	225.3(6)
Zr(3)-O(5)	222.79(15)			Zr(3)-O(12)	228.7(5)
Zr(3)-O(6)	229.33(15)			Zr(3)-O(13)	228.5(5)
Metal to oxygen distances for μ_2- ^{n}butoxo ligands					
Zr(1)-O(7)	223.42(15)	Ti(1)-O(5)	203.5(3)		
Zr(3)-O(7)	212.47(15)	Ti(1)-O(5)*	202.2(3)		
Zr(2)-O(8)	217.53(16)				
Zr(3)-O(8)	213.80(16)				
Metal to oxygen distances for terminal ^{n}butoxo ligands					
Zr(2)-O(9)	191.45(15)			Zr(1)-O(10)	189.8(5)
Zr(2)-O(10)	190.73(15)			Zr(1)-O(11)	189.9(5)

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Zr3Calix		**TiCalix**		**Zr4Calix2**	
Zr(3)-O(11)	190.77(15)			Zr(4A)-O(14)	266(3)
Zr(3)-O(12)	191.54(17)			Zr(4A)-O(15A)	195.41(13)
				Zr(4A)-O(16A)	195.79(17)
				Zr(4A)-O(17A)	203.12(13)
				Zr(4B)-O(14)	204(3)
				Zr(4B)-O(15B)	189.2(16)
				Zr(4B)-O(16B)	207.9(3)
				Zr(4B)-O(17B)	217.1(2)

Table A.18: *Selected angles [°] of **Zr3Calix**, **TiCalix** and **Zr4Calix2**.*

Zr3Calix		**TiCalix**		**Zr4Calix2**	
Zr(3)-Zr(1)-Zr(2)	58.192(6)	Ti(1)-O(5)-Ti(1)*	109.83(12)	Zr(1)-Zr(2)-Zr(3)	60.465(19)
Zr(3)-Zr(2)-Zr(1)	60.812(6)	O(1)-Ti(1)-O(2)	103.25(12)	Zr(1)-Zr(3)-Zr(2)	60.571(19)
Zr(2)-Zr(3)-Zr(1)	60.996(6)	O(1)-Ti(1)-O(3)	90.19(12)	Zr(2)-Zr(1)-Zr(3)	58.97(2)
Zr(2)-O(1)-Zr(1)	98.76(6)	O(1)-Ti(1)-O(4)	80.44(11)	Zr(1)-Zr(3)-Zr(4A)	135.95(3)
Zr(3)-O(5)-Zr(2)	94.27(5)	O(1)-Ti(1)-O(5)	159.32(11)	Zr(1)-Zr(2)-Zr(4B)	135.38(4)
Zr(3)-O(5)-Zr(1)	96.45(5)	O(1)-Ti(1)-O(5)*	93.50(11)	Zr(2)-Zr(3)-Zr(4A)	75.40(3)
Zr(2)-O(5)-Zr(1)	94.79(5)	O(2)-Ti(1)-O(3)	89.73(11)	Zr(3)-Zr(2)-Zr(4B)	75.29(4)
Zr(2)-O(6)-Zr(3)	93.11(5)	O(2)-Ti(1)-O(4)	81.10(11)	Zr(2)-O(1)-Zr(3)	103.1(2)
Zr(2)-O(6)-Zr(1)	95.73(5)	O(2)-Ti(1)-O(5)	92.52(11)	Zr(2)-O(1)-Zr(4A)	150.0(3)
Zr(3)-O(6)-Zr(1)	95.02(5)	O(2)-Ti(1)-O(5)*	162.69(11)	Zr(2)-O(1)-Zr(4B)	105.4(2)
Zr(3)-O(7)-Zr(1)	102.82(6)	O(3)-Ti(1)-O(4)	164.96(10)	Zr(3)-O(1)-Zr(4A)	106.6(2)
Zr(3)-O(8)-Zr(2)	100.53(6)	O(3)-Ti(1)-O(5)	103.35(11)	Zr(3)-O(1)-Zr(4B)	150.5(3)
O(3)-Zr(1)-O(1)	149.44(6)	O(3)-Ti(1)-O(5)*	94.63(11)	Zr(1)-O(2)-Zr(3)	100.82(18)
O(5)-Zr(1)-O(1)	69.74(5)	O(4)-Ti(1)-O(5)	89.02(10)	Zr(3)-O(4)-Zr(4A)	104.2(2)
O(10)-Zr(2)-O(5)	93.00(6)	O(4)-Ti(1)-O(5)*	97.64(10)	Zr(1)-O(6)-Zr(2)	99.43(17)
O(9)-Zr(2)-O(5)	160.73(6)	O(5)-Ti(1)-O(5)*	70.17(12)	Zr(2)-O(8)-Zr(4B)	102.9(2)
O(11)-Zr(3)-O(5)	160.46(6)			Zr(1)-O(12)-Zr(2)	94.97(17)
O(5)-Zr(3)-O(6)	64.46(5)			Zr(1)-O(12)-Zr(3)	94.98(18)
				Zr(2)-O(12)-Zr(3)	93.47(17)
				Zr(1)-O(13)-Zr(2)	97.2(2)
				Zr(1)-O(13)-Zr(3)	96.14(19)
				Zr(2)-O(13)-Zr(3)	94.5(2)

Table A.19: *Selected bond lengths and atom distances [pm] of* ***TiDMSOAllylPA****,* ***TiAllylPP*** *and* ***TiAllylPP2****.*

TiDMSOAllylPA		**TiAllylPP**		**TiAllylPP2**	
Metal-metal distances					
Ti(2)-Ti(3)	308.68(13)	Ti(2)-Ti(3)	310.84(6)	Ti(1)-Ti(2)	311.18(8)
Ti(2)-Ti(4)	309.98(16)	Ti(2)-Ti(4)	310.38(6)	Ti(1)-Ti(3)	311.34(8)
Ti(3)-Ti(4)	311.64(14)	Ti(3)-Ti(4)	310.64(6)	Ti(2)-Ti(3)	310.43(8)
Selected bond lengths					
Ti(1)-O(13)	195.5(4)	Ti(1)-O(10)	195.83(18)	Ti(1)-O(1)	195.0(2)
Ti(1)-O(17)	201.6(3)	Ti(1)-O(13)	194.76(19)	Ti(1)-O(3)	198.9(2)
Ti(1)-O(18)	206.0(3)	Ti(1)-O(16)	203.54(18)	Ti(1)-O(5)	199.2(2)
Ti(1)-O(19)	181.7(4)	Ti(1)-O(17)	196.64(19)	Ti(1)-O(11)	200.6(2)
Ti(1)-O(20)	180.4(3)	Ti(1)-O(18)	177.69(19)	Ti(1)-O(12)	201.3(2)
Ti(1)-O(21)	208.7(3)	Ti(1)-O(20)	200.4(2)	Ti(1)-O(15)	177.9(2)
Ti(2)-O(3)	193.3(4)	Ti(2)-O(1)	195.59(17)	Ti(2)-O(1)	196.2(2)
Ti(2)-O(4)	203.8(4)	Ti(2)-O(3)	204.43(18)	Ti(2)-O(6)	197.1(3)
Ti(2)-O(6)	202.1(3)	Ti(2)-O(4)	202.27(17)	Ti(2)-O(8)	196.5(2)
Ti(2)-O(9)	176.4(4)	Ti(2)-O(7)	178.1(2)	Ti(2)-O(12)	204.7(2)
Ti(2)-O(10)	198.6(4)	Ti(2)-O(12)	197.87(18)	Ti(2)-O(13)	201.5(2)
Ti(2)-O(11)	197.1(4)	Ti(2)-O(14)	196.62(19)	Ti(2)-O(16)	177.0(2)
Ti(3)-O(3)	195.4(3)	Ti(3)-O(1)	195.39(17)	Ti(3)-O(1)	195.9(2)
Ti(3)-O(5)	201.7(4)	Ti(3)-O(2)	202.15(17)	Ti(3)-O(2)	197.4(2)
Ti(3)-O(6)	201.1(3)	Ti(3)-O(3)	202.08(18)	Ti(3)-O(9)	195.7(2)
Ti(3)-O(7)	177.0(3)	Ti(3)-O(6)	177.26(18)	Ti(3)-O(11)	204.3(2)
Ti(3)-O(8)	197.8(4)	Ti(3)-O(9)	198.21(19)	Ti(3)-O(13)	202.7(2)
Ti(3)-O(16)	196.6(3)	Ti(3)-O(11)	197.32(17)	Ti(3)-O(14)	177.7(2)
Ti(4)-O(3)	197.2(4)	Ti(4)-O(1)	196.78(17)	Ti(4)-O(4)	194.7(2)
Ti(4)-O(4)	202.0(4)	Ti(4)-O(2)	203.82(18)	Ti(4)-O(7)	193.2(3)
Ti(4)-O(5)	199.8(4)	Ti(4)-O(4)	202.48(18)	Ti(4)-O(10)	203.0(2)
Ti(4)-O(12)	198.4(3)	Ti(4)-O(5)	176.9(2)	Ti(4)-O(17)	199.7(3)
Ti(4)-O(14)	176.4(5)	Ti(4)-O(8)	196.61(19)	Ti(4)-O(18)	177.1(2)
Ti(4)-O(15)	196.9(3)	Ti(4)-O(15)	196.20(18)	Ti(4)-O(19)	197.9(3)
P(1)-O(11)	151.8(4)	P(1)-O(11)	153.64(18)	P(1)-O(2)	153.3(2)
P(1)-O(12)	153.7(4)	P(1)-C(22)	179.4(3)	P(1)-C(22)	180.9(4)
P(1)-O(13)	151.6(4)				
P(1)-C(7)	182.8(5)				
O(21)-S(1)	153.6(4)				

Table A.20: *Selected angles [°] of* ***TiDMSOAllylPA****,* ***TiAllylPP*** *and* ***TiAllylPP2****.*

TiDMSOAllylPA		**TiAllylPP**		**TiAllylPP2**	
Ti(3)-Ti(2)-Ti(4)	60.49(3)	Ti(3)-Ti(2)-Ti(4)	60.005(14)	Ti(2)-Ti(1)-Ti(3)	59.825(18)
Ti(2)-Ti(3)-Ti(4)	59.96(3)	Ti(2)-Ti(3)-Ti(4)	59.924(14)	Ti(3)-Ti(2)-Ti(1)	60.113(18)
Ti(2)-Ti(4)-Ti(3)	59.55(3)	Ti(2)-Ti(4)-Ti(3)	60.070(14)	Ti(2)-Ti(3)-Ti(1)	60.063(18)
Ti(2)-O(3)-Ti(3)	105.14(16)	Ti(2)-O(1)-Ti(3)	105.32(8)	Ti(1)-O(1)-Ti(3)	105.56(10)
Ti(2)-O(3)-Ti(4)	105.08(18)	Ti(2)-O(1)-Ti(4)	104.57(8)	Ti(1)-O(1)-Ti(2)	105.36(10)
Ti(3)-O(3)-Ti(4)	105.08(19)	Ti(3)-O(1)-Ti(4)	104.76(8)	Ti(3)-O(1)-Ti(2)	104.66(10)
Ti(2)-O(4)-Ti(4)	99.60(16)	Ti(3)-O(2)-Ti(4)	99.84(7)	Ti(1)-O(11)-Ti(3)	100.52(10)
Ti(3)-O(5)-Ti(4)	101.84(17)	Ti(2)-O(3)-Ti(3)	99.75(8)	Ti(1)-O(12)-Ti(2)	100.09(10)
Ti(2)-O(6)-Ti(3)	99.92(14)	Ti(2)-O(4)-Ti(4)	100.14(8)	Ti(2)-O(13)-Ti(3)	100.36(10)
O(7)-P(1)-C(12)	106.8(3)	O(11)-P(1)-O(12)	110.84(10)	O(2)-P(1)-O(3)	111.18(13)
O(11)-P(1)-O(13)	112.5(2)	O(11)-P(1)-C(22)	105.98(12)	O(2)-P(1)-C(22)	107.09(15)
Oxygen atoms in trans position on the octahedrally coordinated Ti atom					
O(13)-Ti(1)-O(21)	173.60(15)	O(10)-Ti(1)-O(17)	176.07(8)	O(1)-Ti(1)-O(15)	176.42(11)
O(17)-Ti(1)-O(19)	173.76(15)	O(13)-Ti(1)-O(20)	175.14(8)	O(3)-Ti(1)-O(12)	164.94(9)
O(18)-Ti(1)-O(20)	170.86(14)	O(16)-Ti(1)-O(18)	177.40(8)	O(5)-Ti(1)-O(11)	163.82(10)
O(3)-Ti(2)-O(9)	174.23(18)	O(1)-Ti(2)-O(7)	174.60(9)	O(1)-Ti(2)-O(16)	173.89(12)
O(4)-Ti(2)-O(10)	163.82(15)	O(3)-Ti(2)-O(14)	163.96(7)	O(6)-Ti(2)-O(13)	164.88(10)
O(6)-Ti(2)-O(11)	165.18(14)	O(4)-Ti(2)-O(12)	163.84(7)	O(8)-Ti(2)-O(12)	163.16(10)
O(3)-Ti(3)-O(7)	174.13(18)	O(6)-Ti(3)-O(1)	175.30(8)	O(1)-Ti(3)-O(14)	172.23(11)
O(5)-Ti(3)-O(8)	163.78(15)	O(11)-Ti(3)-O(2)	164.93(8)	O(2)-Ti(3)-O(13)	163.57(10)
O(6)-Ti(3)-O(16)	163.77(14)	O(9)-Ti(3)-O(3)	163.83(8)	O(9)-Ti(3)-O(11)	163.54(10)
O(3)-Ti(4)-O(14)	176.9(2)	O(1)-Ti(4)-O(5)	174.18(9)	O(4)-Ti(4)-O(19)	176.83(10)
O(4)-Ti(4)-O(15)	163.27(17)	O(2)-Ti(4)-O(15)	163.26(7)	O(7)-Ti(4)-O(17)	174.42(10)
O(5)-Ti(4)-O(12)	163.43(16)	O(4)-Ti(4)-O(8)	164.67(7)	O(10)-Ti(4)-O(18)	176.98(12)
Oxygen atoms in cis position on the octahedrally coordinated Ti atom					
O-Ti(1)-O	83.82(14) - 96.56(15)	O-Ti(1)-O	86.73(8) - 93.91(8)	O-Ti(1)-O	76.78(9) - 102.55(11)
O-Ti(2)-O	76.87(13) - 100.18(19)	O-Ti(2)-O	76.48(7) - 102.00(9)	O-Ti(2)-O	76.10(9) - 100.46(11)
O-Ti(3)-O	75.75(17) - 100.08(15)	O-Ti(3)-O	77.07(7) - 101.92(8)	O-Ti(3)-O	75.73(9) - 101.21(11)
O-Ti(4)-O	75.78(15) - 102.5(2)	O-Ti(4)-O	76.69(7) - 101.46(9)	O-Ti(4)-O	85.95(10) - 93.36(10)

Table A.21: *Selected bond lengths and atom distances [pm] of* ***TiEtPP****,* ***TiClPrPP*** *and* ***TiBzlPP****.*

TiEtPP		**TiClPrPP**		**TiBzlPP**	
Metal-metal distances					
Ti(2)-Ti(3)	310.67(9)	Ti(1)-Ti(2)	310.32(8)	Ti(2)-Ti(3)	310.76(17)
Ti(2)-Ti(4)	310.44(10)	Ti(1)-Ti(3)	310.16(8)	Ti(2)-Ti(4)	311.11(17)
Ti(3)-Ti(4)	310.10(9)	Ti(2)-Ti(3)	311.07(8)	Ti(3)-Ti(4)	310.60(17)
Selected bond lengths					
Ti(1)-O(3)	194.0(3)	Ti(1)-O(1)	195.8(2)	Ti(1)-O(1)	192.8(4)
Ti(1)-O(7)	194.6(3)	Ti(1)-O(2)	198.7(2)	Ti(1)-O(2)	192.5(4)
Ti(1)-O(8)	202.9(3)	Ti(1)-O(9)	198.0(2)	Ti(1)-O(3)	193.7(4)
Ti(1)-O(17)	178.6(3)	Ti(1)-O(11)	201.6(2)	Ti(2)-O(4)	196.7(4)
Ti(1)-O(18)	197.7(3)	Ti(1)-O(13)	202.3(2)	Ti(2)-O(6)	197.2(4)
Ti(1)-O(19)	201.6(3)	Ti(1)-O(14)	177.0(2)	Ti(2)-O(9)	195.3(4)
Ti(2)-O(1)	196.1(3)	Ti(2)-O(1)	196.4(2)	Ti(2)-O(12)	202.7(5)
Ti(2)-O(5)	197.5(3)	Ti(2)-O(3)	197.5(2)	Ti(2)-O(13)	177.5(4)
Ti(2)-O(10)	196.3(3)	Ti(2)-O(5)	197.2(2)	Ti(2)-O(14)	202.7(4)
Ti(2)-O(12)	203.7(3)	Ti(2)-O(11)	202.7(2)	Ti(3)-O(7)	196.9(4)
Ti(2)-O(13)	202.9(3)	Ti(2)-O(12)	201.5(2)	Ti(3)-O(8)	197.9(5)
Ti(2)-O(16)	177.7(3)	Ti(2)-O(15)	176.8(2)	Ti(3)-O(9)	195.6(4)
Ti(3)-O(1)	195.3(2)	Ti(3)-O(1)	195.9(2)	Ti(3)-O(10)	202.0(5)
Ti(3)-O(4)	196.7(3)	Ti(3)-O(6)	197.3(2)	Ti(3)-O(11)	177.5(4)
Ti(3)-O(6)	197.8(3)	Ti(3)-O(8)	198.7(2)	Ti(3)-O(12)	202.4(5)
Ti(3)-O(11)	202.1(3)	Ti(3)-O(12)	202.0(2)	Ti(4)-O(5)	197.4(4)
Ti(3)-O(12)	202.6(3)	Ti(3)-O(13)	201.1(2)	Ti(4)-O(9)	197.0(4)
Ti(3)-O(15)	177.8(3)	Ti(3)-O(16)	177.4(2)	Ti(4)-O(10)	203.0(4)
Ti(4)-O(1)	195.7(2)	Ti(4)-O(4)	192.9(2)	Ti(4)-O(14)	202.4(4)
Ti(4)-O(2)	197.7(3)	Ti(4)-O(7)	193.5(2)	Ti(4)-O(15)	196.9(4)
Ti(4)-O(9)	196.1(3)	Ti(4)-O(10)	192.5(2)	Ti(4)-O(16)	177.2(4)
Ti(4)-O(11)	204.1(3)	P(1)-O(2)	153.4(2)	P(1)-O(2)	151.6(4)
Ti(4)-O(13)	202.1(3)	P(1)-C(1)	179.4(3)	P(1)-C(25)	180.2(7)
Ti(4)-O(14)	178.1(3)				
P(1)-C(1)	179.2(4)				
P(1)-O(2)	153.8(3)				

Table A.22: *Selected angles [°] of* ***TiEtPP****,* ***TiClPrPP*** *and* ***TiBzlPP****.*

TiEtPP		**TiClPrPP**		**TiBzlPP**	
Ti(4)-Ti(2)-Ti(3)	59.90(2)	Ti(3)-Ti(1)-Ti(2)	60.177(18)	Ti(3)-Ti(2)-Ti(4)	59.93(4)
Ti(4)-Ti(3)-Ti(2)	60.01(2)	Ti(1)-Ti(2)-Ti(3)	59.887(18)	Ti(2)-Ti(3)-Ti(4)	60.09(4)
Ti(3)-Ti(4)-Ti(2)	60.09(2)	Ti(1)-Ti(3)-Ti(2)	59.936(18)	Ti(2)-Ti(4)-Ti(3)	59.98(4)
Ti(3)-O(1)-Ti(4)	104.97(12)	Ti(1)-O(1)-Ti(3)	104.71(9)	Ti(2)-O(9)-Ti(3)	105.33(19)
Ti(3)-O(1)-Ti(2)	105.10(11)	Ti(1)-O(1)-Ti(2)	104.63(10)	Ti(2)-O(9)-Ti(4)	104.95(19)
Ti(4)-O(1)-Ti(2)	104.83(11)	Ti(3)-O(1)-Ti(2)	104.92(10)	Ti(3)-O(9)-Ti(4)	104.57(19)
Ti(3)-O(11)-Ti(4)	99.53(11)	Ti(1)-O(11)-Ti(2)	100.28(9)	Ti(3)-O(10)-Ti(4)	100.14(19)
Ti(3)-O(12)-Ti(2)	99.76(12)	Ti(2)-O(12)-Ti(3)	100.91(9)	Ti(2)-O(12)-Ti(3)	100.17(19)
Ti(4)-O(13)-Ti(2)	100.10(12)	Ti(3)-O(13)-Ti(1)	100.51(9)	Ti(2)-O(14)-Ti(4)	100.36(18)
O(2)-P(1)-O(3)	112.11(15)	O(2)-P(1)-O(3)	111.62(12)	O(1)-P(3)-O(6)	112.1(2)
O(2)-P(1)-C(1)	107.41(18)	O(2)-P(1)-C(1)	106.42(15)	O(1)-P(3)-C(1)	107.4(3)
Oxygen atoms in trans position on the octahedrally coordinated Ti atom					
O(3)-Ti(1)-O(19)	175.31(12)	O(1)-Ti(1)-O(14)	173.93(10)	O(1)-Ti(1)-O(1)*	180.0(3)
O(7)-Ti(1)-O(18)	176.08(12)	O(2)-Ti(1)-O(13)	162.81(9)	O(2)-Ti(1)-O(2)*	180.0(3)
O(8)-Ti(1)-O(17)	177.46(13)	O(9)-Ti(1)-O(11)	165.34(9)	O(3)-Ti(1)-O(3)*	180.0(3)
O(1)-Ti(2)-O(16)	174.20(15)	O(1)-Ti(2)-O(15)	175.31(11)	O(4)-Ti(2)-O(12)	164.46(18)
O(5)-Ti(2)-O(13)	164.54(12)	O(3)-Ti(2)-O(12)	164.55(9)	O(6)-Ti(2)-O(14)	164.57(18)
O(10)-Ti(2)-O(12)	163.45(12)	O(5)-Ti(2)-O(11)	162.83(9)	O(13)-Ti(2)-O(9)	172.9(2)
O(1)-Ti(3)-O(15)	175.52(13)	O(1)-Ti(3)-O(16)	175.33(10)	O(7)-Ti(3)-O(10)	163.98(18)
O(4)-Ti(3)-O(12)	164.48(11)	O(6)-Ti(3)-O(13)	164.72(9)	O(8)-Ti(3)-O(12)	163.59(18)
O(6)-Ti(3)-O(11)	164.83(11)	O(8)-Ti(3)-O(12)	163.08(9)	O(9)-Ti(3)-O(11)	175.0(2)
O(1)-Ti(4)-O(14)	175.53(12)	O(4)-Ti(4)-O(4)*	180	O(5)-Ti(4)-O(10)	163.62(18)
O(2)-Ti(4)-O(13)	164.37(11)	O(7)-Ti(4)-O(7)*	180.000(1)	O(9)-Ti(4)-O(16)	176.32(19)
O(9)-Ti(4)-O(11)	164.34(11)	O(10)-Ti(4)-O(10)*	180	O(14)-Ti(4)-O(15)	162.71(18)
Oxygen atoms in cis position on the octahedrally coordinated Ti atom					
O-Ti(1)-O	86.44(11) - 93.47(11)	O-Ti(1)-O	76.62(8) - 101.86(10)	O-Ti(1)-O	88.38(18) - 91.62(18)
O-Ti(2)-O	76.53(11) - 100.29(15)	O-Ti(2)-O	76.46(9) - 102.96(10)	O-Ti(2)-O	76.45(18) - 99.5(2)
O-Ti(3)-O	77.09(11) - 100.97(12)	O-Ti(3)-O	76.44(9) - 102.13(10)	O-Ti(3)-O	76.45(18) - 99.7(2)
O-Ti(4)-O	76.78(10) - 100.78(13)	O-Ti(4)-O	87.72(9) - 92.28(9)	O-Ti(4)-O	76.59(17) - 101.64(19)

Table A.23: *Selected bond lengths and atom distances [pm] of* ***TiBrPrPP****,* ***TiXylPP*** *and* ***TiNpMePP****.*

TiBrPrPP		**TiXylPP**		**TiNpMePP**	
		Metal-metal distances			
Ti(1)-Ti(2)	310.40(12)	Ti(2)-Ti(3)	309.64(11)	Ti(1)-Ti(3)	332.48(11)
Ti(1)-Ti(3)	310.56(12)	Ti(2)-Ti(4)	310.27(11)		
Ti(2)-Ti(3)	311.55(12)	Ti(3)-Ti(4)	311.02(11)		
		Selected bond lengths			
Ti(1)-O(1)	195.6(3)	Ti(1)-O(2)	206.5(3)	Ti(1)-O(1)	201.7(3)
Ti(1)-O(2)	197.7(3)	Ti(1)-O(5)	201.1(3)	Ti(1)-O(8)	220.1(3)
Ti(1)-O(9)	198.8(3)	Ti(1)-O(8)	192.1(3)	Ti(1)-O(13)	194.4(3)
Ti(1)-O(12)	202.4(3)	Ti(1)-O(17)	178.6(3)	Ti(1)-O(14)	192.8(3)
Ti(1)-O(14)	201.7(3)	Ti(1)-O(18)	181.1(3)	Ti(1)-O(18)	175.9(3)
Ti(1)-O(15)	177.0(3)	Ti(1)-O(19)	213.9(3)	Ti(1)-O(21)	192.2(3)
Ti(2)-O(1)	196.3(3)	Ti(2)-O(1)	195.5(3)	Ti(2)-O(1)	232.1(3)
Ti(2)-O(3)	198.8(3)	Ti(2)-O(3)	197.2(3)	Ti(2)-O(2)	201.8(3)
Ti(2)-O(5)	197.5(3)	Ti(2)-O(10)	195.8(3)	Ti(2)-O(3)	180.4(4)
Ti(2)-O(12)	201.6(3)	Ti(2)-O(11)	201.0(3)	Ti(2)-O(4)	176.8(3)
Ti(2)-O(13)	202.5(4)	Ti(2)-O(13)	202.8(3)	Ti(2)-O(5)	193.6(4)
Ti(2)-O(16)	177.5(3)	Ti(2)-O(14)	177.7(3)	Ti(2)-O(6)	205.4(3)
Ti(3)-O(1)	197.0(3)	Ti(3)-O(1)	196.2(3)	Ti(3)-O(8)	219.5(3)
Ti(3)-O(6)	197.7(3)	Ti(3)-O(4)	197.0(3)	Ti(3)-O(10)	177.4(3)
Ti(3)-O(8)	197.9(3)	Ti(3)-O(7)	197.5(3)	Ti(3)-O(11)	206.5(3)
Ti(3)-O(13)	201.9(4)	Ti(3)-O(11)	202.7(3)	Ti(3)-O(12)	178.1(3)
Ti(3)-O(14)	202.1(3)	Ti(3)-O(12)	203.5(3)	Ti(3)-O(13)	209.9(3)
Ti(3)-O(17)	177.1(3)	Ti(3)-O(15)	176.6(3)	Ti(3)-O(20)	195.9(3)
Ti(4)-O(4)	193.5(3)	Ti(4)-O(1)	194.9(3)	Ti(4)-O(7)	202.0(3)
Ti(4)-O(7)	192.7(4)	Ti(4)-O(6)	196.6(3)	Ti(4)-O(15)	205.5(3)
Ti(4)-O(11)	193.4(3)	Ti(4)-O(9)	198.5(3)	Ti(4)-O(16)	189.9(4)
C(1A)-P(1)	179.7(5)	Ti(4)-O(12)	202.5(3)	Ti(4)-O(17)	199.0(3)
O(2)-P(1)	153.1(3)	Ti(4)-O(13)	201.5(3)	Ti(4)-O(22)	176.5(3)
		Ti(4)-O(16)	177.7(3)	Ti(4)-O(23)	201.2(4)
		P(1)-C(1)	179.8(4)	P(1)-O(1)	156.2(3)
		P(1)-O(2)	150.4(3)	P(1)-O(2)	152.9(3)
		Oxygen-oxygen distance of hydrogen bonds		P(1)-O(15)	149.4(3)
		O(19)-O(21)	268.0(4)	P(1)-C(12)	179.4(4)
		O(21)-O(4)	302.9(4)	P(2)-O(5)	152.4(4)
				P(2)-O(19)	150.4(4)
				P(2)-O(21)	153.3(3)
				P(3)-O(6)	151.3(3)
				P(3)-O(7)	151.2(3)
				P(3)-O(8)	156.1(3)
				P(4)-O(14)	153.6(3)
				P(4)-O(17)	151.7(3)
				P(4)-O(20)	152.4(3)

Table A.24: *Selected angles [°] of* ***TiBrPrPP****,* ***TiXylPP*** *and* ***TiNpMePP****.*

TiBrPrPP		**TiXylPP**		**TiNpMePP**	
Ti(2)-Ti(1)-Ti(3)	60.23(3)	Ti(3)-Ti(2)-Ti(4)	60.23(3)	Ti(1)-O(1)-Ti(2)	128.61(14)
Ti(1)-Ti(2)-Ti(3)	59.91(3)	Ti(2)-Ti(3)-Ti(4)	59.99(2)	Ti(1)-O(8)-Ti(3)	98.29(11)
Ti(1)-Ti(3)-Ti(2)	59.86(3)	Ti(2)-Ti(4)-Ti(3)	59.79(2)	Ti(1)-O(13)-Ti(3)	110.59(13)
Ti(1)-O(1)-Ti(2)	104.76(15)	Ti(4)-O(1)-Ti(2)	105.26(13)	O(1)-P(1)-O(15)	114.91(17)
Ti(1)-O(1)-Ti(3)	104.57(14)	Ti(4)-O(1)-Ti(3)	105.36(13)	O(2)-P(1)-O(15)	114.63(19)
Ti(2)-O(1)-Ti(3)	104.79(14)	Ti(2)-O(1)-Ti(3)	104.45(13)	O(1)-P(1)-O(2)	101.16(17)
Ti(2)-O(12)-Ti(1)	100.40(14)	Ti(2)-O(11)-Ti(3)	100.17(12)	O(15)-P(1)-C(12)	108.6(2)
Ti(3)-O(13)-Ti(2)	100.78(14)	Ti(4)-O(12)-Ti(3)	100.00(12)		
Ti(1)-O(14)-Ti(3)	100.55(14)	Ti(4)-O(13)-Ti(2)	100.26(12)		
O(2)-P(1)-O(4)	111.94(19)	O(2)-P(1)-O(3)	114.63(16)		
O(2)-P(1)-C(1A)	107.4(2)	O(2)-P(1)-C(1)	108.36(18)		
		O19-H19-O21	174.42(38)		
		O21-H21-O4	167.83(19)		
Oxygen atoms in trans position on the octahedrally coordinated Ti atom					
O(1)-Ti(1)-O(15)	174.33(15)	O(2)-Ti(1)-O(17)	172.13(13)	O(1)-Ti(1)-O(13)	158.73(12)
O(2)-Ti(1)-O(14)	164.88(14)	O(5)-Ti(1)-O(18)	168.58(13)	O(8)-Ti(1)-O(18)	176.89(12)
O(9)-Ti(1)-O(12)	163.01(14)	O(8)-Ti(1)-O(19)	168.54(13)	O(14)-Ti(1)-O(21)	170.92(13)
O(1)-Ti(2)-O(16)	175.30(15)	O(1)-Ti(2)-O(14)	174.93(13)	O(1)-Ti(2)-O(4)	163.27(13)
O(3)-Ti(2)-O(13)	162.91(14)	O(3)-Ti(2)-O(13)	162.28(12)	O(2)-Ti(2)-O(5)	157.35(14)
O(5)-Ti(2)-O(12)	164.92(14)	O(10)-Ti(2)-O(11)	166.36(12)	O(3)-Ti(2)-O(6)	166.12(15)
O(1)-Ti(3)-O(17)	175.87(16)	O(1)-Ti(3)-O(15)	172.85(13)	O(8)-Ti(3)-O(12)	163.03(13)
O(6)-Ti(3)-O(14)	162.96(14)	O(4)-Ti(3)-O(12)	163.49(12)	O(10)-Ti(3)-O(13)	168.79(14)
O(8)-Ti(3)-O(13)	164.41(14)	O(7)-Ti(3)-O(11)	163.77(12)	O(11)-Ti(3)-O(20)	167.44(13)
O(4)-Ti(4)-O(4)*	180.000(1)	O(1)-Ti(4)-O(16)	175.34(14)	O(7)-Ti(4)-O(16)	175.07(16)
O(7)-Ti(4)-O(7)*	180.00(15)	O(6)-Ti(4)-O(13)	164.04(12)	O(15)-Ti(4)-O(22)	176.38(16)
O(11)-Ti(4)-O(11)*	180.000(1)	O(9)-Ti(4)-O(12)	163.91(12)	O(17)-Ti(4)-O(23)	165.12(18)
Oxygen atoms in cis position on the octahedrally coordinated Ti atom					
O-Ti(1)-O	76.77(13) - 101.61(15)	O-Ti(1)-O	78.06(12) - 97.54(13)	O-Ti(1)-O	74.40(11) - 102.72(13)
O-Ti(2)-O	76.54(13) - 102.10(17)	O-Ti(2)-O	76.18(11) - 101.90(13)	O-Ti(2)-O	66.37(11) - 100.09(16)
O-Ti(3)-O	76.50(13) - 103.16(16)	O-Ti(3)-O	76.33(11) - 100.11(13)	O-Ti(3)-O	71.63(11) - 99.10(15)
O-Ti(4)-O	87.74(14) - 92.26(14)	O-Ti(4)-O	76.64(12) - 101.72(13)	O-Ti(4)-O	81.39(17) - 97.36(16)

Table A.25: *Selected bond lengths and atom distances [pm] of* ***TiCl3MePP****,* ***TiVinylPP*** *and* ***ZrPhPP****.*

TiCl3MePP		**TiVinylPP**		**ZrPhPP**	
Metal-metal distances					
Ti(1)-Ti(2)	310.19(10)	Ti(1)-Ti(2)	308.98(10)	Zr(1)-Zr(2)	335.56(9)
Ti(1)-Ti(3)	309.65(11)	Ti(1)-Ti(3)	308.66(10)	Zr(1)-Zr(3)	335.48(9)
Ti(2)-Ti(3)	309.40(11)	Ti(2)-Ti(3)	310.94(9)	Zr(2)-Zr(3)	340.70(8)
Selected bond lengths					
Ti(1)-O(1)	198.8(3)	Ti(1)-O(1)	194.5(3)	Zr(1)-O(1)	211.5(5)
Ti(1)-O(2)	198.8(3)	Ti(1)-O(2)	198.4(2)	Zr(1)-O(2)	209.2(5)
Ti(1)-O(5)	198.4(3)	Ti(1)-O(10)	198.9(3)	Zr(1)-O(5)	209.9(5)
Ti(1)-O(11)	200.8(3)	Ti(1)-O(12)	204.0(3)	Zr(1)-O(8)	214.6(5)
Ti(1)-O(13)	201.9(3)	Ti(1)-O(14)	200.5(3)	Zr(1)-O(10)	214.3(5)
Ti(1)-O(14)	175.2(3)	Ti(1)-O(15)	177.1(3)	Zr(1)-O(13)	193.0(5)
Ti(2)-O(1)	196.8(3)	Ti(2)-O(1)	195.9(2)	Zr(2)-O(1)	208.6(4)
Ti(2)-O(3)	198.3(3)	Ti(2)-O(7)	199.0(3)	Zr(2)-O(3)	209.1(5)
Ti(2)-O(8)	199.7(3)	Ti(2)-O(9)	200.4(3)	Zr(2)-O(6)	209.4(5)
Ti(2)-O(11)	202.6(3)	Ti(2)-O(12)	199.6(3)	Zr(2)-O(10)	215.7(5)
Ti(2)-O(12)	200.2(3)	Ti(2)-O(13)	200.7(3)	Zr(2)-O(11)	193.4(5)
Ti(2)-O(15)	176.5(3)	Ti(2)-O(16)	176.1(3)	Zr(2)-O(12)	215.8(5)
Ti(3)-O(1)	195.0(3)	Ti(3)-O(1)	196.7(3)	Zr(3)-O(1)	208.1(4)
Ti(3)-O(6)	199.0(3)	Ti(3)-O(3)	196.2(2)	Zr(3)-O(4)	210.2(4)
Ti(3)-O(9)	199.4(3)	Ti(3)-O(6)	198.5(3)	Zr(3)-O(7)	207.6(5)
Ti(3)-O(12)	203.9(3)	Ti(3)-O(13)	203.5(3)	Zr(3)-O(8)	215.9(5)
Ti(3)-O(13)	199.6(3)	Ti(3)-O(14)	202.0(3)	Zr(3)-O(9)	192.7(5)
Ti(3)-O(16)	175.7(3)	Ti(3)-O(17)	177.3(3)	Zr(3)-O(12)	215.6(5)
Ti(4)-O(4)	213.1(3)	Ti(4)-O(4)	197.0(3)	P(1)-O(2)	153.1(5)
Ti(4)-O(7)	204.8(3)	Ti(4)-O(5)	194.9(3)	P(1)-O(3)	151.7(5)
Ti(4)-O(10)	197.6(3)	Ti(4)-O(8)	194.4(3)	P(1)-O(4)	152.9(5)
Ti(4)-O(17)	178.8(3)	Ti(4)-O(11)	191.6(3)	P(1)-C(7)	178.3(6)
Ti(4)-O(18)	176.5(3)	Ti(4)-O(18)	177.6(3)		
Ti(4)-O(19)	209.7(3)	Ti(4)-O(19)	214.8(3)		
P(1)-C(1)	186.3(4)	P(1)-O(2)	155.8(3)		
P(1)-O(2)	152.6(3)	P(1)-O(3)	154.0(3)		
C(28)-O(19)	124.4(5)	P(1)-O(4)	150.5(3)		
C(28)-N(1)	131.7(5)	P(1)-O(5)	154.0(3)		
C(29)-N(1)	145.5(6)	P(2)-O(6)	152.8(3)		
C(30)-N(1)	145.4(6)	P(2)-O(7)	152.8(3)		
		P(2)-O(8)	153.1(3)		
		P(2)-C(1)	178.6(4)		

Table A.26: *Selected angles [°] of **TiCl3MePP**, **TiVinylPP** and **ZrPhPP**.*

TiCl3MePP		**TiVinylPP**		**ZrPhPP**	
Ti(2)-Ti(1)-Ti(3)	59.89(2)	Ti(2)-Ti(1)-Ti(3)	60.45(2)	Zr(2)-Zr(1)-Zr(3)	61.024(19)
Ti(1)-Ti(2)-Ti(3)	59.97(2)	Ti(1)-Ti(2)-Ti(3)	59.72(2)	Zr(1)-Zr(2)-Zr(3)	59.475(18)
Ti(1)-Ti(3)-Ti(2)	60.14(2)	Ti(1)-Ti(3)-Ti(2)	59.82(2)	Zr(1)-Zr(3)-Zr(2)	59.501(18)
Ti(1)-O(1)-Ti(2)	103.25(12)	Ti(1)-O(1)-Ti(2)	104.63(12)	Zr(3)-O(1)-Zr(2)	109.7(2)
Ti(1)-O(1)-Ti(3)	103.66(12)	Ti(1)-O(1)-Ti(3)	104.19(12)	Zr(3)-O(1)-Zr(1)	106.17(19)
Ti(2)-O(1)-Ti(3)	104.31(12)	Ti(2)-O(1)-Ti(3)	104.74(11)	Zr(2)-O(1)-Zr(1)	106.01(19)
Ti(1)-O(11)-Ti(2)	100.53(11)	Ti(2)-O(12)-Ti(1)	99.92(11)	Zr(1)-O(10)-Zr(2)	102.59(18)
Ti(1)-O(13)-Ti(3)	100.92(12)	Ti(2)-O(13)-Ti(3)	100.57(11)	Zr(1)-O(8)-Zr(3)	102.38(19)
Ti(2)-O(12)-Ti(3)	99.91(12)	Ti(1)-O(14)-Ti(3)	100.15(11)	Zr(2)-O(12)-Zr(3)	104.34(19)
O(2)-P(1)-O(3)	112.09(15)	O-P(1)-O	106.25(14) - 111.44(14)	P(1)-O(2)-Zr(1)	132.3(3)
O(2)-P(1)-C(1)	102.31(17)	O(6)-P(2)-O(7)	112.01(15)	P(1)-O(3)-Zr(2)	148.3(3)
O(19)-C(28)-N(1)	123.0(4)	O(6)-P(2)-C(1)	107.09(18)	O(3)-P(1)-O(2)	110.7(3)
				O(2)-P(1)-C(7)	106.4(3)
Oxygen atoms in trans position on the octahedrally coordinated Ti atom					
O(1)-Ti(1)-O(14)	175.10(13)	O(15)-Ti(1)-O(1)	175.82(12)	O(1)-Zr(1)-O(13)	167.1(2)
O(2)-Ti(1)-O(13)	161.98(11)	O(2)-Ti(1)-O(12)	163.51(11)	O(2)-Zr(1)-O(10)	161.76(18)
O(5)-Ti(1)-O(11)	163.02(11)	O(10)-Ti(1)-O(14)	164.81(12)	O(5)-Zr(1)-O(8)	162.45(18)
O(1)-Ti(2)-O(15)	177.62(13)	O(1)-Ti(2)-O(16)	176.89(12)	O(1)-Zr(2)-O(11)	157.3(2)
O(8)-Ti(2)-O(11)	164.46(11)	O(7)-Ti(2)-O(12)	165.30(10)	O(3)-Zr(2)-O(10)	168.32(19)
O(3)-Ti(2)-O(12)	163.79(11)	O(9)-Ti(2)-O(13)	163.71(10)	O(6)-Zr(2)-O(12)	160.22(18)
O(1)-Ti(3)-O(16)	175.70(13)	O(1)-Ti(3)-O(17)	173.23(12)	O(1)-Zr(3)-O(9)	157.1(2)
O(6)-Ti(3)-O(12)	164.06(11)	O(3)-Ti(3)-O(13)	164.92(11)	O(4)-Zr(3)-O(12)	161.01(18)
O(9)-Ti(3)-O(13)	164.98(12)	O(6)-Ti(3)-O(14)	162.31(11)	O(7)-Zr(3)-O(8)	168.55(18)
O(4)-Ti(4)-O(17)	170.58(12)	O(4)-Ti(4)-O(18)	171.02(11)		
O(7)-Ti(4)-O(18)	171.35(13)	O(5)-Ti(4)-O(8)	169.57(11)		
O(10)-Ti(4)-O(19)	168.61(11)	O(11)-Ti(4)-O(19)	174.98(11)		
Oxygen atoms in cis position on the octahedrally coordinated Ti atom					
O-Ti(1)-O	76.33(11) - 105.53(12)	O-Ti(1)-O	76.89(11) - 101.20(12)	O-Zr(1)-O	73.97(18) - 100.9(2)
O-Ti(2)-O	77.58(11) - 102.48(13)	O-Ti(2)-O	77.12(10) - 101.03(12)	O-Zr(2)-O	72.84(17) - 105.0(2)
O-Ti(3)-O	77.12(11) - 99.90(13)	O-Ti(3)-O	76.28(10) - 101.60(12)	O-Zr(3)-O	72.98(18) - 104.6(2)
O-Ti(4)-O	79.64(11) - 98.05(12)	O-Ti(4)-O	82.40(11) - 95.57(12)		

Table A.27: *Selected bond lengths and atom distances [pm] of* ***TiOAcEtPP****,* ***TiOAcNpMePP*** *and* ***TiOAcVinylPP****.*

TiOAcEtPP		**TiOAcNpMePP**		**TiOAcVinylPP**	
		Metal-metal distances			
Ti(1)-Ti(2)	313.75(2)	Ti(1)-Ti(2)	312.00(4)	Ti(1)-Ti(2)	308.65(7)
Ti(1)-Ti(3)	309.51(2)	Ti(1)-Ti(3)	310.32(4)	Ti(1)-Ti(3)	313.58(7)
Ti(2)-Ti(3)	375.16(2)	Ti(2)-Ti(3)	374.52(4)	Ti(2)-Ti(3)	375.69(6)
Ti(2)-Ti(3)*	344.03(2)	Ti(2)-Ti(3)*	344.15(4)	Ti(2)-Ti(3)*	345.85(7)
		Selected bond lengths			
Ti(1)-O(1)	198.03(6)	Ti(1)-O(1)	198.63(9)	Ti(1)-O(1)	197.73(19)
Ti(1)-O(3)	207.86(6)	Ti(1)-O(3)	207.02(11)	Ti(1)-O(3)	207.54(19)
Ti(1)-O(5)	195.83(7)	Ti(1)-O(5)	198.56(10)	Ti(1)-O(5)	197.31(19)
Ti(1)-O(6)	197.62(7)	Ti(1)-O(6)	195.98(10)	Ti(1)-O(6)	195.68(19)
Ti(1)-O(7)	177.81(6)	Ti(1)-O(7)	176.49(10)	Ti(1)-O(7)	177.75(19)
Ti(1)-O(12)*	194.95(6)	Ti(1)-O(12)	196.08(10)	Ti(1)-O(12)	194.9(2)
Ti(2)-O(1)	199.58(5)	Ti(2)-O(1)	199.07(9)	Ti(2)-O(1)	190.14(19)
Ti(2)-O(2)	186.29(6)	Ti(2)-O(2)	187.03(10)	Ti(2)-O(2)	175.9(2)
Ti(2)-O(4)	211.71(6)	Ti(2)-O(4)	211.20(11)	Ti(2)-O(6)	202.79(19)
Ti(2)-O(6)	203.57(6)	Ti(2)-O(5)	202.19(10)	Ti(2)-O(9)	180.7(2)
Ti(2)-O(9)	179.65(6)	Ti(2)-O(8)	179.01(10)	Ti(2)-O(10)	196.6(2)
Ti(2)-O(11)	195.54(6)	Ti(2)-O(10)	195.39(10)	Ti(3)-O(1)	199.69(19)
Ti(3)-O(1)	190.61(6)	Ti(3)-O(1)	190.35(10)	Ti(3)-O(2)	185.6(2)
Ti(3)-O(2)*	175.77(6)	Ti(3)-O(2)	175.51(10)	Ti(3)-O(4)	212.1(2)
Ti(3)-O(5)	203.15(6)	Ti(3)-O(6)	204.51(10)	Ti(3)-O(5)	203.5(2)
Ti(3)-O(8)	181.16(6)	Ti(3)-O(9)	182.23(11)	Ti(3)-O(8)	179.39(19)
Ti(3)-O(10)	196.23(6)	Ti(3)-O(11)	196.57(10)	Ti(3)-O(11)	196.0(2)
P(1)-O(10)	152.66(6)	P(1)-O(10)	152.89(10)	P(1)-O(10)	152.6(2)
P(1)-C(18)	179.34(8)	P(1)-C(18)	180.19(14)	P(1)-C(18A)	177.9(3)

Table A.28: *Selected angles [°] of **TiOAcEtPP**, **TiOAcNpMePP** and **TiOAcVinylPP**.*

TiOAcEtPP		**TiOAcNpMePP**		**TiOAcVinylPP**	
Ti(2)-Ti(1)-Ti(3)	74.013(5)	Ti(2)-Ti(1)-Ti(3)	73.999(8)	Ti(2)-Ti(1)-Ti(3)	74.277(16)
Ti(1)-Ti(2)-Ti(3)	52.477(4)	Ti(1)-Ti(2)-Ti(3)	52.795(7)	Ti(1)-Ti(2)-Ti(3)	53.460(14)
Ti(1)-Ti(3)-Ti(2)	53.510(4)	Ti(1)-Ti(3)-Ti(2)	53.206(7)	Ti(1)-Ti(3)-Ti(2)	52.262(13)
Ti(1)-Ti(2)-Ti(3)*	90.826(5)	Ti(1)-Ti(2)-Ti(3)*	92.473(9)	Ti(1)-Ti(2)-Ti(3)*	98.319(17)
Ti(1)-Ti(3)-Ti(2)*	97.834(5)	Ti(1)-Ti(3)-Ti(2)*	98.119(9)	Ti(1)-Ti(3)-Ti(2)*	90.636(17)
Ti(1)-O(1)-Ti(2)	104.20(3)	Ti(1)-O(1)-Ti(2)	103.35(4)	Ti(2)-O(1)-Ti(1)	105.44(9)
Ti(1)-O(1)-Ti(3)	105.56(3)	Ti(3)-O(1)-Ti(1)	105.82(4)	Ti(2)-O(1)-Ti(3)	149.03(11)
Ti(2)-O(1)-Ti(3)	148.08(3)	Ti(3)-O(1)-Ti(2)	148.19(5)	Ti(1)-O(1)-Ti(3)	104.19(8)
Ti(2)-O(2)-Ti(3)*	143.66(4)	Ti(3)-O(2)-Ti(2)	143.33(6)	Ti(2)-O(2)-Ti(3)	146.07(12)
Ti(1)-O(5)-Ti(3)	101.73(3)	Ti(1)-O(5)-Ti(2)	102.25(4)	Ti(1)-O(5)-Ti(3)	102.96(8)
Ti(1)-O(6)-Ti(2)	102.88(3)	Ti(1)-O(6)-Ti(3)	101.56(4)	Ti(1)-O(6)-Ti(2)	101.52(8)
O(10)-P(1)-O(11)	112.29(3)	O(11)-P(1)-O(10)	112.30(6)	O(10)-P(1)-O(11)	112.11(11)
O(10)-P(1)-C(18)	106.49(4)	O(10)-P(1)-C(18)	106.48(6)	O(10)-P(1)-C(18A)	107.23(13)
Oxygen atoms in trans position on the octahedrally coordinated Ti atom					
O(1)-Ti(1)-O(7)	171.35(3)	O(1)-Ti(1)-O(7)	173.87(5)	O(1)-Ti(1)-O(7)	171.16(9)
O(3)-Ti(1)-O(12)	179.18(3)	O(3)-Ti(1)-O(12)	178.05(5)	O(3)-Ti(1)-O(12)	179.28(8)
O(5)-Ti(1)-O(6)	152.86(3)	O(5)-Ti(1)-O(6)	153.34(4)	O(5)-Ti(1)-O(6)	152.94(8)
O(1)-Ti(2)-O(9)	164.55(3)	O(8)-Ti(2)-O(1)	165.04(5)	O(1)-Ti(3)-O(8)	164.25(9)
O(2)-Ti(2)-O(4)	175.03(3)	O(2)-Ti(2)-O(4)	175.00(4)	O(2)-Ti(3)-O(4)	175.97(9)
O(6)-Ti(2)-O(11)	162.43(3)	O(10)-Ti(2)-O(5)	163.40(4)	O(5)-Ti(3)-O(11)	161.45(8)
Oxygen atoms in cis position on the octahedrally coordinated Ti atom					
O-Ti(1)-O	76.38(2) - 104.18(3)	O-Ti(1)-O	76.35(4) - 104.39(4)	O-Ti(1)-O	76.45(8) - 106.34(9)
O-Ti(2)-O	74.94(2) - 99.41(3)	O-Ti(2)-O	76.18(4) - 99.03(4)	O-Ti(3)-O	74.74(7) - 100.69(9)

Table A.29: *Selected bond lengths and atom distances [pm] of* ***TiOAcAllylPP****,* ***TiOAcCl-PrPP*** *and* ***TiOAcBzlPP****.*

TiOAcAllylPP		**TiOAcClPrPP**		**TiOAcBzlPP**	
Metal-metal distances					
Ti(1)-Ti(2)	312.20(3)	Ti(1)-Ti(2)	312.79(10)	Ti(1)-Ti(2)	309.98(6)
Ti(1)-Ti(3)	307.59(3)	Ti(1)-Ti(3)	309.03(10)	Ti(1)-Ti(3)	312.58(7)
Ti(2)-Ti(3)	375.06(4)	Ti(2)-Ti(3)	373.02(11)	Ti(2)-Ti(3)	371.85(8)
Ti(2)-Ti(3)*	341.78(4)	Ti(2)-Ti(3)*	342.82(11)	Ti(2)-Ti(3)*	343.14(7)
Selected bond lengths					
Ti(1)-O(1)	197.01(6)	Ti(1)-O(1)	197.5(2)	Ti(1)-O(1)	199.30(16)
Ti(1)-O(3)	207.90(7)	Ti(1)-O(3)	208.5(3)	Ti(1)-O(3)	206.41(17)
Ti(1)-O(5)	198.25(6)	Ti(1)-O(5)	197.7(3)	Ti(1)-O(5)	197.10(19)
Ti(1)-O(6)	196.21(6)	Ti(1)-O(6)	195.9(3)	Ti(1)-O(6)	196.99(19)
Ti(1)-O(7)	177.53(6)	Ti(1)-O(7)	177.2(3)	Ti(1)-O(7)	177.10(17)
Ti(1)-O(12)	194.65(7)	Ti(1)-O(12)	194.3(3)	Ti(1)-O(12)	195.26(17)
Ti(2)-O(1)	200.84(6)	Ti(2)-O(1)	199.2(3)	Ti(2)-O(1)	190.07(17)
Ti(2)-O(2)	188.27(7)	Ti(2)-O(2)	186.1(3)	Ti(2)-O(2)	176.91(17)
Ti(2)-O(4)	213.31(7)	Ti(2)-O(4)	213.8(3)	Ti(2)-O(5)	202.35(17)
Ti(2)-O(5)	202.13(6)	Ti(2)-O(5)	202.9(3)	Ti(2)-O(8)	180.5(2)
Ti(2)-O(8)	176.59(7)	Ti(2)-O(8)	178.0(3)	Ti(2)-O(10)	195.93(17)
Ti(2)-O(10)	195.71(6)	Ti(2)-O(10)	195.7(3)	Ti(3)-O(1)	197.99(17)
Ti(3)-O(1)	190.52(6)	Ti(3)-O(1)	189.6(3)	Ti(3)-O(2)	186.26(18)
Ti(3)-O(2)*	175.23(6)	Ti(3)-O(2)	175.4(3)	Ti(3)-O(4)	211.83(18)
Ti(3)-O(6)	203.42(6)	Ti(3)-O(6)	202.7(3)	Ti(3)-O(6)	203.18(17)
Ti(3)-O(9)	182.31(7)	Ti(3)-O(9)	179.6(3)	Ti(3)-O(9)	179.78(18)
Ti(3)-O(11)	197.72(7)	Ti(3)-O(11)	194.8(3)	Ti(3)-O(11)	196.25(17)
P(1)-O(10)	152.80(7)	P(1)-O(10)	151.4(4)	P(1)-O(10)	152.77(18)
P(1)-C(18)	180.03(9)	P(1)-C(18A)	182.1(11)	P(1)-C(18)	180.3(2)

*Table A.30: Selected angles [°] of **TiOAcAllylPP**, **TiOAcClPrPP** and **TiOAcBzlPP**.*

TiOAcAllylPP		**TiOAcClPrPP**		**TiOAcBzlPP**	
Ti(2)-Ti(1)-Ti(3)	74.473(8)	Ti(3)-Ti(1)-Ti(2)	73.72(2)	Ti(2)-Ti(1)-Ti(3)	73.354(16)
Ti(1)-Ti(2)-Ti(3)	52.202(5)	Ti(1)-Ti(2)-Ti(3)	52.68(2)	Ti(1)-Ti(2)-Ti(3)	53.646(13)
Ti(1)-Ti(3)-Ti(2)	53.324(5)	Ti(1)-Ti(3)-Ti(2)	53.60(2)	Ti(1)-Ti(3)-Ti(2)	53.000(12)
Ti(1)-Ti(2)-Ti(3)*	90.442(6)	Ti(1)-Ti(2)-Ti(3)*	91.2(3)	Ti(1)-Ti(2)-Ti(3)*	98.485(17)
Ti(1)-Ti(3)-Ti(2)*	98.722(6)	Ti(1)-Ti(3)-Ti(2)*	98.06(3)	Ti(1)-Ti(3)-Ti(2)*	91.290(15)
Ti(1)-O(1)-Ti(2)	103.39(3)	Ti(1)-O(1)-Ti(2)	104.07(12)	Ti(2)-O(1)-Ti(3)	146.77(9)
Ti(1)-O(1)-Ti(3)	105.06(3)	Ti(1)-O(1)-Ti(3)	105.92(12)	Ti(2)-O(1)-Ti(1)	105.50(8)
Ti(2)-O(1)-Ti(3)	146.80(3)	Ti(2)-O(1)-Ti(3)	147.17(14)	Ti(3)-O(1)-Ti(1)	103.77(8)
Ti(2)-O(2)-Ti(3)*	140.16(4)	Ti(2)-O(2)-Ti(3)*	142.99(18)	Ti(2)-O(2)-Ti(3)	141.76(11)
Ti(1)-O(5)-Ti(2)	102.47(3)	Ti(1)-O(5)-Ti(2)	102.69(13)	Ti(1)-O(5)-Ti(2)	101.79(7)
Ti(1)-O(6)-Ti(3)	100.64(3)	Ti(1)-O(6)-Ti(3)	101.63(12)	Ti(1)-O(6)-Ti(3)	102.71(8)
O(10)-P(1)-O(11)	112.26(4)	O(10)-P(1)-O(11)	111.96(17)	O(10)-P(1)-O(11)	111.88(10)
O(10)-P(1)-C(18)	107.06(4)	O(10)-P(1)-C(18A)	115.5(4)	O(10)-P(1)-C(18)	108.13(11)
Oxygen atoms in trans position on the octahedrally coordinated Ti atom					
O(1)-Ti(1)-O(7)	170.82(3)	O(1)-Ti(1)-O(7)	171.76(13)	O(7)-Ti(1)-O(1)	175.51(8)
O(3)-Ti(1)-O(12)	177.48(3)	O(3)-Ti(1)-O(12)	179.08(12)	O(12)-Ti(1)-O(3)	177.34(7)
O(5)-Ti(1)-O(6)	154.20(3)	O(5)-Ti(1)-O(6)	152.65(12)	O(6)-Ti(1)-O(5)	152.18(7)
O(1)-Ti(2)-O(8)	167.73(3)	O(1)-Ti(2)-O(8)	164.35(13)	O(9)-Ti(3)-O(1)	164.37(8)
O(2)-Ti(2)-O(4)	174.99(3)	O(2)-Ti(2)-O(4)	176.74(13)	O(2)-Ti(3)-O(4)	177.20(8)
O(5)-Ti(2)-O(10)	162.77(3)	O(5)-Ti(2)-O(10)	162.39(13)	O(11)-Ti(3)-O(6)	163.49(8)
Oxygen atoms in cis position on the octahedrally coordinated Ti atom					
O-Ti(1)-O	76.97(3) - 102.77(3)	O-Ti(1)-O	76.13(11) - 103.17(16)	O-Ti(1)-O	75.89(7) - 104.61(8)
O-Ti(2)-O	75.75(2) - 98.76(3)	O-Ti(2)-O	75.24(11) - 99.43(16)	O-Ti(3)-O	75.49(7) - 97.84(8)

Table A.31: *Selected bond lengths and atom distances [pm] of* ***TiOAcBrPrPP****,* ***TiOAcPhPA*** *and* ***TiOAcBrPrPP2****.*

TiOAcBrPrPP		**TiOAcPhPA**		**TiOAcBrPrPP2**	
		Metal-metal distances			
Ti(1)-Ti(2)	312.66(2)	Ti(1)-Ti(2)	311.00(5)	Ti(1)-Ti(2)	309.95(5)
Ti(1)-Ti(3)	308.02(2)	Ti(1)-Ti(3)	310.08(5)	Ti(1)-Ti(3)	309.78(4)
Ti(2)-Ti(3)	374.61(2)	Ti(2)-Ti(3)	374.64(5)	Ti(2)-Ti(3)	310.71(5)
Ti(2)-Ti(3)*	342.84(2)	Ti(2)-Ti(3)*	344.36(5)	Ti(4)-Ti(5)	333.02(5)
		Selected bond lengths			
Ti(1)-O(1)	198.18(7)	Ti(1)-O(1)	198.80(13)	Ti(1)-O(1)	195.73(12)
Ti(1)-O(3)	206.86(7)	Ti(1)-O(3)	206.06(14)	Ti(1)-O(4)	201.82(12)
Ti(1)-O(5)	197.94(7)	Ti(1)-O(5)	198.20(13)	Ti(1)-O(5)	201.53(12)
Ti(1)-O(6)	195.09(7)	Ti(1)-O(6)	196.30(14)	Ti(1)-O(8)	177.09(13)
Ti(1)-O(7)	176.79(7)	Ti(1)-O(7)	176.57(13)	Ti(1)-O(15)	195.97(12)
Ti(1)-O(12)	194.02(7)	Ti(1)-O(12)	196.40(13)	Ti(1)-O(18)	200.07(12)
Ti(2)-O(1)	199.46(7)	Ti(2)-O(1)	198.79(12)	Ti(2)-O(1)	196.85(12)
Ti(2)-O(2)	185.60(7)	Ti(2)-O(2)	186.40(13)	Ti(2)-O(4)	202.14(12)
Ti(2)-O(4)	213.84(7)	Ti(2)-O(4)	211.65(13)	Ti(2)-O(6)	202.19(13)
Ti(2)-O(5)	202.09(7)	Ti(2)-O(5)	201.48(13)	Ti(2)-O(9)	176.60(13)
Ti(2)-O(8)	180.39(7)	Ti(2)-O(8)	180.57(13)	Ti(2)-O(19)	198.00(13)
Ti(2)-O(10)	195.27(7)	Ti(2)-O(10)	195.94(13)	Ti(2)-O(21)	196.76(13)
Ti(3)-O(1)	190.28(7)	Ti(3)-O(1)	190.66(13)	Ti(3)-O(1)	194.45(12)
Ti(3)-O(2)	176.78(7)	Ti(3)-O(2)	176.15(13)	Ti(3)-O(5)	203.13(12)
Ti(3)-O(6)	203.06(7)	Ti(3)-O(6)	203.82(14)	Ti(3)-O(6)	203.23(13)
Ti(3)-O(9)	179.95(8)	Ti(3)-O(9)	181.76(13)	Ti(3)-O(10)	177.06(13)
Ti(3)-O(11)	197.14(7)	Ti(3)-O(11)	196.56(13)	Ti(3)-O(16)	199.39(13)
P(1)-O(10)	152.93(7)	P(1)-C(18)	179.51(18)	Ti(3)-O(22)	197.89(13)
P(1)-C(18)	179.45(10)	P(1)-O(10)	152.73(14)	Ti(4)-O(2)	206.85(13)
				Ti(4)-O(7)	202.99(13)
				Ti(4)-O(11)	176.88(13)
				Ti(4)-O(12)	180.52(13)
				Ti(4)-O(17)	195.69(13)
				Ti(4)-O(20)	219.25(12)
				Ti(5)-O(3)	207.95(14)
				Ti(5)-O(7)	202.14(13)
				Ti(5)-O(13)	177.62(13)
				Ti(5)-O(14)	179.83(14)
				Ti(5)-O(20)	219.61(12)
				Ti(5)-O(23)	194.65(13)
				P(1)-C(36A)	180.24(18)
				P(1)-O(15)	153.33(13)

Table A.32: *Selected angles [°] of **TiOAcBrPrPP**, **TiOAcPhPA** and **TiOAcBrPrPP2**.*

TiOAcBrPrPP		**TiOAcPhPA**		**TiOAcBrPrPP2**	
Ti(2)-Ti(1)-Ti(3)	74.244(6)	Ti(3)-Ti(1)-Ti(2)	74.197(11)	Ti(3)-Ti(1)-Ti(2)	60.179(10)
Ti(1)-Ti(2)-Ti(3)	52.312(5)	Ti(1)-Ti(2)-Ti(3)	52.788(9)	Ti(1)-Ti(2)-Ti(3)	59.884(10)
Ti(1)-Ti(3)-Ti(2)	53.444(5)	Ti(1)-Ti(3)-Ti(2)	53.014(9)	Ti(1)-Ti(3)-Ti(2)	59.937(10)
Ti(1)-Ti(2)-Ti(3)*	90.262(6)	Ti(1)-Ti(2)-Ti(3)*	91.539(11)	Ti(1)-O(1)-Ti(2)	104.28(6)
Ti(1)-Ti(3)-Ti(2)*	98.024(6)	Ti(1)-Ti(3)-Ti(2)*	98.071(12)	Ti(1)-O(1)-Ti(3)	105.11(6)
Ti(1)-O(1)-Ti(2)	103.68(3)	Ti(2)-O(1)-Ti(1)	102.93(6)	Ti(2)-O(1)-Ti(3)	105.13(6)
Ti(1)-O(1)-Ti(3)	104.90(3)	Ti(3)-O(1)-Ti(1)	105.52(6)	Ti(1)-O(4)-Ti(2)	100.22(5)
Ti(2)-O(1)-Ti(3)	147.96(4)	Ti(3)-O(1)-Ti(2)	148.28(7)	Ti(1)-O(5)-Ti(3)	99.91(5)
Ti(2)-O(2)-Ti(3)*	142.19(4)	Ti(3)-O(2)-Ti(2)	143.53(8)	Ti(2)-O(6)-Ti(3)	100.06(5)
Ti(1)-O(5)-Ti(3)	102.81(3)	Ti(1)-O(5)-Ti(2)	102.18(6)	Ti(4)-O(7)-Ti(5)	110.57(6)
Ti(1)-O(6)-Ti(2)	101.34(3)	Ti(1)-O(6)-Ti(3)	101.59(6)	Ti(4)-O(20)-Ti(5)	98.72(5)
O(10)-P(1)-O(11)	111.86(4)	O(10)-P(1)-O(11)	112.35(7)	O(15)-P(1)-O(16)	111.51(7)
O(10)-P(1)-C(18)	106.42(4)	O(10)-P(1)-C(18)	106.41(8)	O(15)-P(1)-C(36A)	106.34(8)
Oxygen atoms in trans position on the octahedrally coordinated Ti atom					
O(1)-Ti(1)-O(7)	170.88(3)	O(1)-Ti(1)-O(7)	175.67(6)	O(8)-Ti(1)-O(1)	173.30(6)
O(3)-Ti(1)-O(12)	178.36(3)	O(3)-Ti(1)-O(12)	178.49(6)	O(18)-Ti(1)-O(5)	161.63(5)
O(5)-Ti(1)-O(6)	153.39(3)	O(5)-Ti(1)-O(56)	153.16(6)	O(1)-Ti(2)-O(9)	173.84(6)
O(1)-Ti(2)-O(8)	165.66(3)	O(1)-Ti(2)-O(8)	166.57(6)	O(6)-Ti(2)-O(19)	160.87(5)
O(2)-Ti(2)-O(4)	176.36(3)	O(2)-Ti(2)-O(4)	175.70(6)	O(1)-Ti(3)-O(10)	173.51(6)
O(5)-Ti(2)-O(10)	161.77(3)	O(5)-Ti(2)-O(10)	163.73(5)	O(5)-Ti(3)-O(22)	164.24(5)
				O(2)-Ti(4)-O(17)	168.38(5)
				O(12)-Ti(4)-O(20)	165.17(6)
				O(3)-Ti(5)-O(23)	171.08(5)
				O(7)-Ti(5)-O(13)	164.64(6)
Oxygen atoms in cis position on the octahedrally coordinated Ti atom					
O-Ti(1)-O	76.81(3) - 106.59(3)	O-Ti(1)-O	76.41(5) - 103.60(6)	O-Ti(1)-O	76.70(5) - 103.14(5)
O-Ti(2)-O	75.58(3) - 100.80(3)	O-Ti(2)-O	76.49(5) - 99.60(6)	O-Ti(2)-O	76.45(5) - 99.69(6)
				O-Ti(3)-O	76.61(5) - 99.97(6)
				O-Ti(4)-O	73.91(5) - 98.65(6)
				O-Ti(5)-O	74.00(5) - 99.18(6)

Table A.33: *Selected bond lengths and atom distances [pm] of* ***TiOAcXylPP*** *and* ***TiOPhPP****.*

TiOAcXylPP		**TiOPhPP**	
Metal-metal distances			
Ti(1)-Ti(2)	318.82(6)	Ti(1)-Ti(2)	313.03(7)
Ti(1)-Ti(3)	347.46(6)	Ti(1)-Ti(3)	310.24(6)
Ti(2)-Ti(3)	353.50(5)	Ti(2)-Ti(3)	374.35(6)
Ti(2)-Ti(4)	346.78(6)	Ti(2)-Ti(3)*	358.73(7)
Ti(3)-Ti(4)	352.78(5)		
Ti(3)-Ti(5)	347.00(6)		
Ti(4)-Ti(5)	318.24(6)		
Selected bond lengths			
Ti(1)-O(1)	199.99(16)	Ti(1)-O(1)	196.64(18)
Ti(1)-O(4)	204.7(2)	Ti(1)-O(3)	204.73(19)
Ti(1)-O(6)	202.5(2)	Ti(1)-O(6)	199.75(18)
Ti(1)-O(12)	195.6(2)	Ti(1)-O(7)	196.70(17)
Ti(1)-O(14)	178.02(19)	Ti(1)-O(8)	178.92(18)
Ti(1)-O(18)	193.98(19)	Ti(1)-O(13)	194.46(19)
Ti(2)-O(1)	211.10(16)	Ti(2)-O(1)	197.52(18)
Ti(2)-O(3)	178.91(18)	Ti(2)-O(2)	188.84(19)
Ti(2)-O(5)	211.56(19)	Ti(2)-O(4)	209.26(19)
Ti(2)-O(12)	205.6(2)	Ti(2)-O(6)	202.52(18)
Ti(2)-O(15)	180.53(18)	Ti(2)-O(9)	178.12(18)
Ti(2)-O(21)	196.32(18)	Ti(2)-O(11)	197.03(18)
Ti(3)-O(1)	183.87(16)	Ti(3)-O(1)	192.51(17)
Ti(3)-O(2)	183.22(15)	Ti(3)-O(2)	172.59(19)
Ti(3)-O(7)	207.36(16)	Ti(3)-O(7)	205.68(18)
Ti(3)-O(8)	206.91(16)	Ti(3)-O(10)	181.06(18)
Ti(3)-O(19)	197.07(16)	Ti(3)-O(12)	198.36(18)
Ti(3)-O(22)	196.90(16)	P(1)-O(3)	150.61(19)
Ti(4)-O(2)	207.15(16)	P(1)-O(4)	150.8(2)
Ti(4)-O(3)	183.21(17)	P(1)-O(5)	158.6(2)
Ti(4)-O(10)	210.59(18)	P(1)-C(1)	179.0(3)
Ti(4)-O(13)	203.91(19)	P(2)-O(11)	152.78(19)
Ti(4)-O(16)	176.38(17)	P(2)-O(12)	152.74(19)
Ti(4)-O(20)	197.19(18)	P(2)-O(13)	152.09(19)
Ti(5)-O(2)	202.64(16)	P(2)-C(25)	180.2(3)
Ti(5)-O(9)	201.75(18)		
Ti(5)-O(11)	203.88(18)		
Ti(5)-O(13)	196.35(19)		
Ti(5)-O(17)	175.70(17)		
Ti(5)-O(23)	194.14(16)		
P(1)-O(18)	154.71(19)		
P(1)-C(27)	177.9(2)		

Table A.34: *Selected angles [°] of* ***TiOAcXylPP*** *and* ***TiOPhPP****.*

TiOAcXylPP		**TiOPhPP**	
Ti(2)-Ti(1)-Ti(3)	63.918(13)	Ti(2)-Ti(1)-Ti(3)	73.828(16)
Ti(1)-Ti(2)-Ti(3)	61.984(13)	Ti(1)-Ti(2)-Ti(3)	52.747(12)
Ti(1)-Ti(2)-Ti(4)	93.467(15)	Ti(1)-Ti(3)-Ti(2)	53.426(12)
Ti(3)-Ti(2)-Ti(4)	60.490(11)	Ti(1)-Ti(2)-Ti(3)*	90.087(16)
Ti(1)-Ti(3)-Ti(2)	54.098(11)	Ti(1)-Ti(3)-Ti(2)*	97.929(16)
Ti(1)-Ti(3)-Ti(4)	87.682(13)	Ti(1)-O(1)-Ti(2)	105.15(8)
Ti(1)-Ti(3)-Ti(5)	137.515(16)	Ti(1)-O(1)-Ti(3)	105.73(8)
Ti(2)-Ti(3)-Ti(4)	58.811(11)	Ti(2)-O(1)-Ti(3)	147.40(10)
Ti(2)-Ti(3)-Ti(5)	87.185(12)	Ti(2)-O(2)-Ti(3)*	165.97(11)
Ti(2)-Ti(4)-Ti(3)	60.698(11)	Ti(1)-O(6)-Ti(2)	102.18(7)
Ti(2)-Ti(4)-Ti(5)	93.062(13)	Ti(1)-O(7)-Ti(3)	100.87(8)
Ti(3)-Ti(4)-Ti(5)	62.026(11)	O(3)-P(1)-O(4)	117.06(11)
Ti(3)-Ti(5)-Ti(4)	63.881(12)	O(3)-P(1)-O(5)	104.09(11)
Ti(1)-O(1)-Ti(2)	101.67(7)	O(4)-P(1)-O(5)	110.30(11)
Ti(1)-O(1)-Ti(3)	129.65(9)	O(3)-P(1)-C(1)	109.63(12)
Ti(2)-O(1)-Ti(3)	126.89(8)	O(4)-P(1)-C(1)	108.67(12)
Ti(3)-O(2)-Ti(4)	129.20(8)	O(5)-P(1)-C(1)	106.55(12)
Ti(3)-O(2)-Ti(5)	128.06(8)	O(13)-P(2)-O(12)	111.20(10)
Ti(4)-O(2)-Ti(5)	101.90(7)	O(13)-P(2)-O(11)	112.99(10)
Ti(2)-O(3)-Ti(4)	146.51(10)	O(12)-P(2)-O(11)	111.54(10)
Ti(1)-O(12)-Ti(2)	105.22(8)	O(13)-P(2)-C(25)	106.28(12)
Ti(4)-O(13)-Ti(5)	105.31(7)	O(12)-P(2)-C(25)	108.04(11)
O(18)-P(1)-O(19)	109.36(10)	O(11)-P(2)-C(25)	106.40(12)
O(18)-P(1)-C(27)	107.72(11)		
Oxygen atoms in trans position on the octahedrally coordinated Ti atom			
O(1)-Ti(1)-O(14)	171.93(9)	O(1)-Ti(1)-O(8)	168.28(8)
O(4)-Ti(1)-O(18)	172.06(8)	O(3)-Ti(1)-O(13)	177.49(8)
O(6)-Ti(1)-O(12)	165.62(8)	O(6)-Ti(1)-O(7)	152.78(7)
O(1)-Ti(2)-O(15)	169.70(8)	O(1)-Ti(2)-O(9)	168.13(8)
O(3)-Ti(2)-O(5)	174.54(8)	O(2)-Ti(2)-O(4)	175.09(8)
O(12)-Ti(2)-O(21)	158.46(7)	O(6)-Ti(2)-O(11)	162.87(7)
O(1)-Ti(3)-O(8)	170.76(7)		
O(2)-Ti(3)-O(7)	171.43(7)		
O(19)-Ti(3)-O(22)	174.87(7)		
O(2)-Ti(4)-O(16)	169.40(8)		
O(3)-Ti(4)-O(10)	170.36(8)		
O(13)-Ti(4)-O(20)	161.12(7)		
O(2)-Ti(5)-O(17)	172.24(8)		
O(9)-Ti(5)-O(13)	164.86(7)		
O(11)-Ti(5)-O(23)	168.54(7)		
Oxygen atoms in cis position on the octahedrally coordinated Ti atom			
O-Ti(1)-O	77.14(7) - 99.23(9)	O-Ti(1)-O	76.21(7) - 104.42(8)
O-Ti(2)-O	72.59(7) - 99.25(9)	O-Ti(2)-O	75.82(7) - 99.74(8)
O-Ti(3)-O	80.49(7) - 98.19(7)		
O-Ti(4)-O	73.72(6) - 98.24(8)		
O-Ti(5)-O	76.33(7) - 97.96(9)		

Table A.35: *Selected bond lengths and atom distances [pm] of* ***TiOMcEtPP*** *and* ***TiOMcAllylPP****.*

TiOMcEtPP		**TiOMcAllylPP**	
Metal-metal distances			
Ti(1)-Ti(2)	309.73(7)	Ti(2)-Ti(5)	330.88(9)
Ti(1)-Ti(3)	311.32(7)	Ti(3)-Ti(4)	387.64(11)
Ti(2)-Ti(3)	309.97(7)		
Ti(4)-Ti(5)	331.85(7)		
Selected bond lengths			
Ti(1)-O(1)	195.98(19)	Ti(1)-O(2)	193.6(2)
Ti(1)-O(3)	196.97(19)	Ti(1)-O(3)	195.9(2)
Ti(1)-O(5)	198.48(18)	Ti(1)-O(4)	202.1(2)
Ti(1)-O(13)	202.08(19)	Ti(1)-O(8)	195.8(2)
Ti(1)-O(14)	200.94(19)	Ti(1)-O(12)	200.9(2)
Ti(1)-O(17)	178.0(2)	Ti(1)-O(20)	175.6(2)
Ti(2)-O(1)	193.96(18)	Ti(2)-O(1)	192.6(2)
Ti(2)-O(2)	195.49(19)	Ti(2)-O(6)	188.8(2)
Ti(2)-O(8)	198.1(2)	Ti(2)-O(7)	216.5(2)
Ti(2)-O(13)	204.4(2)	Ti(2)-O(19)	206.3(3)
Ti(2)-O(15)	202.41(19)	Ti(2)-O(21)	195.1(2)
Ti(2)-O(18)	177.88(19)	Ti(2)-O(22)	175.2(2)
Ti(3)-O(1)	196.53(18)	Ti(3)-O(9)	193.5(2)
Ti(3)-O(7)	198.03(19)	Ti(3)-O(10)	221.1(2)
Ti(3)-O(10)	195.3(2)	Ti(3)-O(11)	198.2(2)
Ti(3)-O(14)	203.54(19)	Ti(3)-O(14)	191.2(2)
Ti(3)-O(15)	202.61(19)	Ti(3)-O(17)	202.8(2)
Ti(3)-O(19)	176.75(19)	Ti(3)-O(23)	175.1(2)
Ti(4)-O(6)	218.42(19)	Ti(4)-O(5)	193.1(2)
Ti(4)-O(9)	195.37(19)	Ti(4)-O(10)	212.4(2)
Ti(4)-O(11)	208.49(19)	Ti(4)-O(15)	203.6(2)
Ti(4)-O(16)	202.13(19)	Ti(4)-O(16)	209.6(2)
Ti(4)-O(20)	177.04(19)	Ti(4)-O(24)	177.8(2)
Ti(4)-O(21)	178.4(2)	Ti(4)-O(25)	180.3(2)
Ti(5)-O(4)	195.26(19)	Ti(5)-O(7)	217.4(2)
Ti(5)-O(6)	221.18(19)	Ti(5)-O(13)	193.3(2)
Ti(5)-O(12)	208.84(19)	Ti(5)-O(18)	206.8(3)
Ti(5)-O(16)	200.9(2)	Ti(5)-O(21)	208.0(2)
Ti(5)-O(23)	176.2(2)	Ti(5)-O(26)	178.5(2)
Ti(5)-O(22)	179.81(19)	Ti(5)-O(27)	175.8(2)
P(1)-O(2)	153.8(2)	P(1)-O(1)	152.5(2)
P(1)-C(1)	179.6(3)	P(1)-C(1A)	178.7(4)

***Table A.36:** Selected angles [°] of **TiOMcEtPP** and **TiOMcAllylPP**.*

TiOMcEtPP		**TiOMcAllylPP**	
Ti(2)-Ti(1)-Ti(3)	59.880(16)	Ti(2)-O(7)-Ti(5)	99.38(9)
Ti(1)-Ti(2)-Ti(3)	60.315(16)	Ti(2)-O(21)-Ti(5)	110.31(10)
Ti(2)-Ti(3)-Ti(1)	59.804(16)	Ti(3)-O(10)-Ti(4)	126.79(10)
Ti(2)-O(1)-Ti(1)	105.18(8)	O(1)-P(1)-O(2)	110.68(13)
Ti(2)-O(1)-Ti(3)	105.08(9)	O(1)-P(1)-C(1A)	107.31(16)
Ti(1)-O(1)-Ti(3)	104.96(8)	O(10)-P(4)-O(11)	99.11(12)
Ti(4)-O(6)-Ti(5)	98.03(7)	O(10)-P(4)-O(12)	114.61(13)
Ti(1)-O(13)-Ti(2)	99.27(8)	O(11)-P(4)-O(12)	115.63(14)
Ti(1)-O(14)-Ti(3)	100.65(8)		
Ti(2)-O(15)-Ti(3)	99.87(8)		
Ti(5)-O(16)-Ti(4)	110.85(9)		
O(2)-P(1)-O(3)	110.80(11)		
O(2)-P(1)-C(1)	106.15(13)		
Oxygen atoms in trans position on the octahedrally coordinated Ti atom			
O(1)-Ti(1)-O(17)	174.76(9)	O(2)-Ti(1)-O(12)	175.07(10)
O(5)-Ti(1)-O(13)	162.32(8)	O(8)-Ti(1)-O(3)	172.61(10)
O(1)-Ti(2)-O(18)	173.62(9)	O(20)-Ti(1)-O(4)	174.75(12)
O(8)-Ti(2)-O(13)	163.51(8)	O(1)-Ti(2)-O(21)	161.56(10)
O(1)-Ti(3)-O(19)	171.44(9)	O(6)-Ti(2)-O(19)	171.11(10)
O(7)-Ti(3)-O(15)	160.66(8)	O(7)-Ti(2)-O(22)	171.61(10)
O(6)-Ti(4)-O(21)	164.31(8)	O(9)-Ti(3)-O(17)	168.66(10)
O(9)-Ti(4)-O(11)	169.18(8)	O(10)-Ti(3)-O(23)	158.70(10)
O(4)-Ti(5)-O(12)	168.51(8)	O(11)-Ti(3)-O(14)	163.03(10)
O(6)-Ti(5)-O(22)	165.70(8)	O(5)-Ti(4)-O(16)	168.23(10)
		O(10)-Ti(4)-O(24)	171.72(10)
		O(15)-Ti(4)-O(25)	173.24(10)
		O(7)-Ti(5)-O(26)	161.72(10)
		O(13)-Ti(5)-O(18)	170.57(10)
		O(21)-Ti(5)-O(27)	166.70(10)
Oxygen atoms in cis position on the octahedrally coordinated Ti atom			
O-Ti(1)-O	76.89(8) - 99.50(8)	O-Ti(1)-O	84.52(10) - 94.92(10)
O-Ti(2)-O	76.79(8) - 100.78(9)	O-Ti(2)-O	74.74(9) - 97.91(10)
O-Ti(3)-O	76.31(8) - 102.30(9)	O-Ti(3)-O	68.37(9) - 105.37(10)
O-Ti(4)-O	74.75(7) - 99.58(9)	O-Ti(4)-O	80.29(9) - 97.29(10)
O-Ti(5)-O	74.37(7) - 98.62(9)	O-Ti(5)-O	72.08(8) - 101.03(11)

Appendix B

Crystallographic Data

Table B.1: *Crystal data, data collection parameters and refinement details for **TiCycloBu**, **TiBenzCl** and **TiTPA**.*

	TiCycloBu	**TiBenzCl**	**TiTPA**
Crystal data			
Empirical formula	$Ti_6O_{28}C_{56}H_{82}$	$Ti_2O_{10}C_{30}H_{33}Cl_3$	$Ti_3O_{15}C_{110}H_{98}Cl_2$
M_r	1490.62	755.71	1874.48
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P2_1/c$
a (pm)	961.36(4)	2326.3(6)	1509.26(14)
b (pm)	1290.95(7)	2444.5(6)	2491.3(3)
c (pm)	1357.06(7)	1393.7(3)	2477.7(3)
α (°)	95.160(2)	90	90
β (°)	96.711(2)	96.421(9)	97.736(4)
γ (°)	105.180(2)	90	90
V ($10^6 \cdot pm^3$)	1601.48(14)	7876(3)	9231.4(17)
Z	1	8	4
D_x ($Mg \cdot m^{-3}$)	1.546	1.275	1.349
μ (mm^{-1})	0.797	0.655	0.379
crystal size (mm)	0.2 x 0.1 x 0.05	0.3 x 0.25 x 0.2	0.6 x 0.5 x 0.4
Data collection			
no. of measured refl.	12864	4101	171490
no. of independent refl.	5603	4101	18625
no. of observed refl. [$I > 2 \cdot \sigma(I)$]	3421	1940	13707
R_{int}	0.0561	0.1775	0.0648
Θ_{max} (°)	25.01	20.88	26.28
Refinement			
$R[F^2 > 2 \cdot \sigma(F)], \omega R(F^2), S$	0.0637, 0.1445, 1.017	0.0657, 0.1298, 0.915	0.0477, 0.1179, 1.034
no. of reflections	5603	4101	18625
no. of parameters	408	444	1226
no. of restraints	0	215	4
weighting scheme values*	a = 0.0739, b = 2.2854	a = 0.0611	a = 0.0605, b = 10.6792
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (10^{-6} $e \cdot pm^{-3}$)	0.969, -0.819	0.535, -0.378	1.153, -0.841

* $\omega = [\sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P]^{-1}$ where $P = \frac{(F_0^2 + 2 \cdot F_c^2)}{3}$

Table B.2: *Crystal data, data collection parameters and refinement details for* ***TiAda****,* ***ZrAda*** *and* ***TiBenzMeCl****.*

	TiAda	**ZrAda**	**TiBenzMeCl**
Crystal data			
Empirical formula	$Ti_6O_{31}C_{128}H_{212}$	$Zr_6O_{37}C_{154}H_{218}$	$Ti_2O_{11}C_{37}H_{62}Cl_2$
M_r	2534.38	3208.6	849.57
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (pm)	2296.59(9)	2244.4(2)	2008.03(12)
b (pm)	2304.89(9)	3192.5(3)	1249.31(8)
c (pm)	2535.04(10)	2508.5(2)	1949.92(12)
α (°)	90	90	90
β (°)	103.813(2)	90.027(3)	113.092(3)
γ (°)	90	90	90
V ($10^6 \cdot pm^3$)	13030.9(9)	17974(3)	4499.7(5)
Z	4	4	4
D_x ($Mg\cdot m^{-3}$)	1.292	1.186	1.254
μ (mm^{-1})	0.423	0.399	0.524
crystal size (mm)	0.4 x 0.4 x 0.3	0.37 x 0.32 x 0.27	0.8 x 0.5 x 0.4
Data collection			
no. of measured refl.	503074	455653	90356
no. of independent refl.	39867	36960	13876
no. of observed refl. [$I > 2\cdot\sigma(I)$]	27534	26953	8474
R_{int}	0.0528	0.0537	0.0452
Θ_{max} (°)	30.54	26.46	30.8
Refinement			
$R[F^2 > 2\cdot\sigma(F)], \omega R(F^2), S$	0.049, 0.1259, 1.029	0.0658, 0.1861, 1.103	0.0619, 0.1637, 1.044
no. of reflections	39867	36960	13876
no. of parameters	1947	2126	555
no. of restraints	2047	1325	279
weighting scheme values*	a = 0.0680, b = 9.5710	a = 0.1151, b = 26.6251	a = 0.1046, b = 4.4384
$\Delta\rho_{max}, \Delta\rho_{min}$ ($10^{-6}\ e\cdot pm^{-3}$)	1.032, -0.894	1.803, -0.951	2.035, -0.981

* $\omega = [\sigma^2(F_0^2) + (a\cdot P)^2 + b\cdot P]^{-1}$ where $P = \frac{(F_0^2 + 2\cdot F_c^2)}{3}$

Table B.3: *Crystal data, data collection parameters and refinement details for* ***ZrBenzMeCl****,* ***ZrPentin*** *and* ***TiBuImid****.*

	ZrBenzMeCl	**ZrPentin**	**TiBuImid**
Crystal data			
Empirical formula	$Zr_{10}O_{40}C_{128}H_{192}Cl_8$	$Zr_9O_{36}C_{102}H_{192}$	$TiO_5N_2C_{16}H_{30}$
M_r	3566.62	2815.54	378.32
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (pm)	1691.59(11)	1542.59(7)	956.79(6)
b (pm)	1707.15(11)	2845.87(16)	1072.38(6)
c (pm)	3091.6(2)	2918.08(16)	1121.04(7)
α (°)	103.938(2)	90	85.272(2)
β (°)	91.761(2)	94.987(2)	65.808(3)
γ (°)	117.788(2)	90	68.423(2)
V ($10^6 \cdot pm^3$)	7558.7(8)	12761.9(12)	972.53(10)
Z	2	4	2
D_x ($Mg \cdot m^{-3}$)	1.567	1.465	1.292
μ (mm^{-1})	0.874	0.774	0.466
crystal size (mm)	0.35 x 0.25 x 0.23	0.39 x 0.35 x 0.34	0.2 x 0.14 x 0.12
Data collection			
no. of measured refl.	246972	305291	20370
no. of independent refl.	44190	48678	5298
no. of observed refl. [$I > 2 \cdot \sigma(I)$]	28898	34598	4207
R_{int}	0.0428	0.0622	0.0359
Θ_{max} (°)	30.68	33.23	29.62
Refinement			
$R[F^2 > 2 \cdot \sigma(F)], \omega R(F^2), S$	0.0727, 0.171, 1.126	0.0515, 0.1097, 1.162	0.0374, 0.0849, 1.05
no. of reflections	44190	48678	5298
no. of parameters	1945	1553	253
no. of restraints	272	20	1
weighting scheme values*	a = 0.0643, b = 65.8448	a = 0.0461, b = 25.9016	a = 0.0387, b = 0.3848
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (10^{-6} $e \cdot pm^{-3}$)	2.78, -2.302	2.126, -1.326	0.501, -0.481

* $\omega = [\sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P]^{-1}$ where $P = \frac{(F_0^2 + 2 \cdot F_c^2)}{3}$

Table B.4: *Crystal data, data collection parameters and refinement details for* ***TiOMc1****,* ***TiOMc2****,* ***TiOMc6*** *and* ***TiOMc8****.*

	TiOMc1	**TiOMc2**	**TiOMc6**	**TiOMc8**
Crystal data				
Empirical formula	$Ti_2O_{11}C_{29}H_{60}$	$Ti_6O_{28}C_{56}H_{96}$	$Ti_9O_{48.50}C_{85.50}H_{123}$	$Ti_8O_{40}C_{64}H_{80}$
M_r	680.57	1504.73	2357.94	1872.48
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/c$
a (pm)	1065.27(5)	1155.03(4)	1182.0(3)	2401.73(16)
b (pm)	1819.00(8)	1895.81(5)	1626.7(3)	1662.84(16)
c (pm)	1961.76(8)	1702.46(5)	3060.3(7)	2430.81(18)
α (°)	90	90	87.652(5)	90
β (°)	100.688(2)	105.1810(10)	88.160(6)	90.459(6)
γ (°)	90	90	72.026(5)	90
V $(10^6 \cdot pm^3)$	3735.4(3)	3597.81(19)	5591(2)	9707.6(14)
Z	4	2	2	4
D_x $(Mg{\cdot}m^{-3})$	1.21	1.389	1.401	1.281
μ (mm^{-1})	0.476	0.71	0.693	0.699
crystal size (mm)	0.5 x 0.5 x 0.5	0.4 x 0.25 x 0.2	0.2 x 0.15 x 0.05	0.65 x 0.64 x 0.33
Data collection				
no. of measured refl.	244599	103239	108932	9827
no. of independent refl.	30570	14090	10435	9827
no. of observed refl. $[I > 2{\cdot}\sigma(I)]$	20685	10638	6190	7847
R_{int}	0.0498	0.0523	0.1637	0.054
Θ_{max} (°)	44.89	33.5	20.02	26.38
Refinement				
$R[F^2 > 2{\cdot}\sigma(F)], \omega R(F^2), S$	0.054, 0.1177, 1.102	0.0361, 0.0889, 1.032	0.0824, 0.2002, 1.087	0.1195, 0.2594, 3.502
no. of reflections	30570	14090	10435	9827
no. of parameters	435	418	1223	506
no. of restraints	44	0	49	24
weighting scheme values*	a = 0.0447, b = 1.7418	a = 0.0459, b = 1.6781	a = 0.1135, b = 28.5259	a = 0.0275, b = 11.5003
$\Delta\rho_{max}, \Delta\rho_{min}$ $(10^{-6}\ e{\cdot}pm^{-3})$	1.076, -0.516	0.955, -0.592	0.867, -0.905	1.445, -0.95

* $\omega = [\sigma^2(F_0^2) + (a{\cdot}P)^2 + b{\cdot}P]^{-1}$ where $P = \frac{(F_0^2 + 2{\cdot}F_c^2)}{3}$

Table B.5: *Crystal data, data collection parameters and refinement details for* ***TiPhthal1****,* ***TiPhthal2****,* ***TiMal*** *and* ***Zr3Calix****.*

	TiPhthal1	**TiPhthal2**	**TiMal**	**Zr3Calix**
Crystal data				
Empirical formula	$Ti_2O_{15}C_{43}H_{71}$	$Ti_3O_{18}C_{42}H_{54}$	$Ti_6O_{25}C_{50}H_{102}$	$Zr_3O_{12}C_{76}H_{123}$
M_r	923.8	1036.92	1390.72	1502.4
crystal system	triclinic	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a (pm)	1148.9(2)	1292.21(15)	1259.72(3)	1652.46(8)
b (pm)	1177.70(10)	1366.70(16)	1565.63(3)	2117.02(9)
c (pm)	1944.0(3)	1457.26 (13)	1990.53(4)	2198.71(10)
α (°)	103.090(8)	85.597(7)	73.2380(10)	90
β (°)	97.570(9)	66.419 (7)	76.7970(10)	90
γ (°)	99.780(8)	78.107(7)	83.5880(10)	90
V ($10^6 \cdot pm^3$)	2484.7(7)	2308.0(4)	3655.25(13)	7691.7(6)
Z	2	2	2	4
D_x ($Mg \cdot m^{-3}$)	1.236	1.492	1.264	1.297
μ (mm^{-1})	0.382	0.581	0.69	0.455
crystal size (mm)	0.4 x 0.32 x 0.3	0.2 x 0.18 x 0.14	0.3 x 0.27 x 0.2	0.72 x 0.64 x 0.43
Data collection				
no. of measured refl.	72908	15330	102190	142609
no. of independent refl.	14419	7542	12570	13545
no. of observed refl. $[I > 2 \cdot \sigma(I)]$	11404	4285	9709	13147
R_{int}	0.0356	0.0728	0.0369	0.0422
Θ_{max} (°)	30.02	23.2	24.82	25
Refinement				
$R[F^2 > 2 \cdot \sigma(F)], \omega R(F^2), S$	0.0439, 0.1210, 1.028	0.0759, 0.2426, 1.000	0.047, 0.1371, 1.055	0.0209, 0.0575, 1.112
no. of reflections	14419	7542	12570	13545
no. of parameters	602	580	758	841
no. of restraints	36	0	15	0
weighting scheme values*	a = 0.0536, b = 1.8273	a = 0.1398	a = 0.0886, b = 2.9622	a = 0.0390, b = 2.8125
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (10^{-6} $e \cdot pm^{-3}$)	1.331, -0.693	0.816, -0.923	0.969, -0.406	0.759, -0.537

* $\omega = [\sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P]^{-1}$ where $P = \frac{(F_0^2 + 2 \cdot F_c^2)}{3}$

Table B.6: *Crystal data, data collection parameters and refinement details for **TiCalix**, **Zr4Calix2**, **ZrHexOx** and **TiDMSOAllylPA**.*

	TiCalix	**Zr4Calix2**	**ZrHexOx**	**TiDMSOAllylPA**
Crystal data				
Empirical formula	$Ti_2O_{12}C_{120}H_{158}$	$Zr_4O_{17}C_{120}H_{177}$	$Zr_{10}O_{42}N_8C_{108}H_{212}$	$Ti_8O_{38}P_6S_2C_{70}H_{155}$
M_r	1888.2	2256.5	3207.06	2238.08
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P\ 2/n$	$P2_1/c$
a (pm)	1262.96(9)	1303.39(3)	1647.07(9)	3366.33(17)
b (pm)	1346.57(10)	4931.52(12)	1334.70(9)	1270.76(7)
c (pm)	1798.78(13)	1866.79(5)	3338.8(2)	2763.86(14)
α (°)	85.990(3)	90	90	90
β (°)	73.640(3)	91.9870(10)	97.663(2)	114.257(2)
γ (°)	64.020(3)	90	90	90
V ($10^6 \cdot pm^3$)	2633.6(3)	11991.9(5)	7274.2(8)	10779.4(10)
Z	1	4	2	4
D_x ($Mg \cdot m^{-3}$)	1.191	1.25	1.464	1.379
μ (mm^{-1})	0.212	0.398	0.759	0.762
crystal size (mm)	0.4 x 0.3 x 0.2	0.57 x 0.37 x 0.36	0.22 x 0.2 x 0.15	0.3 x 0.2 x 0.2
Data collection				
no. of measured refl.	21201	123565	189576	116818
no. of independent refl.	6831	20496	12947	32005
no. of observed refl. [$I > 2 \cdot \sigma(I)$]	4840	15935	9267	16463
R_{int}	0.0465	0.0425	0.0871	0.1066
Θ_{max} (°)	22.59	25.03	25.13	30.56
Refinement				
$R[F^2 > 2 \cdot \sigma(F)], \omega R(F^2), S$	0.0593, 0.1525, 1.026	0.096, 0.217, 1.179	0.0695, 0.1612, 1.202	0.0633, 0.1665, 0.939
no. of reflections	6831	20496	12947	32005
no. of parameters	699	1360	935	1205
no. of restraints	299	53	422	248
weighting scheme values*	a = 0.0921, b = 3.2969	a = 0.0524, b = 97.5620	a = 0.0565, b = 61.3137	a = 0.0761
$\Delta\rho_{max}$, $\Delta\rho_{min}$ ($10^{-6}\ e \cdot pm^{-3}$)	0.765, -0.621	1.164, -0.916	1.343, -1.095	1.551, -1.760

* $\omega = [\sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P]^{-1}$ where $P = \frac{(F_0^2 + 2 \cdot F_c^2)}{3}$

*Table B.7: Crystal data, data collection parameters and refinement details for **TiAllylPP**, **TiAllylPP2**, **TiEtPP** and **TiClPrPP**.*

	TiAllylPP	**TiAllylPP2**	**TiEtPP**	**TiClPrPP**
Crystal data				
Empirical formula	$Ti_8O_{40}P_8C_{72}H_{152}$	$Ti_8O_{40}P_8C_{72}H_{152}$	$Ti_4O_{20}P_4C_{32}H_{76}$	$Ti_{3.50}O_{16}P_3C_{27}H_{60}Cl_3$
M_r	2288.9	2288.9	1096.41	1007.66
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (pm)	1192.63(4)	1260.81(4)	1173.14(3)	1474.51(4)
b (pm)	1315.97(4)	1873.03(6)	1266.27(4)	1506.18(4)
c (pm)	1888.04(8)	2282.43(8)	1870.42(5)	2021.22(6)
α (°)	95.737(2)	90	90.5310(10)	90
β (°)	93.920(2)	93.6370(10)	95.6330(10)	104.184(2)
γ (°)	114.5600(10)	90	114.4040(10)	90
V ($10^6 \cdot pm^3$)	2661.77(17)	5379.18	2514.25(12)	4352.0(2)
Z	1	2	2	4
D_x ($Mg \cdot m^{-3}$)	1.428	1.413	1.448	1.538
μ (mm^{-1})	0.766	0.758	0.807	0.978
crystal size (mm)	0.4 x 0.3 x 0.2	0.4 x 0.4 x 0.3	0.6 x 0.5 x 0.4	0.3 x 0.2 x 0.2
Data collection				
no. of measured refl.	52732	121493	99598	113501
no. of independent refl.	19103	18194	16665	8719
no. of observed refl. [$I > 2 \cdot \sigma(I)$]	12969	13342	13216	6723
R_{int}	0.0337	0.0517	0.0282	0.0593
Θ_{max} (°)	32.64	31.75	31.55	26.24
Refinement				
$R[F^2 > 2 \cdot \sigma(F)], \omega R(F^2), S$	0.0548, 0.1685, 1.019	0.0682, 0.1966, 1.098	0.0601, 0.1840, 1.074	0.0465, 0.1306, 1.049
no. of reflections	19103	18194	16665	8719
no. of parameters	719	663	820	517
no. of restraints	197	144	274	49
weighting scheme values*	a = 0.0861, b = 2.4222	a = 0.0673, b = 17.5872	a = 0.0863, b = 6.1747	a = 0.0606, b = 11.9306
$\Delta\rho_{max}, \Delta\rho_{min}$ ($10^{-6}\ e \cdot pm^{-3}$)	1.619, -1.634	2.329, -1.886	2.944, -1.597	1.477, -0.690

* $\omega = [\sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P]^{-1}$ where $P = \frac{(F_0^2 + 2 \cdot F_c^2)}{3}$

Table B.8: *Crystal data, data collection parameters and refinement details for* ***TiBzlPP****,* ***TiBrPrPP****,* ***TiXylPP*** *and* ***TiNpMePP****.*

	TiBzlPP	**TiBrPrPP**	**TiXylPP**	**TiNpMePP**
Crystal data				
Empirical formula	$Ti_7O_{32}P_6C_{78}H_{126}$	$Ti_7O_{32}P_6C_{54}H_{120}Br_6$	$Ti_8O_{41}P_6C_{111}H_{204}$	$Ti_4O_{23}P_4C_{77}H_{113}$
M_r	2096.91	2282.08	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)	1348.84(17)	1505.94(17)	1416.99(12)	1327.97(14)
b (pm)	1496.1(2)	1519.44(17)	2272.53(18)	1421.57(15)
c (pm)	2399.1(3)	2013.5(2)	2227.81(17)	2497.7(3)
α (°)	90	90	90	83.599(4)
β (°)	98.141(4)	104.169(4)	101.300(4)	74.598(4)
γ (°)	90	90	90	83.251(4)
V ($10^6 \cdot pm^3$)	4792.4(11)	4467.1(9)	7034.8(10)	4498.5(9)
Z	2	2	2	2
D_x ($Mg \cdot m^{-3}$)	1.453	1.697	1.305	1.27
μ (mm^{-1})	0.73	3.457	0.571	0.479
crystal size (mm)	0.2 x 0.2 x 0.1	0.5 x 0.5 x 0.4	0.5 x 0.3 x 0.2	0.6 x 0.5 x 0.4
Data collection				
no. of measured refl.	62552	123226	105744	116779
no. of independent refl.	8294	11112	12938	18623
no. of observed refl. [$I > 2 \cdot \sigma(I)$]	5573	8456	7468	12241
R_{int}	0.0847	0.063	0.169	0.0538
Θ_{max} (°)	24.87	28.32	25.41	26.63
Refinement				
$R[F^2 > 2 \cdot \sigma(F)], \omega R(F^2), S$	0.0704, 0.2205, 1.035	0.0673, 0.1537, 1.046	0.0528, 0.1229, 1.000	0.0715, 0.2450, 1.041
no. of reflections	8294	11112	12938	18623
no. of parameters	556	567	799	1124
no. of restraints	106	26	6	142
weighting scheme values*	a = 0.1079, b = 27.4456	a = 0.0628, b = 27.8261	a = 0.0371, b = 10.814	a = 0.1379, b = 7.4926
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (10^{-6} $e \cdot pm^{-3}$)	1.767, -1.104	1.736, -1.682	0.662, -0.533	1.539, -0.705

* $\omega = [\sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P]^{-1}$ where $P = \frac{(F_0^2 + 2 \cdot F_c^2)}{3}$

Table B.9: *Crystal data, data collection parameters and refinement details for* ***TiCl3MePP****,* ***TiVinylPP****,* ***ZrPhPP*** *and* ***TiOAcEtPP****.*

	TiCl3MePP	**TiVinylPP**	**ZrPhPP**	**TiOAcEtPP**
Crystal data				
Empirical formula	$Ti_4O_{19}P_3NC_{30}H_{63}Cl_9$	$Ti_8O_{38}P_6C_{59.50}H_{133}Cl_7$	$Zr_6O_{26}P_4C_{72}H_{128}$	$Ti_6O_{24}P_2C_{38}H_{86}$
M_r	1345.37	2273.82	2080.94	1276.22
crystal system	orthorhombic	triclinic	triclinic	monoclinic
space group	*Pccn*	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (pm)	4555.0(7)	1291.14(4)	1302.35(6)	1226.23(6)
b (pm)	1238.77(18)	1350.40(4)	1332.92(6)	1649.58(9)
c (pm)	2078.0(3)	1774.80(5)	1411.35(7)	1464.69(7)
α (°)	90	72.343(2)	70.526(3)	90
β (°)	90	72.146(2)	81.574(3)	98.272(3)
γ (°)	90	63.430(2)	80.357(3)	90
V ($10^6 \cdot pm^3$)	11725(3)	2583.69(13)	2266.34(18)	2931.9(3)
Z	8	1	1	2
D_x ($Mg \cdot m^{-3}$)	1.524	1.461	1.525	1.446
μ (mm^{-1})	1.078	0.932	0.804	0.904
crystal size (mm)	0.45 x 0.4 x 0.35	0.5 x 0.4 x 0.4	0.4 x 0.3 x 0.2	0.5 x 0.5 x 0.5
Data collection				
no. of measured refl.	112978	61573	58806	121208
no. of independent refl.	10431	13068	11418	21197
no. of observed refl. [$I > 2 \cdot \sigma(I)$]	8816	9149	7843	16514
R_{int}	0.0595	0.053	0.0549	0.0336
Θ_{max} (°)	25.11	28.58	28.59	42.84
Refinement				
$R[F^2 > 2 \cdot \sigma(F)], \omega R(F^2), S$	0.0502, 0.1207, 1.167	0.0552, 0.1473, 1.114	0.0741, 0.184, 1.093	0.0323, 0.0862, 1.037
no. of reflections	10431	13068	11418	21197
no. of parameters	671	588	607	418
no. of restraints	84	10	176	8
weighting scheme values*	a = 0.0481, b = 32.5100	a = 0.0729, b = 6.0547	a = 0.1044, b = 21.0763	a = 0.0344, b = 1.2
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (10^{-6} $e \cdot pm^{-3}$)	1.45, -0.896	1.801, -0.625	4.065, -1.379	0.885, -1.307

* $\omega = [\sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P]^{-1}$ where $P = \frac{(F_0^2 + 2 \cdot F_c^2)}{3}$

Table B.10: *Crystal data, data collection parameters and refinement details for* ***TiOAcNpMePP****,* ***TiOAcVinylPP****,* ***TiOAcAllylPP*** *and* ***TiOAc-ClPrPP****.*

	TiOAcNpMePP	**TiOAcVinylPP**	**TiOAcAllylPP**	**TiOAcClPrPP**
Crystal data				
Empirical formula	$Ti_6O_{24}P_2C_{56}H_{94}$	$Ti_6O_{24}P_2C_{38}H_{82}$	$Ti_6O_{24}P_2C_{40}H_{86}$	$Ti_6O_{24}P_2C_{40}H_{88}Cl_2$
M_r	1500.65	1272.38	1300.43	1373.34
crystal system	monoclinic	monoclinic	Triclinic	monoclinic
space group	$C2/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (pm)	2259.5(2)	1206.87(6)	1146.80(9)	1376.54(5)
b (pm)	1682.61(13)	1664.31(8)	1223.83(10)	1571.04(5)
c (pm)	1830.97(15)	1460.95(8)	1228.22(10)	1653.85(5)
α (°)	90	90	106.880(4)	90
β (°)	91.538(3)	97.193(2)	110.202(3)	112.1300(10)
γ (°)	90	90	97.601(4)	90
V ($10^{6} \cdot pm^3$)	6958.5(10)	2911.4(3)	1495.2(2)	3313.13(19)
Z	4	2	1	2
D_x ($Mg \cdot m^{-3}$)	1.432	1.451	1.444	1.377
μ (mm^{-1})	0.774	0.91	0.888	0.883
crystal size (mm)	0.5 x 0.5 x 0.4	0.5 x 0.4 x 0.3	0.3 x 0.3 x 0.3	0.5 x 0.4 x 0.4
Data collection				
no. of measured refl.	93315	43475	62482	88173
no. of independent refl.	13284	5971	14474	8720
no. of observed refl. [$I > 2 \cdot \sigma(I)$]	10942	5034	12261	5416
R_{int}	0.0414	0.0261	0.0229	0.0466
Θ_{max} (°)	33.22	26.41	36.35	28.95
Refinement				
$R[F^2 > 2 \cdot \sigma(F)], \omega R(F^2), S$	0.0356, 0.1004, 1.043	0.0424, 0.1002, 1.106	0.0263, 0.0726, 1.036	0.0647, 0.2177, 1.094
no. of reflections	13284	5971	14474	8720
no. of parameters	408	448	336	443
no. of restraints	0	0	0	7
weighting scheme values*	a = 0.0417, b = 14.8148	a = 0.0344, b = 9.7385	a = 0.0313, b = 0.6556	a = 0.0889, b = 3.5722
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (10^{-6} $e \cdot pm^{-3}$)	1.246, -0.424	1.641, -0.957	1.272, -0.362	0.741, -0.477

* $\omega = [\sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P]^{-1}$ where $P = \frac{(F_0^2 + 2 \cdot F_c^2)}{3}$

Table B.11: *Crystal data, data collection parameters and refinement details for* ***TiOAcBzlPP****,* ***TiOAcBrPrPP****,* ***TiOAcPhPA*** *and* ***TiOAcBrPrPP2****.*

	TiOAcBzlPP	**TiOAcBrPrPP**	**TiOAcPhPA**	**TiOAcBrPrPP2**
Crystal data				
Empirical formula	$Ti_6O_{24}P_2C_{50}H_{94}Cl_4$	$Ti_6O_{24}P_2C_{40}H_{88}Br_2$	$Ti_6O_{24}P_2C_{48}H_{90}Cl_4$	$Ti_5O_{23}P_3C_{44}H_{98}Br_3$
M_r	1570.39	1462.26	1542.34	1567.36
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/c$	*Pbca*	*Pbca*	$P2_1/n$
a (pm)	2643.8(3)	1632.40(3)	1213.82(8)	1308.99(7)
b (pm)	1259.66(14)	1585.18(3)	2359.25(16)	2291.37(13)
c (pm)	2280.3(3)	2401.10(4)	2438.60(17)	2346.81(13)
α (°)	90	90	90	90
β (°)	108.761(4)	90	90	102.299(2)
γ (°)	90	90	90	90
V ($10^6 \cdot pm^3$)	7190.8(14)	6213.2(2)	6983.4(8)	6877.4(7)
Z	4	4	4	4
D_x ($Mg \cdot m^{-3}$)	1.451	1.563	1.467	1.514
μ (mm^{-1})	0.896	2.142	0.921	2.434
crystal size (mm)	0.32 x 0.27 x 0.23	0.6 x 0.5 x 0.5	0.5 x 0.4 x 0.3	0.6 x 0.4 x 0.35
Data collection				
no. of measured refl.	287456	196724	53232	127718
no. of independent refl.	21997	13047	10147	16623
no. of observed refl. [$I > 2 \cdot \sigma(I)$]	16780	10744	8860	13683
R_{int}	0.0599	0.046	0.0265	0.0293
Θ_{max} (°)	30.58	34.37	30	28.32
Refinement				
$R[F^2 > 2 \cdot \sigma(F)], \omega R(F^2), S$	0.044, 0.1256, 1.068	0.0222, 0.0571, 1.049	0.0371, 0.094, 1.044	0.0567, 0.1487, 1.031
no. of reflections	21997	13047	10147	16623
no. of parameters	894	345	390	727
no. of restraints	54	0	63	106
weighting scheme values*	a = 0.0517, b = 11.3637	a = 0.0251, b = 2.6246	a = 0.0452, b = 8.1234	a = 0.0552, b = 46.4092
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (10^{-6} $e \cdot pm^{-3}$)	1.5, -1.368	0.681, -0.423	1.161, -0.898	5.461, -5.769

* $\omega = [\sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P]^{-1}$ where $P = \frac{(F_0^2 + 2 \cdot F_c^2)}{3}$

Table B.12: *Crystal data, data collection parameters and refinement details for* ***TiOAcXylPP****,* ***TiOPhPP****,* ***TiOMcEtPP*** *and* ***TiOMcAllylPP****.*

	TiOAcXylPP	**TiOPhPP**	**TiOMcEtPP**	**TiOMcAllylPP**
Crystal data				
Empirical formula	$Ti_5O_{23}P_2C_{42}H_{72}$	$Ti_6O_{26}P_4C_{60}H_{104}$	$Ti_5O_{23}P_3C_{43}H_{97}$	$Ti_{10}O_{54}P_{10}C_{94}H_{182}$
M_r	1246.44	1652.53	1314.62	2965.1
crystal system	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (pm)	1210.96(6)	1367.65(7)	2756.55(14)	1366.83(13)
b (pm)	1284.46(7)	1524.89(9)	1861.84(10)	1403.15(13)
c (pm)	1908.81(11)	1839.29(10)	2600.75(11)	2110.25(17)
α (°)	101.464(3)	90	90	73.525(4)
β (°)	96.661(3)	93.246(2)	105.268(2)	75.199(4)
γ (°)	96.627(3)	90	90	64.922(5)
V ($10^6 \cdot pm^3$)	2860.8(3)	3829.7(4)	12876.6(11)	3472.3(5)
Z	2	2	8	1
D_x ($Mg{\cdot}m^{-3}$)	1.447	1.433	1.356	1.418
μ (mm^{-1})	0.797	0.752	0.735	0.739
crystal size (mm)	0.7 x 0.6 x 0.4	0.23 x 0.23 x 0.15	0.25 x 0.2 x 0.15	0.25 x 0.15 x 0.1
Data collection				
no. of measured refl.	137433	65957	230762	76823
no. of independent refl.	27635	7847	22815	12361
no. of observed refl. [$I > 2{\cdot}\sigma(I)$]	19253	5866	17441	8533
R_{int}	0.0463	0.063	0.0657	0.0806
Θ_{max} (°)	36.37	26.43	25.07	25.15
Refinement				
$R[F^2 > 2{\cdot}\sigma(F)], \omega R(F^2), S$	0.063, 0.1544, 1.084	0.0376, 0.0898, 1.033	0.0355, 0.0809, 1.053	0.0429, 0.0922, 1.035
no. of reflections	27635	7847	22815	12361
no. of parameters	789	445	1413	828
no. of restraints	8	0	84	0
weighting scheme values*	a = 0.0160, b = 9.9669	a = 0.0463, b = 4.1838	a = 0.0409, b = 14.5476	a = 0.0457, b = 3.3285
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (10^{-6} $e{\cdot}pm^{-3}$)	1.701, -1.112	0.538, -0.449	1.004, -0.922	0.779, -0.492

* $\omega = [\sigma^2(F_0^2) + (a{\cdot}P)^2 + b{\cdot}P]^{-1}$ where $P = \frac{(F_0^2 + 2{\cdot}F_c^2)}{3}$

Appendix C

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Curriculum Vitae

Matthias Czakler

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Education

February 2011 – current	**PhD** in Technical Science, Technical Chemistry, Vienna University of Technology
Thesis:	Carboxylate- and Phosphonate-Substituted Titanium and Zirconium Oxo Clusters Supervisor: Prof. Ulrich Schubert
October 2005 – January 2011	**Diploma study** in Technical Chemistry, Vienna University of Technology
Thesis:	Verknüpfte Metallnanopartikel für neue Hybridmaterialien Supervisor: Prof. Marie-Alexandra Néouze-Gauthey
October 1999 – June 2004	Graduation at the Technical High School HTL TGM, Vienna with Focus on Technical Informatics

Employment

February 2011 – October 2014	**Project Assistant**, Vienna University of Technology, Institute of Materials Chemistry
Summer 2002, 2003	Internships at Siemens Austria

Personal Skills and Interests

Languages	**German**: native speaker, **English**: excellent, **French**: basics
Interests	Climbing, Soccer, Cycling, Swimming

Honors and Memberships

2011	Diploma Thesis Award of the City of Vienna
2011 – current	Austrian Chemical Society (GÖCH - Gesellschaft Österreichischer Chemiker)