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Ketoximate Derivatives of Titanium Alkoxides and Partial Hydrolysis Products Thereof

Stefan O. Baumann,*[a] Maria Bendova,[a] Helmut Fric,[a] Michael Puchberger,[a] Claudia Visinescu,[a] and Ulrich Schubert*[a]

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Crystalline oximate derivatives of titanium alkoxides $[Ti(OR)_2(ON{=}CR'R'')_2]_2$ were obtained when $Ti(OR)_4$ (R = *i*Pr, Et) was treated with various oximes (cyclopentanone oxime, cyclohexanone oxime, acetoxime, ethyl methyl ketoxime or 2,4-pentandione dioxime). Formation of bis-substituted derivatives was favored in each case, and only one mono-substituted derivative, $[Ti(OiPr)_3(ON{=}C_6H_{10})]_2$, was isolated. Two isomers were observed for $[Ti(OR)_2(ON{=}CR'R'')_2]_2$, differing by the mutual orientation of the oximate ligands. The NO groups of the oximate ligands are side-on coordinated to one titanium atom in each case. Three partially hydrolyzed derivatives, viz. $Ti_6O_6(OiPr)_6(ON{=}CR_2)_6$ (CR_2 = CMe_2 or C_5H_8) and $Ti_4O_2(OiPr)_8(ON{=}CMe{-}CH_2{-}CMe{=}NO)_2$ were also structurally characterized. In these derivatives the NO groups bridge two titanium atoms.

Introduction

Metal alkoxides with bidentate anionic co-ligands (BL), $M(OR)_{x-y}(BL)_y$, are often employed in sol-gel processes because their reactivity towards water is lower, and thus better controllable, than that of the parent alkoxides $M(OR)_x$. Often used BL are carboxylates, β-diketonates or β-keto esterates.[1,2] Partial substitution of alkoxo groups by reaction of metal alkoxides with protic compounds (BL–H) is rather general [Equation (1)] and occurs if the entering ligand is more strongly bonded than the leaving alkoxo group.

$$M(OR)_x + y\ BL{-}H \rightarrow M(OR)_{x-y}(BL)_y + y\ ROH \qquad (1)$$

In most practical sol-gel protocols, the organically modified precursors $M(OR)_{x-y}(BL)_y$ are prepared in situ without being isolated or characterized. The (structural) chemistry of only few organically modified precursors, essentially some carboxylate- and β-diketonate substituted metal alkoxides, was systematically investigated.[1,3] Structures of some phosphonate and phosphinate-substituted titanium alkoxide derivatives are also known.[4] Own recent work extended these studies to nitrogen-containing bidentate ligands, such as aminoethanolate-substituted titanium and zirconium alkoxides and some of their partial hydrolysis products.[5]

In this contribution, we report on oximate derivatives. A wide range of oximes can be prepared easily by various methods, including functional derivatives.[6] We focus on titanium alkoxide derivatives for comparison of their structures with the known structures of other titanium alkoxides with nitrogen-containing ligands. Several $Ti(OR)_{4-x}(ON{=}CR'_2)_x$ or $Ti(OR)_{4-x}(ON{=}CR'R'')_x$ (x = 1–4) derivatives were reported in the early literature,[7] but structural evidence was not provided. The reaction of $Ti(OBu)_4$ with acetoxime was recently repeated.[8] Based on infrared and NMR spectra the authors claim that they obtained $Ti(OBu)_{4-x}(ON{=}CMe_2)_x$, with x = 1 or 2, and bridging oximate ligands.

Structural investigation of titanium oximate complexes $[Cp_2Ti(H_2O)(oximato)]^+$ showed side-on coordination of the oximate ligands.[9] More recently, $Ti(OiPr)_4$ was treated with salicylaldoxime or *syn*-pyridine-2-aldoxime (L–H).[10] With salicylaldoxime, trinuclear complexes $Ti_3(OiPr)_8L_2$ were obtained, where each oximate ligand is di-anionic (deprotonation of both the NOH and OH group) and bridges the three titanium centers. In contrast, dinuclear complexes $Ti_2(OiPr)_4L_4$ with side-on coordinated oximate ligand and pending pyridyl groups were obtained from pyridine-2-aldoxime.[10] This structure type will be discussed in more detail below.

The different substitution possibilities ($R'R''C{=}NOH$, $R'_2C{=}NOH$, $R'HC{=}NOH$) allow easy variation of the organic groups both in terms of steric demand and chemical composition. However, hydrolytic stability of the metal-oximate link must be taken into account because oximate ligands cannot form chelate systems as other BL. On the other hand, the easy changing to a bridging coordination or from side-on to end-on coordination, i.e. the possibility

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[a] Institute of Materials Chemistry,
Vienna University of Technology
Getreidemarkt 9, 1060 Wien, Austria

to easily adjust to the requirements of a particular metal moiety, may compensate this potential disadvantage.

Solid-state structures of titanium alkoxide derivatives with simple oximes are discussed in this work as well as investigations in solution by NMR spectroscopy. Metal alkoxide oximate derivatives with functional organic groups will be subject of later publications. Structures of some partially hydrolyzed products are included which shed light on the structural development during hydrolysis reactions and also provide preliminarily information on the hydrolytic stability of the metal-oximate groups.

Results and Discussion

Mehrotra et al. reported that the derivatives $Ti(OiPr)_{4-x}$-$(ON{=}CMeR)_x$ (x = 1–4, R = Me or Et) were obtained when $Ti(OiPr)_4$ was treated with corresponding proportions of acetoxime or ethyl methyl ketoxime in benzene.[7] Our results were different. Even when *one* molar equivalent of cyclopentanone oxime, acetoxime, or ethyl methyl ketoxime was treated with $Ti(OiPr)_4$ in dichloromethane solution, only the *di*-substituted derivatives $[Ti(OiPr)_2(ON{=}CR'R'')_2]_2$ (i.e., x = 2) crystallized from the reaction solution [Equation (2)]. As expected, the same compounds were obtained with *two* molar equivalents of the oximes, although in higher yields.

$$2\ Ti(OiPr)_4 + 4\ R''R'C{=}NOH \longrightarrow [Ti(OiPr)_2(ON{=}CR'R'')_2]_2 + 4\ iPrOH \qquad (2)$$

1: $CR'R'' = C_5H_8$
2: R', R'' = Me
3: R' = Me, R'' = Et

A slightly different situation was encountered when the reaction of cyclohexanone oxime was examined. With an under-stoichiometric proportion of the oxime, the mono- and the disubstituted derivative co-crystallized from the solution in a 1:1 ratio, i.e. $[Ti(OiPr)_3(ON{=}C_6H_{10})]_2$ (**4**)·$[Ti(OiPr)_2(ON{=}C_6H_{10})_2]_2$ (**5**). We were not able to obtain **4** void of the di-substituted derivative. The pure di-substituted derivative **5** was formed with an excess of the oxime. When $Ti(OEt)_4$ was used instead of $Ti(OiPr)_4$, the di-substituted derivative $[Ti(OEt)_2(ON{=}C_6H_{10})_2]_2$ (**6**) was exclusively obtained, even when oxime and alkoxide were reacted in an equimolar ratio.

The derivatives **1**–**6** were characterized by single-crystal X-ray structure analyses. Both the mono- and the di-substituted derivatives are alkoxo-bridged dimers (Figure 1), as found for $Ti_2(OiPr)_4$(pyridine-2-aldoximate)$_4$ (see above), contrary to monomeric compounds postulated from molecular weight measurements.[7] The structures can formally be derived from dimeric $[Ti(OiPr)_4]_2$,[11] with one or two O*i*Pr groups replaced by side-on coordinated oximate ligands. The C–N–O angle of the oximate ligands is close to 120° in all derivatives [118.3(5)–123.9(3)°], and the N–O distance between 134.3(5) and 139.3(5) pm without an obvious correlation with structural details.

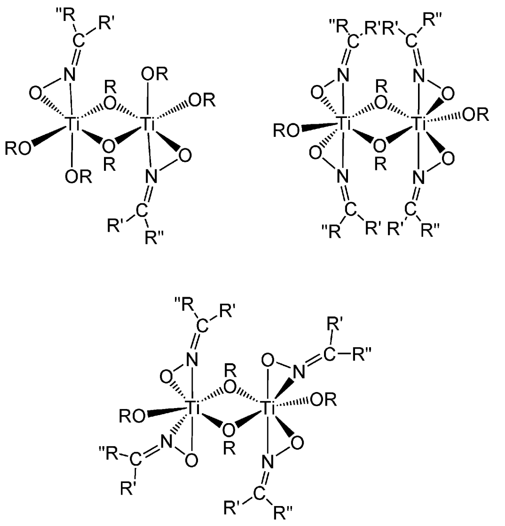

Figure 1. Schematic structures of **4** (top, left), **1**, **2** ("isomer 1", top right) and **3**, **5**, **6** ("isomer 2", bottom).

The structure of the only mono-substituted derivative $[Ti(OiPr)_3(ON{=}C_6H_{10})]_2$ (**4**) (Figure 2) is a centrosymmetric O*i*Pr-bridged dimer with the oximate ligands *trans* with regard to the central Ti_2O_2 ring. The titanium atoms have a distorted trigonal-bipyramidal coordination, with the η^2-coordinated O*i*Pr ligand [O(6)] and one of the bridging O*i*Pr ligands [O(8)*] in axial positions [O(6)–Ti–O(8)* 168.6(1)°]. Consequently, the angles between O(7), O(8) and the center of the η^2-coordinated oximate ligand are in the range of 120° [O(7)–Ti–O(8) 114.28(9)°].

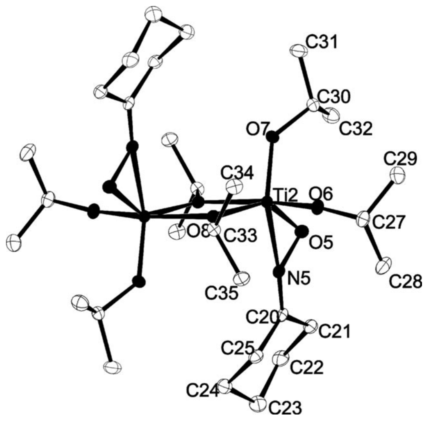

Figure 2. Molecular structure of $Ti_2(OiPr)_6(ON{=}C_6H_{10})_2$ (**4**).

Two isomeric forms were found for the di-substituted derivatives $[Ti(OiPr)_2(ON{=}CR_2)_2]_2$ (Figure 1). Both are O*i*Pr-bridged dimers with a terminal O*i*Pr ligand in the Ti_2O_2 plane and both oximate ligands perpendicular to this plane. The isomers differ by the mutual orientation of the oximate ligands bonded to the same titanium atom. In the compounds **1** and **2**, the two nitrogen atoms are *trans* (N–Ti–N 162–164° and $O_{oximate}$–Ti–$O_{oximate}$ ≈ 85°) ("isomer 1"), while in **3**, **5** and **6** the N–Ti–N and $O_{oximate}$–Ti–$O_{oximate}$ are around 130°, and a nearly linear O–Ti–N axis was observed [N–Ti–O 168–171°] ("isomer 2"). Figure 3 and Figure 4 show the molecular structures for **2** and **6**, as examples for both isomers. The structures of compounds **1** (isomer 1) and **3**/**5** (isomer 2) are very similar. Isomer 2 was also observed in $Ti_2(OiPr)_4$(pyridine-2-aldoximate)$_4$.[10] As in the mono-substituted derivative **4**, the titanium atom has a distorted trigonal-bipyramidal coordination, with the terminal O*i*Pr ligand and one bridging O*i*Pr ligand in axial positions (O–Ti–O ≈ 170°) and the other bridging O*i*Pr ligand and the centers of the η^2-coordinated oximate ligands in equatorial positions.

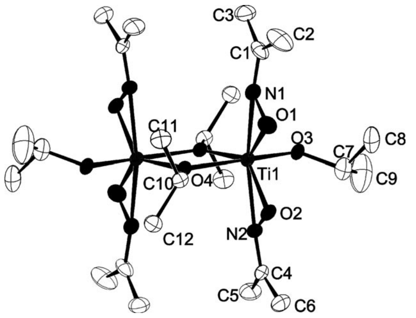

Figure 3. Molecular structure of $Ti_2(OiPr)_4(ON{=}CMe_2)_4$ (**2**).

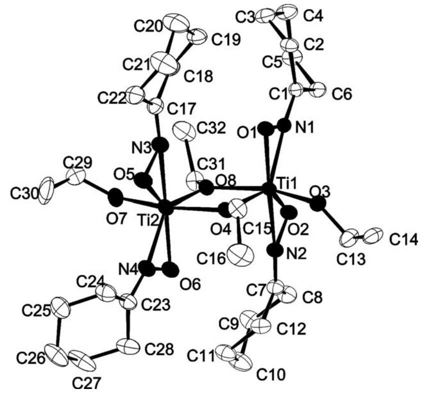

Figure 4. Molecular structure of $Ti_2(OEt)_4(ON{=}C_6H_{10})_4$ (**6**).

The tetrameric compound **7** was obtained from the reaction of $Ti(OiPr)_4$ with 2,4-pentandione dioxime [Equation (3)] and consists of two "isomer 1" type subunits which are interconnected by two dioximate ligands (Figure 5). The other two dioximate ligands bridge the two titanium atoms of each sub-unit. Each of the titanium atoms is thus coordinated by two oximate groups of different dioximate ligands with N–Ti–N angles of 161.7 ± 0.9° and $O_{oximate}$–Ti–$O_{oximate}$ 84.0 ± 0.5°. Bridging of the two metal centers of each sub-unit by a dioximate ligand results in a slight distortion of the central Ti_2O_2 ring towards a butterfly structure with a distance of 40 pm of Ti(2) off the Ti(1),O(6),O(8) plane. This distortion was not observed in the other "isomer 1" type compounds.

$$4\ Ti(OiPr)_4 + 4\ HON{=}CMe\text{-}CH_2\text{-}CMe{=}NOH \longrightarrow \underset{\mathbf{7}}{Ti_4(OiPr)_8(ON{=}CMe\text{-}CH_2\text{-}CMe{=}NO)_4} + 8\ iPrOH \qquad (3)$$

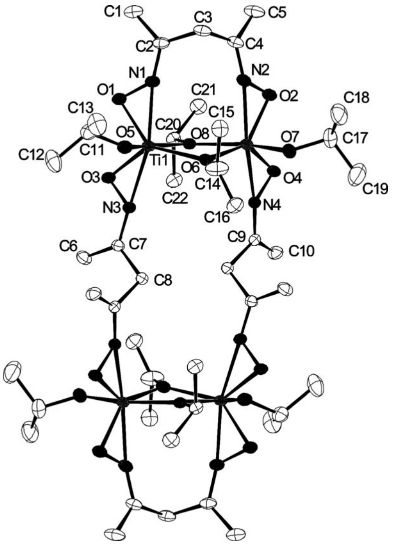

Figure 5. Molecular structure of $Ti_4(OiPr)_8(ON{=}CMe{-}CH_2{-}CMe{=}NO)_4$ (**7**).

NMR investigations were performed to find out whether the dimeric structures are retained in solution. Data are exemplarily discussed for **5**, those of the other compounds are very similar. According to the solid-state structure both of the two possible isomers (1 and 2 in Figure 1) have an inversion center and should therefore each give rise to signals for two non-equivalent O*i*Pr groups and two non-equivalent cyclohexanone oximate groups. The ^{1}H NMR spectroscopic data of **5** in [D$_8$]toluene solution at room temperature show three different sets of O*i*Pr ligands, two of them at δ_{CH} = 4.75 ppm, and one at δ = 4.41 ppm as shown in the COSY spectrum at room temperature (Figure 6). An EXSY spectrum of compound **5** at room temperature shows exchange signals between the O*i*Pr and the oximate ligands (Figure 7). Dynamic exchange can be explained by the conversion of the two possible isomers 1 and 2.

In an attempt to gain information on how the structures change upon partial hydrolysis, we exposed **2** to ambient humidity. To this end, a solution of $Ti(OiPr)_4$ and three molar equivalents of acetoxime was stored in a flask permitting access to ambient humidity. Moderate yields of the polynuclear compound $Ti_6O_6(OiPr)_6(ON{=}CMe_2)_6\cdot 2CH_2Cl_2$ (**8**) were reproducibly obtained (i.e. the experiment was repeated several times). The same cluster type, viz. $Ti_6O_6(OBu)_6(ON{=}C_5H_8)_6\cdot 3CH_2Cl_2$ (**9**) was obtained in the same experiment, starting from $Ti(OBu)_4$ and cyclopentanone oxime. Since both structures are nearly identical, only **8** is shown in Figure 8.

The Ti_6O_6 core of the clusters **8** and **9** is a hexagonal prism of alternating titanium and oxygen atoms. A notable difference to the dimeric oximate-substituted alkoxides **1**–**7** is that the oximate ligands are bridging rather than side-on

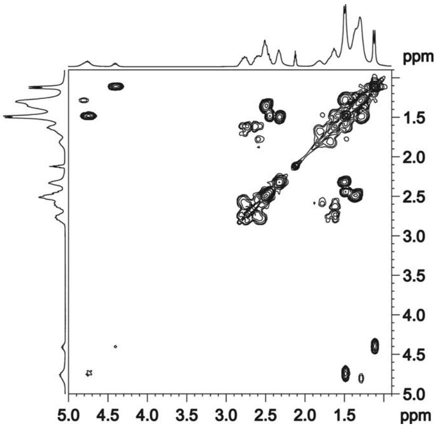

Figure 6. COSY spectrum of **5** in [D$_8$]toluene at room temperature.

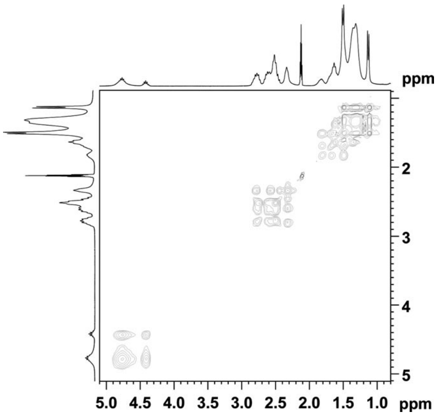

Figure 7. EXSY spectrum of **5** in [D$_8$]toluene at room temperature.

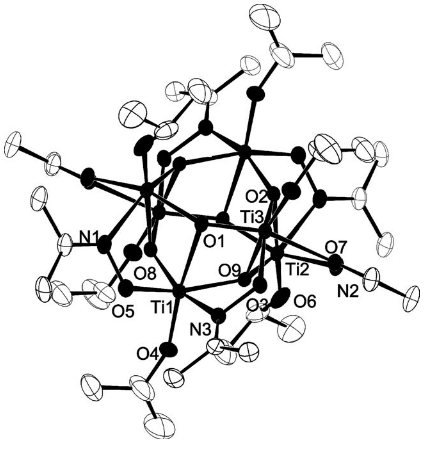

Figure 8. Molecular structure of $Ti_6O_6(OiPr)_6(ON{=}CMe_2)_6$ (**8**).

coordinated. As a consequence of the different coordination mode, the methyl group signal of the acetoximate ligand shifts from 2.04 ppm in dimeric **2** to 1.68 ppm in the hexanuclear cluster **8** in the solution ^{1}H NMR spectra. The six oximate ligands bridge the six four-membered Ti_2O_2 rings of the hexagonal prism (Figure 9) in an alternating orientation, i.e. each titanium atom is coordinated to only one nitrogen atom. Each titanium atom is additionally coordinated by a terminal OR ligand that is oriented perpendicular to the Ti_3O_3 rings. The same cluster type was already found for $Ti_6O_6(OR)_6(OOCR')_6$ (various OR and carboxylate ligands), with bridging carboxylate instead of oximate ligands.[12]

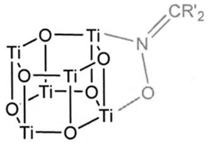

Figure 9. Schematic drawing of the cluster core of $Ti_6O_6(OR)_6(ON{=}CR'_2)_6$ (**8** and **9**). Only one oximate ligand is drawn for simplicity.

The different coordination of the oximate ligands allows an unambiguous assignment of the C=N absorptions in the infrared spectra. C=N absorptions of about 1640 cm^{-1} were previously assigned to terminally coordinated ligands,[13] and about 1650 cm^{-1} for bridging NO groups.[8] In the compounds **1**–**7**, which contain side-on coordinated ligands, C=N absorptions of 1643 ± 10 cm^{-1} were observed. In contrast, a lower value of 1617 cm^{-1} was observed in **9** where the NO group bridges two neighboring titanium atoms.

The composition of **8** and **9** is remarkable, as the Ti/oximate ratio is 1:1, although an excess of oximate was employed in the syntheses and despite the fact that only 1:2 compounds were isolated in the absence of water. There are two possible explanations: (i) the mono-substitution product $[Ti(OR)_3(ON{=}CR'R'')]_n$ could be kinetically trapped by the reaction with water before bis-substitution can occur, or (ii) the second oximate ligand per titanium atom in the bis-substitution products $[Ti(OR)_2(ON{=}CR'R'')_2]_2$ is cleaved during the hydrolysis reaction. Distinction between both possibilities will be subject to further work.

While **8** and **9** can be reproducibly obtained by the protocol discussed above, we obtained another partial hydrolysis products, viz. $Ti_4O_2(OiPr)_8(ON{=}CMe{-}CH_2{-}CMe{=}NO)_2$ (**10**), fortuitously in small yields when $Ti(OiPr)_4$ was treated with 2,4-pentandione dioxime without rigorously excluding moisture. This compound is nevertheless included here because each of such structures is a snapshot on stages of the hydrolysis reaction; the whole set of structures on partially hydrolyzed compounds is thus a structural "library" for the structural development from molecular precursors to gels.

The centrosymmetric tetramer (Figure 10) has two non-equivalent, octahedrally coordinated titanium atoms. Each dioximate ligand coordinates to three titanium atoms with pairwise bridging N–O groups. Thus, Ti(1) is chelated by both nitrogen atoms of the same dioximate, while two oxygen atoms of different dioximate ligands coordinate to Ti(2) in *trans* positions. When comparing the oxo cluster **10** to its non-hydrolyzed counterpart **7**, the lower titanium/oximate group ratio is again striking, as for the acetoximate and cyclopentanone oximate derivative described above. Compound **10** has the same Ti/oximate group ratio of 1:1 as in

8 and **9**, but the degree of hydrolysis is lower. Common to both cluster types is the presence of μ_3-O ions, typical of most titanium oxo clusters.

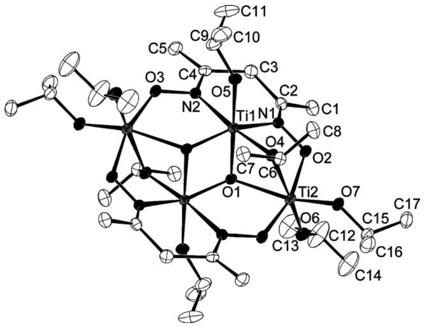

Figure 10. Molecular structure of $Ti_4O_2(OiPr)_8(ON{=}CMe{-}CH_2{-}CMe{=}NO)_2$ (**10**).

Conclusions

We have shown in this paper that mono- and dioximates are versatile ligands for the modification of titanium alkoxides. The basic structural motif of the oximate derivatives, i.e. an alkoxo-bridged dimer, is similar to what has been found for acetylacetonate,[14] aminoethanolate,[5] aminocarboxylate[15] or amine derivatives[16] of titanium alkoxides. However, there are some major differences. Bis-substitution (i.e. substitution of each Ti atom by two oximate ligands) appears to proceed much easier than with the other ligands mentioned. As a matter of fact, bis-substituted derivatives $[Ti(OR)_2(ON{=}CR'R'')_2]_2$ were found even if a 1:1 ratio of $Ti(OR)_4$ and oxime was employed, and a mono-substitution product $[Ti(OR)_3(ON{=}CR'R'')]_2$ was only obtained in a special case (compound **4** co-crystallized with **5**). The easier bis-substitution may be due to steric reasons. In all non-hydrolyzed derivatives (**1–7**), the NO group of the oximate ligands is side-on coordinated to one titanium atom. Thus, substitution of an OR group by a R′R′′C=NO ligand does not increase steric crowding or the coordination number of the metal atoms to the same extent as substitution by chelating ligands.

The oximate ligands are always positioned perpendicular to the central Ti_2O_2 unit. However, there is no preferred mutual orientation of the two oximate ligands in the bis-substituted derivatives $[Ti(OR)_2(ON{=}CR'R'')_2]_2$. Two isomers were found in the crystal structures, with no obvious correlation to chemical or steric properties of the ligands. In one isomer, the Ti atom is an inversion center with regard to the orientation of the oximate ligands, and in the other the two oximate ligands are related by a mirror plane through the Ti atom. NMR experiments in solution suggest interconversion of the two isomers.

Although hydrolysis studies were not in the focus of the present work, we isolated three partially hydrolyzed derivatives, which allow interesting, albeit preliminary comparisons with regard to coordination of the oximate ligands in the non-hydrolyzed compounds. First, the Ti/oximate ratio was 1:1, although the non-hydrolyzed compounds had 1:2 compositions. We currently cannot decide whether this is due to faster reaction of the mono-substituted derivatives with water or easier cleavage of the second oximate ligand during hydrolysis. This question will be subject to further work. Second, while the NO groups in the non-hydrolyzed compounds **1–7** are side-on coordinated to one titanium atom, they are bridging two titanium atoms in the partially hydrolyzed compounds **8–10**. This change in the coordination mode may be due to some *trans* influence of the μ_2 or μ_3 oxygen atoms, which results in significantly longer Ti–N distances (220–228 pm in **8–10**, compared to 204–206 pm in **1–7**, see Table 1) and thus disfavors side-on coordination.

Experimental Section

General: All operations were carried out in a moisture- and oxygen-free argon atmosphere using Schlenk and glovebox techniques. $Ti(OiPr)_4$ (Acros, 98+%), $Ti(OEt)_4$ (Aldrich, techn.), $Ti(OBu)_4$ (Aldrich, 97%), acetoxime (Aldrich, 98%), cyclopentanone oxime (Aldrich, 97%), cyclohexanone oxime (Aldrich, 97%) and 2,4-pentanedione oxime (ABCR, 98+%) were used as received. All solvents were dried and purified by standard methods. Ethyl methyl ketone *E*-oxime was synthesized from the ketone by usual methods following the procedure of Bousquet.[17] The solvents for NMR spectroscopy (Eurisotop) were degassed prior to use and stored over molecular sieve.

Table 1. Comparison of the Ti–O and Ti–N distances [pm], and N–Ti–N and $O_{oximate}$–Ti–$O_{oximate}$ bond angles [°] in the derivatives **1–7**.

	4	**1**	**2**	**3**	**5** (co-crystallized with **4**)	**5**	**6**	**7**
Ti–O	194.9(2)	194.9(4)	192.5(4)	196(1)	194.3(2)	197.4(1)	196.4(1)	195.7(2)
		195.9(4)	193.2(4)	198(1)	199.2(2)	198.2(1)	194.9(2)	193.3(2)
				200(1)		196.6(1)	194.6(2)	193.9(2)
				196(1)		198.9(1)	199.6(2)	197.2(2)
Ti–N	209.5(3)	209.2(5)	210.3(4)	205(2)	203.7(3)	209.5(1)	204.2(2)	208.7(2)
		211.6(5)	211.0(4)	209(2)	212.2(3)	204.9(1)	211.1(2)	209.4(2)
				204(2)		204.4(1)	211.3(2)	211.9(2)
				216(1)		210.4(1)	202.8(2)	207.6(2)
N–Ti–N	–	164.3(2)	162.0(2)	130.5(6)	129.9(1)	132.18(5)	131.70(7)	162.56(8)
				131.0(6)		132.35(5)	130.39(8)	160.86(7)
O–Ti–O	–	85.3(2)	84.5(2)	131.0(6)	129.67(9)	132.42(4)	131.98(6)	84.47(7)
				131.2(6)		132.45(4)	130.45(7)	83.47(6)

^{1}H and ^{13}C solution NMR spectra were recorded on a Bruker AVANCE 250 (250.13 MHz {^{1}H}, 62.86 MHz {^{13}C}) and a Bruker DPX 300 spectrometer (300.13 MHz {^{1}H}, 75.47 MHz {^{13}C}) equipped with a 5 mm inverse-broadband probe head and a *z*-gradient unit. 2D NMR spectra were measured with Bruker standard pulse programs COSY (Correlation Spectroscopy), TOCSY (Total Correlation Spectroscopy), HSQC (Heteronuclear Single Quantum Correlation), and HMBC (Heteronuclear Multiple-Bond Correlation). A numbering scheme for the carbon atoms of the oximate ligands is given in Figure 11.

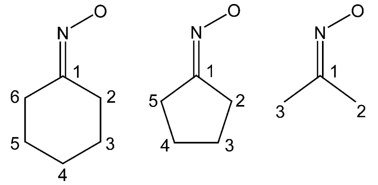

Figure 11. Numbering of the carbon atoms of cyclohexanone, cyclopentanone and acetoximate ligands.

FT-IR spectra were recorded on a Bruker Tensor 27 working in ATR MicroFocusing MVP-QL with a ZnSe crystal or in dichloromethane solution, using OPUS version 4.0 software for analysis. Reliable elemental analyses were not obtained due to the high moisture sensitivity of the complexes.

Synthesis of [Ti(O*i*Pr)$_2$(ON=C$_5$H$_8$)$_2$]$_2$ (1): An amount of 389 mg (4.93 mmol) cyclopentanone oxime was dissolved in 0.79 mL of dichloromethane at room temperature followed by dropwise addition of 701 mg (2.47 mmol) of Ti(O*i*Pr)$_4$. The pale yellow reaction mixture was stirred for 5 min. Colorless crystals were obtained from the solution after two days which were washed with several portions of pentane at –20 °C and dried in vacuo; yield 383 mg (43 %). ^{1}H NMR (CDCl$_3$, 20 °C): δ = 4.50 (q, *J* = 6.0 Hz, 1 H, C*H*Me$_2$), 2.52 (m, 2 H, C^{2}*H*), 2.42 (m, 2 H, C^{5}*H*), 1.76 (s, 4 H, C^{3,4}*H*), 1.17 (d, *J* = 5.5 Hz, 4 H, C*H*$_3$), 1.06 (d, *J* = 6.1 Hz, 2 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 158.3 (*C*=N), 76.2/77.7 [*C*H(CH$_3$)$_2$], 30.1 (*C*^{5}), 29.2 (*C*^{2}), 24.9 (*C*H$_3$), 24.6/24.8 (*C*^{3,4}), 23.7 (*C*H$_3$) ppm. IR (CH$_2$Cl$_2$): ṽ = 2970 (s), 2874 (s), 1668 (m), 1634 (w), 1453 (m), 1426 (m), 1376 (m), 1362 (m), 1330 (m), 1214 (w), 1162 (s), 1125 (vs), 1073 (w), 998 (vs), 947 (s), 851 (sh), 814 (w), 623 (s), 582 (s), 567 (s) cm^{-1}.

Synthesis of [Ti(O*i*Pr)$_2$(ON=CMe$_2$)$_2$]$_2$ (2): An amount of 156 mg (2.13 mmol) acetoxime was dissolved in 0.30 mL of dichloromethane at room temperature followed by dropwise addition of 307 mg (1.08 mmol) of Ti(O*i*Pr)$_4$. A white crystalline solid precipitated immediately which was re-dissolved by addition of 0.40 mL of dichloromethane. Colorless crystals were obtained from the yellow solution after one day which were washed with several portions of hexane at –20 °C and dried in vacuo; yield 126 mg (30 %). ^{1}H NMR (CDCl$_3$, 20 °C): δ = 4.60 (q, *J* = 5.9 Hz, 1 H, C*H*Me$_2$), 2.07 (s, 3 H, C^{2}*H*), 2.04 (s, 3 H, C^{3}*H*), 1.22 [d, *J* = 5.2 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.09 [d, *J* = 5.8 Hz, 3 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 147.7 (*C*=N), 76.3 (*C*HMe$_2$), 25.7/26.3 [CH(*C*H$_3$)$_2$], 21.7 (*C*^{2}H), 18.5 (*C*^{3}H) ppm. IR (CH$_2$Cl$_2$): ṽ = 2970 (s), 2874 (s), 1667 (m), 1453 (m), 1426 (w), 1375 (m), 1362 (m), 1330 (w), 1214 (w), 1161 (s), 1125 (vs), 1073 (w), 998 (vs), 947 (m), 851 (sh), 814 (w), 623 (m), 582 (s), 567 (m) cm^{-1}.

Synthesis of [Ti(O*i*Pr)$_2$(ON=C(Me)Et)$_2$]$_2$ (3): An amount of 530 mg (6.08 mmol) ethyl methyl ketoxime was dissolved in 0.45 mL of dichloromethane at room temperature followed by dropwise addition of 864 mg (3.04 mmol) of Ti(O*i*Pr)$_4$. A colorless microcrystalline solid precipitated upon evaporation of the solvent in vacuo which was re-dissolved by addition of 0.20 mL of dichloromethane. Colorless crystals were obtained from the yellow solution after one day of storing the reaction mixture at 2 °C. The crystals were washed with several portions of pentane at –20 °C and dried in vacuo; yield 968 mg (94 %). ^{1}H NMR (CDCl$_3$, 20 °C): δ = 4.55/4.46 (q, *J* = 6.2 Hz, 1 H, C*H*Me$_2$), 2.44/2.29 (q, *J* = 7.6 Hz, 2 H, C*H*$_2$Me), 1.99/1.96 (s, 3 H, CC*H*$_3$), 1.18/1.16 [s, 3 H, CH(C*H*$_3$)$_2$], 1.06/1.02 [d, *J* = 6.2 Hz, 6 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 152 (*C*=N), 77.2/76.3 (*C*HMe$_2$), 29.1 (*C*H$_2$Me), 26.4/25.7 (*C*HMe$_2$), 17.1 (C*C*H$_3$), 9.7 (CH$_2$*C*H$_3$) ppm. IR (CH$_2$Cl$_2$): ṽ = 2873 (s), 2880 (s), 1648 (m), 1461 (m), 1438 (w), 1376 (m), 1161 (m), 1128 (vs), 1074 (w), 1003 (s), 947 (m), 851 (sh), 813 (w), 627 (s), 562 (s), 508 (w) cm^{-1}.

Synthesis of [Ti(O*i*Pr)$_3$(ON=C$_6$H$_{10}$)]$_2$·[Ti(O*i*Pr)$_2$(ON=C$_6$H$_{10}$)$_2$]$_2$ (4+5): An amount of 346 mg (3.05 mmol) cyclohexanone oxime was dissolved in 0.49 mL of dichloromethane at room temperature followed by dropwise addition of 1.306 g (4.59 mmol) of Ti(O*i*Pr)$_4$. The reaction mixture was stirred for 20 min. Colorless crystals of **4+5** were obtained from the yellow solution after one day beside crystals of **5**. The crystals were washed with several portions of hexane at –20 °C and dried in vacuo. ^{1}H NMR (CDCl$_3$, 20 °C): δ = 4.45 (m, 1 H, C*H*$_2$Me), 2.55 (m, 1 H, C^{2}*H*), 2.32 (m, 1 H, C^{6}*H*), 1.58 (s, 3 H, C$^{3-5}$*H*), 1.17 (d, *J* = 6.2 Hz, 5 H, C*H*$_3$), 1.03 (d, *J* = 6.1 Hz, 1 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 152.8 (*C*=N), 77.2 (*C*HMe$_2$), 32.4 (*C*^{6}), 28.6 (*C*^{2}), 25.8/26.4 (*C*$^{3-5}$), 25.7/26.9 (*C*H$_3$) ppm. IR (CH$_2$Cl$_2$): ṽ = 2971 (s), 2936 (s), 2863 (s), 1652 (w), 1449 (m), 1377 (m), 1363 (m), 1331 (m), 1162 (s), 1123 (vs), 1075 (w), 999 (s), 949 (m), 901 (w), 851 (sh), 619 (m), 535 (m) cm^{-1}.

Synthesis of [Ti(O*i*Pr)$_2$(ON=C$_6$H$_{10}$)$_2$]$_2$ (5): An amount of 339 mg (3.00 mmol) cyclohexanone oxime was dissolved in 0.50 mL of dichloromethane at room temperature followed by dropwise addition of 423 mg (1.49 mmol) of Ti(O*i*Pr)$_4$. The reaction mixture was stirred for 20 min. Colorless crystals were obtained from the yellow solution after one day which were washed with several portions of hexane at –20 °C and dried in vacuo; yield 452 mg (78 %). ^{1}H NMR ([D$_8$]toluene, 20 °C): δ = 4.75 (q, *J* = 6.1 Hz, 3 H, C*H*Me$_2$), 4.41 (q, *J* = 6.1 Hz, 1 H, C*H*Me$_2$), 2.76 (t, *J* = 6.7 Hz, 3 H, C^{2}*H*), 2.60 (t, *J* = 7.2 Hz, 5 H, C^{2}*H*), 2.50 (t, *J* = 6.3 Hz, 5 H, C^{6}*H*), 2.32 (t, *J* = 5.8 Hz, 3 H, C^{6}*H*), 1.62 (s, 6 H, C$^{3-5}$*H*), 1.49 (d, *J* = 6.2 Hz, 16 H, C*H*$_3$), 1.30 (s, 18 H, C$^{3-5}$*H*), 1.11 (d, *J* = 6.0 Hz, 8 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_8$]toluene, 20 °C): δ = 146.2/148.8 (*C*=N), 72.9/76.3 (*C*HMe$_2$), 31.9 (*C*^{6}), 28.1 (*C*^{2}), 25.8/26.0 (*C*$^{3-5}$), 25.0/26.7 (*C*H$_3$) ppm. IR (CH$_2$Cl$_2$): ṽ = 2970 (s), 2940 (s), 2861 (s), 1655 (w), 1449 (sh), 1377 (m), 1326 (w), 1129 (m), 1074 (w), 1002 (s), 948 (m), 902 (w), 847 (w), 589 (s), 537 (m) cm^{-1}.

Synthesis of [Ti(OEt)$_2$(ON=C$_6$H$_{10}$)$_2$]$_2$ (6): An amount of 511 mg (4.51 mmol) cyclohexanone oxime was dissolved in 0.75 mL of dichloromethane at room temperature followed by dropwise addition of 518 mg (2.27 mmol) of Ti(OEt)$_4$ and stirring for 30 min. A fawn solid precipitated upon evaporation of the solvent which was re-dissolved in 0.25 mL of CH$_2$Cl$_2$ upon heating. Colorless crystals were obtained from the yellow solution after 30 min which were washed with several portions of hexane at –20 °C and dried in vacuo; yield 541 mg (66 %). ^{1}H NMR (CDCl$_3$, 20 °C): δ = 4.54 (q, *J* = 6.0 Hz, 1 H, C*H*$_2$Me), 2.55 (m, 4 H, C^{2}*H*), 2.32 (m, 4 H, C^{6}*H*), 1.58 (s, 12 H, C$^{3-5}$*H*), 1.15 (d, *J* = 5.0 Hz, 3 H, C*H*$_3$), 1.03 (d, *J* = 5.8 Hz, 3 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 151.0/152.8 (*C*=N), 76.1/77.2 (*C*H$_2$CH$_3$), 32.2/32.4 (*C*^{6}), 28.6 (*C*^{2}), 25.8 (*C*$^{3-5}$), 25.7/26.9 (*C*H$_3$) ppm. IR (CH$_2$Cl$_2$): ṽ = 2969 (s), 2941 (s), 2860 (s), 1656 (m), 1449 (m), 1422 (m), 1376 (w), 1161 (m), 1129 (s), 1002 (s), 949 (m), 897 (sh), 847 (m), 620 (m), 589 (s), 537 (s) cm^{-1}.

Synthesis of [Ti$_2$(O*i*Pr)$_4$(ON=CMe-CH$_2$-CMe = NO)$_2$]$_2$ (7): An amount of 284 mg (2.18 mmol) 2,4-pentanedione dioxime was dissolved in 5 mL of hot *i*PrOH to give a colorless solution. Dropwise addition of 624 mg (2.20 mmol) Ti(O*i*Pr)$_4$ to the refluxing solution yielded a claret red discoloration. Heating was continued for 10 min. The crystals obtained when the reaction mixture was slowly cooled to room temperature overnight were washed with several portions of pentane at –20 °C and dried in vacuo; yield 475 mg (74%). ^{1}H NMR (CDCl$_3$, 20 °C): δ = 3.96 (q, J = 6.2 Hz, 1 H, C*H*Me$_2$), 2.29 (s, 2 H, C*H*$_2$), 1.14 (d, J = 5.7 Hz, 6 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 148.3 (*C*=N), 77.2 (*C*HMe$_2$), 64.4 (*C*H$_2$), 29.7 (*C*H$_3$), 25.4 [C(*C*H$_3$)$_2$] ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2926 (s), 2854 (s), 1647 (m), 1422 (s), 1339 (w), 1121 (s), 1009 (m), 896 (sh), 589 (m), 536 (m) cm^{-1}.

Synthesis of Ti$_6$O$_6$(O*i*Pr)$_6$(ON=CMe$_2$)$_6$ (8): An amount of 121 mg (1.66 mmol) acetoxime was dissolved in 0.26 mL of CH$_2$Cl$_2$ at room temperature followed by dropwise addition of 154 mg (0.54 mmol) of Ti(O*i*Pr)$_4$. Colorless crystals of **7**·2CH$_2$Cl$_2$ were obtained from the yellow solution after two months upon slow diffusion of water. To this end, the reaction mixture was exposed to ambient moisture by keeping the solution in a vessel capped by a perforated rubber seal. The crystals were washed with several portions of pentane at –20 °C and dried in vacuo; yield 34 mg (5.4%). ^{1}H NMR (CDCl$_3$, 20 °C): δ = 5.00 (q, J = 6.1 Hz, 1 H, C*H*Me$_2$),

Table 2. Crystallographic and structural parameters of **1**–**10**.

	1·2CH$_2$Cl$_2$	**2**	**3**	**4+5**	**5**
Empirical formula	C$_{34}$H$_{64}$Cl$_4$N$_4$O$_8$Ti$_2$	C$_{24}$H$_{52}$N$_4$O$_8$Ti$_2$	C$_{28}$H$_{60}$N$_4$O$_8$Ti$_2$	C$_{66}$H$_{130}$N$_6$O$_{16}$Ti$_4$	C$_{36}$H$_{68}$N$_4$O$_8$Ti$_2$
Formula weight	894.5	620.5	676.6	1455.4	780.7
Temperature /K	173	100	100	173	100
Crystal system	monoclinic	monoclinic	triclinic	triclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$Pna2_1$
Unit cell dimensions					
a /pm	1369.5(1)	1020.3(2)	1004.1(3)	1051.8(2)	2042.74(8)
b /pm	961.31(8)	1758.7(4)	1013.7(3)	1130.1(2)	1024.07(4)
c /pm	1807.6(2)	1029.9(2)	1044.7(3)	1727.4(3)	1972.46(8)
α /°			96.614(5)	89.192(3)	
β /°	105.185(2)	115.528(4)	103.641(5)	84.723(3)	
γ /°			113.170(4)	73.183(3)	
Volume /pm^3 × 10^6	2296.6(3)	1667.7(6)	923.9(5)	1956.9(6)	4126.2(3)
Z	2	2	1	1	4
Calcd. density /g cm^{-3}	1.294	1.236	1.216	1.235	1.257
Absorption coeff. μ /mm^{-1}	0.627	0.524	0.478	0.456	0.438
Crystal size /mm	0.04 × 0.04 × 0.04	0.30 × 0.25 × 0.20	0.15 × 0.15 × 0.10	0.30 × 0.30 × 0.30	0.60 × 0.50 × 0.20
θ range /°	2.33–24.99	2.32–28.33	2.32–28.36	2.26–28.30	2.22–28.28
Reflections collected/unique	11870/4038	16047/4137	7992/4494	13247/9400	38794/8995
Data/parameters	4038/235	4137/180	4494/198	9400/451	8995/459
GOF on F^2	1.095	0.958	1.000	0.962	1.052
R [$I > 2\sigma(I)$]	0.092	0.070	0.062	0.052	0.025
$wR2$	0.263	0.149	0.135	0.106	0.064
Largest diff. peak/hole /e Å^{-3}	1.994/–1.433	0.525/–0.522	0. 698/–0. 472	0.433/–0.510	0.383/–0.152

	6	**7**	**8**·2CH$_2$Cl$_2$	**9**·3CH$_2$Cl$_2$	**10**
Empirical formula	C$_{32}$H$_{60}$N$_4$O$_8$Ti$_2$	C$_{44}$H$_{88}$N$_8$O$_{16}$Ti$_4$	C$_{38}$H$_{82}$Cl$_4$N$_6$O$_{18}$Ti$_6$	C$_{57}$H$_{108}$Cl$_6$N$_6$O$_{18}$Ti$_6$	C$_{34}$H$_{72}$N$_4$O$_{14}$Ti$_4$
Formula weight	724.64	1176.82	1340.3	1665.6	952.6
Temperature /K	173	100	173	173	173
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
Unit cell dimensions					
a /pm	1947.42(8)	1099.9(2)	1110.79(5)	1756.2(1)	995.22(6)
b /pm	1068.17(5)	1142.8(2)	1279.24(6)	2323.9(1)	1750.1(1)
c /pm	2053.63(9)	2475.2(5)	1302.90(6)	1916.4(1)	1408.10(9)
α /°			62.790(1)		
β /°	115.048(1)	102.012(3)	71.598(1)	100.876(1)	108.057(1)
γ /°			86.117(1)		
Volume /pm^3 × 10^6	3870.2(3)	3043.0(11)	1555.9(1)	7680.5(8)	2331.7(2)
Z	4	4	1	4	2
Calcd. density /g cm^{-3}	1.244	1.284	1.430	1.440	1.357
Absorption coeff. μ /mm^{-1}	0.461	0.570	0.968	0.867	0.721
Crystal size /mm	0.30 × 0.30 × 0.30	0.29 × 0.28 × 0.08	0.30 × 0.30 × 0.20	0.30 × 0.30 × 0.20	0.30 × 0.30 × 0.30
θ range /°	2.19–28.28	2.61–28.32	2.39–25.00	2.26–25.00	2.45–25.00
Reflections collected/unique	26085/9594	29671/7552	11687/5443	38987/13473	12376/4092
Data/parameters	9594/448	7552/348	5443/362	13473/838	4092/253
GOF on F^2	1.016	1.025	1.057	0.742	1.052
R [$I > 2\sigma(I)$]	0.050	0.044	0.038	0.052	0.041
$wR2$	0.130	0.115	0.109	0.088	0.104
Largest diff. peak/hole /e Å^{-3}	0.416/–0.200	0.378/–0.246	0.838/–0.472	0.558/–0.365	0.777/–0.599

2.07 (s, 3 H, C^2H), 1.68 (s, 3 H, C^3H), 1.30/1.28 [d, J = 5.6 Hz, 6 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ = 150.2 (C=N), 75.8 (CHMe$_2$), 24.0 [$CH(CH_3)_2$], 20.2 (C^2H), 15.9 (C^3H) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2972 (s), 2918 (s), 2866 (s), 1617 (m), 1558 (w), 1435 (m), 1378 (m), 1364 (m), 1329 (w), 1163 (m), 1135 (s), 1082 (m), 1001 (s), 855 (m), 610 (s) cm^{-1}.

Synthesis of $Ti_6O_6(OBu)_6(ON=C_5H_8)_6$ (9): An amount of 431 mg (4.35 mmol) cyclopentanone oxime was dissolved in 0.80 mL of CH_2Cl_2 at room temperature followed by dropwise addition of 490 mg (1.44 mmol) of $Ti(OBu)_4$. Few colorless crystals of **9**·3CH_2Cl_2 were obtained from the yellow solution after two months upon slow diffusion of water. To this end, the reaction mixture was exposed to ambient moisture by keeping the solution in a vessel capped by a perforated rubber seal.

Synthesis of $Ti_4O_2(OiPr)_8(ON=CMe-CH_2-CMe=NO)_2$ (10): $Ti(OiPr)_4$ was added to a suspension of an equimolar amount of 2,4-pentandione dioxime in dry CH_2Cl_2. The mixture was stirred at room temperature for several hours. The pale red solution was decanted from the solid and stored at 4 °C for several days. This resulted in the crystallization of a small amount of **10**.

X-ray Structure Analyses: See Table 2; single-crystal X-ray diffraction experiments were performed on a Siemens SMART and a Bruker-AXS APEX diffractometer with CCD area detectors and a crystal-to-detector distance of 5.0 cm using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm). The data collection covered a hemisphere of the reciprocal space by recording three sets of exposures, each of them exhibiting a different Φ angle. The times for each exposure were 5 to 30 s, each of them covering 0.3° in ω. 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. The structures were solved with direct methods (SHELXS97) and refinement to convergence was carried out with the full-matrix least-squares method based on F^2 (SHELXL97) with anisotropic structure parameters for all non-hydrogen atoms. The hydrogen atoms were placed on calculated positions and refined riding on their parent atoms.

In the crystal structure of **6** two ethoxy ligands are disordered. Most of the residual electron density was close to these disordered groups. In **4+5** and **9** one O*i*Pr group is disordered.

CCDC-729640 (for **1**), -729641 (for **2**), -729642 (for **3**), -729643 (for **4+5**), -729644 (for **5**), -729645 (for **6**), -729646 (for **7**), -729647 (for **8**), -729648 (for **9**), -729649 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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