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Modification of Titanium Isopropoxide with Aromatic Aldoximes

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Dimeric $[Ti(OiPr)_2(benzaldoximate)_2]_2$ was obtained upon reaction of titanium isopropoxide with two molar equivalents of benzaldehyde (*E*)- or (*Z*)-oxime or *m*-anisaldoxime. Two isomers were formed differing by the mutual orientation of the oximate ligands. Reaction with perillaldoxime or *trans*-cinnamaldoxime resulted in the corresponding derivatives with functional ligands. The degree of substitution was higher when *o*- or *p*-anisaldoxime were employed in the same molar ratio, and dimeric $Ti_2(OiPr)_3(o\text{-anisaldoximate})_5$ with a bridging oximate ligand and monomeric $Ti(oximate)_4$ (oximate = *o*-anisaldoximate or *p*-anisaldoximate) were obtained. Dissolution of the *p*-anisaldoximate derivative upon heating in $[D_6]$DMSO led to deoximation reactions.

Introduction

The use of oximes as ligands for the complexation of late transition metals has been investigated intensively. Less attention, however, has been paid to oximate derivatives of earlier transition metals. Addition products of oximes to titanium halides were described in early literature, viz. $TiF_4(Me_2C{=}NOH)_2$ formed by coordination of acetone oxime to TiF_4.[1] The dimethylglyoxime ($dmgH_2$) adduct to $TiCl_4$, $TiCl_4(dmgH_2)_n$, was converted into the oximate derivative $TiCl_3(dmgH)$ by moderate heating.[2] Several alkoxide derivatives $Ti(OR)_{4-x}(ON{=}CR'R'')_x$ (x = 1–4) have been reported, but they were only characterized by infrared spectroscopy and elemental analysis.[3] The first structural analysis of a titanium oximate derivative, with side-on coordinated oximate ligand, was carried out by Thewalt et al. for $[Cp_2Ti(H_2O)(ON{=}CR'R'')]^+$.[4] More recently, reaction of $Ti(OiPr)_4$ with salicylaldoxime resulted in a trinuclear complex in which the oximate groups, as dianionic ligands, bridge the three titanium centers.[5] In the same work, dinuclear complexes with side-on coordinated oximate ligands, $[Ti(\mu\text{-}OiPr)(OiPr)(ON{=}CHR')_2]_2$, were obtained from the reaction of $Ti(OiPr)_4$ with pyridine-2-aldoxime. The latter compounds are part of the structural family of oximate derivatives described below.

We reported recently the synthesis and structures of dimeric oximate derivatives with aliphatic ketoximate ligands, $[Ti(OiPr)_2(oximate)_2]_2$.[6] Disubstituted derivatives (two oximate ligands per titanium atom) were found even if a 1:1 ratio of $Ti(OR)_4$ and oxime was employed. Two isomers were observed (Figure 1), which differ by the mutual orientation of the side-on coordinated oximate ligands. In "isomer 1" the oximate ligands are mirror-symmetric with regard to the Ti_2O_2 plane. The N–Ti–N angle in this isomer with an idealized C_{2h} symmetry is 162–164°, and the Ti–$O_{oximate}$ bonds are nearly perpendicular to each other. The C_i symmetric "isomer 2"-type compounds have a nearly linear N–Ti–$O_{oximate}$ arrangement.

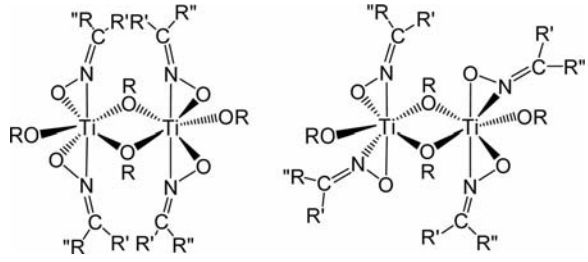

Figure 1. Schematic structures of isomeric $[Ti(OiPr)_2(oximate)_2]_2$ derivatives: "isomer 1" (left) and "isomer 2" (right).

Oximates are powerful ligands for the modification of metal alkoxides. They are easily prepared, show versatile coordination behavior, and, most notably, allow organic functionalities in inorganic–organic hybrid materials to be introduced. We have recently shown that sol–gel processing of acetaldoximate-modified titanium alkoxides in the presence of the nonionic surfactants results in mesoporous anatase with superior properties.[7] A simple example of "organic functionalization" is the use of long-chain oximate derivatives with surfactant properties.[8]

In this article we will show that derivatives $Ti(OiPr)_{4-x}(oximate)_x$ with $x \geq 2$ can be isolated for reactions with aromatic aldoximes and that aromatic oximes allow easy introduction of unsaturated organic groups. The ligands used in this work are shown in Figure 2.

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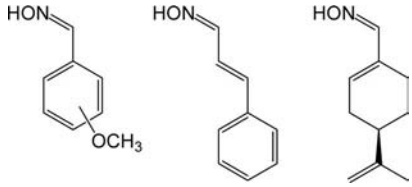

Figure 2. Anisaldoxime (left), *trans*-cinnamaldoxime (center), and perillaldoxime (right).

Results and Discussion

Reaction of Ti(O*i*Pr)$_4$ with benzaldehyde-(*Z*)-oxime (2 equiv.) in CH_2Cl_2 at room temperature resulted in the formation of dimeric [Ti(O*i*Pr)$_2${benzaldehyde-(*Z*)-oximate}$_2]_2$ (**1**). The molecular structure of **1** is of the "isomer 1"-type (Figure 3). In contrast, "isomer 2"-type [Ti(O*i*Pr)$_2${benzaldehyde-(*E*)-oximate}$_2]_2$ (**2**) was obtained from Ti(O*i*Pr)$_4$ and (*E*)-benzaldoxime (Figure 4). Only one isomer crystallized exclusively in either case. As for the reactions with aliphatic oximes,[6] there is no apparent correlation of the formed isomer with the properties of the applied oxime. As the isomers interconvert in solution (see below) the preferred crystallization of one isomer is obviously a crystal packing effect. The Ti–O and Ti–N bond lengths of **1** and **2** (Table 1) are in the same range as that of derivatives with aliphatic oximate ligands.[6] The alkoxido bridges are asymmetric; the bridging Ti–O bond lengths differ by up to 13 pm (in **1**; see Table 1) with the longer Ti–O distance *trans* to the terminal O*i*Pr ligand. In all structures discussed in this article, the phenyl rings are coplanar with the C=N–O groups, and oximate ligands bonded to the same titanium atom are nearly coplanar with each other.

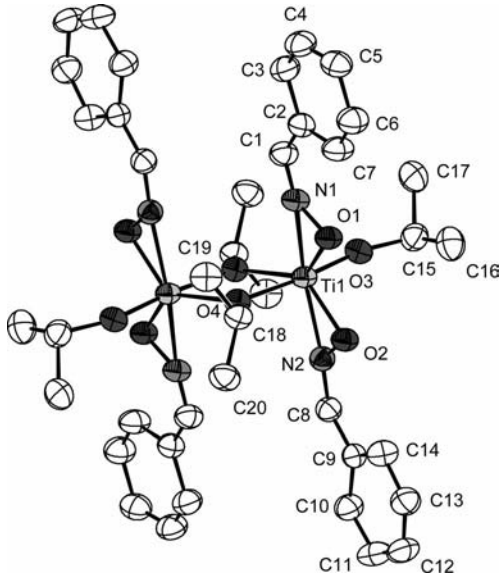

Figure 3. Molecular structure of [Ti(O*i*Pr)$_2${benzaldehyde-(*Z*)-oximate}$_2]_2$ (**1**).

The same structure as that of **2** was found for crystalline [Ti(O*i*Pr)$_2$(*m*-anisaldoximate)$_2]_2$ (**3**) obtained by the same reaction (Figure 5). The behavior of **3** in solution was investigated by NMR spectroscopy and serves as an example for the other derivatives. As also observed for [Ti(O*i*Pr)$_2$-(ON=C_6H_{10})$_2]_2$,[6] signals corresponding to exchange of the O*i*Pr groups (δ_{CH} = 4.58 and 4.06 ppm) were present in the EXSY spectrum (Figure 6). Furthermore, the oximate ligands are dynamic in solution; this can possibly be explained by interconversion of the two isomers (Figure 1). Equilibria between derivatives with different degrees of substitution (see below) may also play a role. Such exchange reactions were also observed for titanium alkoxides modified with other organic ligands, for example, amino alcoholates[9] or β-diketonates.[10]

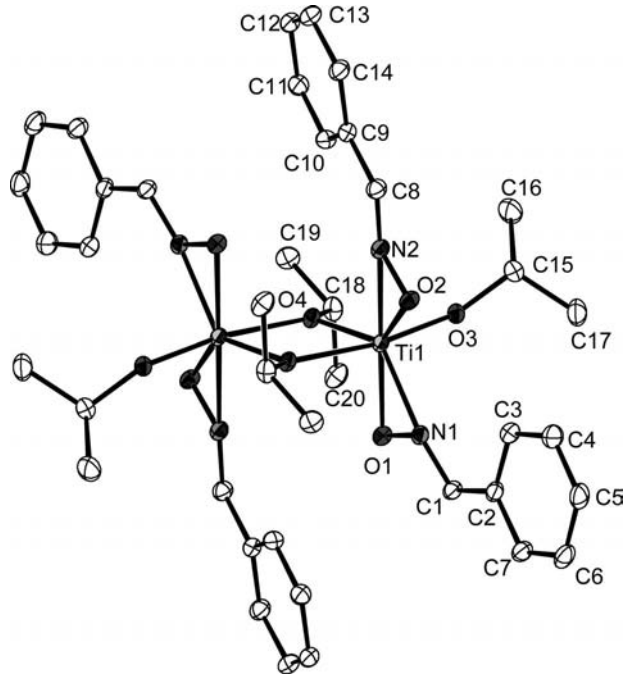

Figure 4. Molecular structure of [Ti(O*i*Pr)$_2${benzaldehyde-(*E*)-oximate}$_2]_2$ (**2**).

^{1}H NMR spectroscopic experiments were performed between –80 and 80 °C to study the solution behavior and the exchange of the ligands in **3** at different temperatures. As shown in Figure 7, the signals of the O*i*Pr and oximate ligands merge upon heating of the solution. For instance, the room temperature signals of the O*i*Pr methyl groups at δ_{CH_3} = 0.98, 1.29, and 1.54 ppm coincide with a signal at δ_{CH_3} = 1.26 ppm at 80 °C, whereas the signal corresponding to the methine groups at δ_{CH} = 3.51 ppm sharpens upon heating due to faster exchange reactions. In contrast, cooling leads to splitting of the signals. Three sets of signals are present for the methine protons of the isopropoxido ligands at temperatures below 0 °C. This means that at low temperatures the exchange of the ligands is blocked and each ligand can be detected individually.

Similar observations were made for amine adducts of titanium alkoxides.[11] The methine ^{1}H NMR signal of dimeric [Ti(O*i*Pr)$_4$(NH_2CH_2Ph)]$_2$ is averaged at room temperature. It splits into four signals when cooled to –80 °C, corresponding to the C_i symmetry of the complex.

Table 1. Comparison of the Ti–O and Ti–N distances [pm] and N–Ti–O and N–Ti–N bond angles [°] in derivatives **1**–**4**, **7**, and **8** (atoms with an asterisk are inversion related).

	1	**2**	**3**	**4**	**7**	**8**
Ti1–O1	197.2(3)	197.43(13)	197.7(2)	196.7(3)	194.8(5)	196.2(2)
Ti1–O2	197.8(3)	196.53(13)	194.9(2)	195.2(2)	197.3(5)	195.5(2)
Ti1–O4	210.6(7)	207.37(12)	206.6(2)	200.7(2)	179.6(4)	179.3(2)
Ti1–O4*	197.7(8)	200.65(12)	197.7(2)		208.8(4)	
Ti2–O4				205.9(2)		205.3(2)
Ti1–O5				209.7(2)		
Ti2–O5				204.1(2)		
Ti2–O6				195.4(3)		
Ti2–O7				194.2(2)		
Ti1–N1	208.6(3)	206.45(14)	206.2(2)	206.3(3)	217.6(5)	208.0(3)
Ti1–N2	208.7(4)	210.96(15)	222.4(2)	215.7(3)	206.7(6)	208.9(3)
Ti2–N4				209.7(3)		
Ti2–N5				210.3(3)		
O2–Ti1–N1	124.93(14)	94.51(6)	90.10(8)	91.94(11)	167.24(19)	125.41(11)
O1–Ti1–N2	125.21(14)	171.86(5)	166.08(8)	169.21(11)	91.3(2)	125.39(11)
O6–Ti2–N5				124.90(11)		
O7–Ti2–N4				124.66(11)		
N1–Ti1–N2	163.59(15)	133.49(6)	127.86(8)	130.67(12)	129.2(2)	164.24(12)
N4–Ti2–N5				163.96(12)		

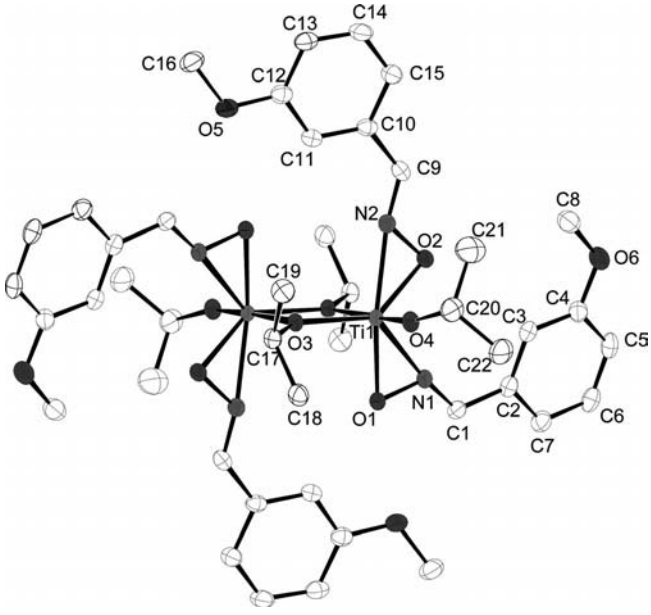

Figure 5. Molecular structure of $[Ti(OiPr)_2(m\text{-anisaldoximate})_2]_2$ (**3**).

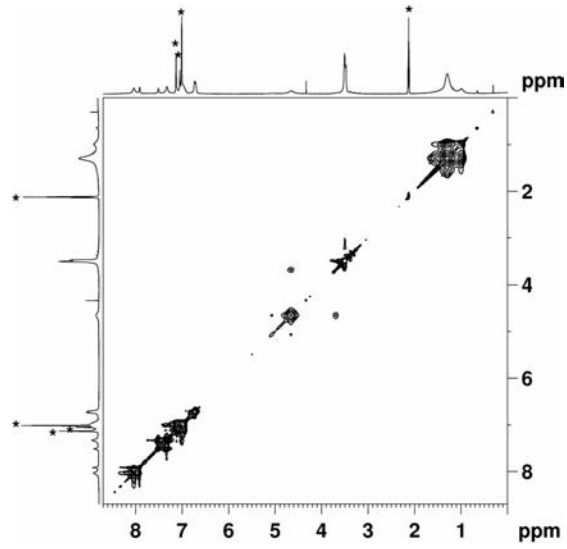

Figure 6. EXSY spectrum of **3** in $[D_8]$toluene at room temperature. Solvent signals are marked by asterisks.

Contrary to the reaction of $Ti(OiPr)_4$ with *m*-anisaldoxime, where only **3** was isolated, compounds with a higher degree of substitution were observed when *o*-anisaldoxime was employed in the same molar ratio (Ti/oxime = 1:2). Due to the low solubility of *o*-anisaldoxime in CH_2Cl_2 an alternative solvent was used, viz. 1,2-dichloroethane. This allowed higher reaction temperatures. $Ti_2(OiPr)_3(o\text{-anisaldoximate})_5$ (**4**, Figure 8) crystallized from a concentrated solution. The increased temperature can be taken into account for the higher degree of substitution.

Compound **4** is formally derived from disubstituted compounds **1**–**3** by replacing one of the bridging O*i*Pr ligands with an oximate ligand. Different to $Ti_6O_6(OiPr)_6(ON{=}CR_2)_6$ ($CR_2{=}CMe_2$ or C_5H_8),[6] for example, the two titanium atoms are not bridged by the NO group, but instead only by the oxygen atom of the oximate. Another noteworthy difference to the structures of **1**–**3** is that the mutual orientation of the side-on coordinated oximate ligands in the two halves of the compound are different. Whereas the angles around Ti1 are 169.2(1)° for O1–Ti1–N2 and 91.9(1)° for O2–Ti1–N1, corresponding to "isomer 2", Ti2 is coordinated as in the "isomer 1"-type compounds with a N4–Ti2–N5 angle of 164.0(1)°. The Ti–O distances in the Ti_2O_2 ring are again asymmetric, the longer distances being *trans* to the terminal O*i*Pr groups.

Complete substitution of the O*i*Pr ligands of $Ti(OiPr)_4$ against oximates was observed upon reaction with *o*- or *p*-anisaldoxime in dichloromethane. Because of its low solubility in CH_2Cl_2 compared to that of the *m*- and *p*-isomers, *o*-anisaldoxime was treated at elevated temperatures. For-

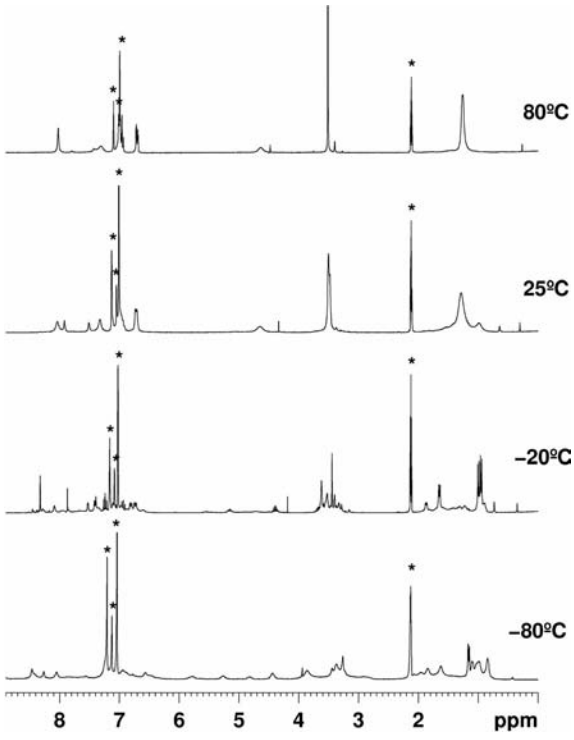

Figure 7. Temperature-dependent ^{1}H NMR spectra of **3** in [D_8]toluene from 80 °C (top) to –80 °C (bottom). Solvent signals are marked by asterisks.

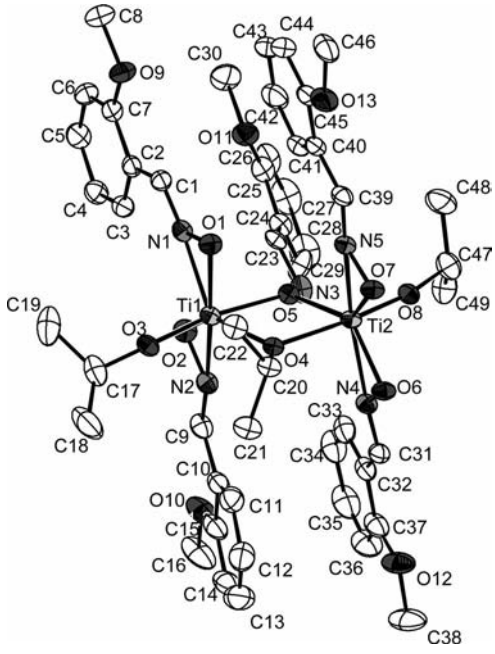

Figure 8. Molecular structure of $Ti_2(OiPr)_3$(*o*-anisaldoximate)$_5$ (**4**).

mation of Ti(*o*-anisaldoximate)$_4$ (**5**) was also observed in 1,2-dichloroethane solution, instead of **4**, when the reaction solution was not concentrated before crystallization. This shows that compound **4** is just an intermediate stage on the way to the fully substituted derivatives and can only be crystallized after minor modifications of the preparation protocol.

In tetrasubstituted derivatives Ti(*o*-anisaldoximate)$_4$ (**5**) and Ti(*p*-anisaldoximate)$_4$ (**6**), the titanium atoms are coordinated by four oximate ligands (Figure 9), with the Ti–O and Ti–N bond length in the same range as that in **1**–**4**. The oximate ligands are pairwise nearly coplanar with each other, as in the structures discussed before, with a N1–Ti1–O3 angle of 172.96(3)° (in **6**, similar values in **5**). The two planes containing two oximate ligands each are nearly perpendicular to each other. The core of the complexes resembles that of $Ti(ONMe_2)_4$ in contrast to S_4-symmetric $Ti(ONEt_2)_4$.[12,13]

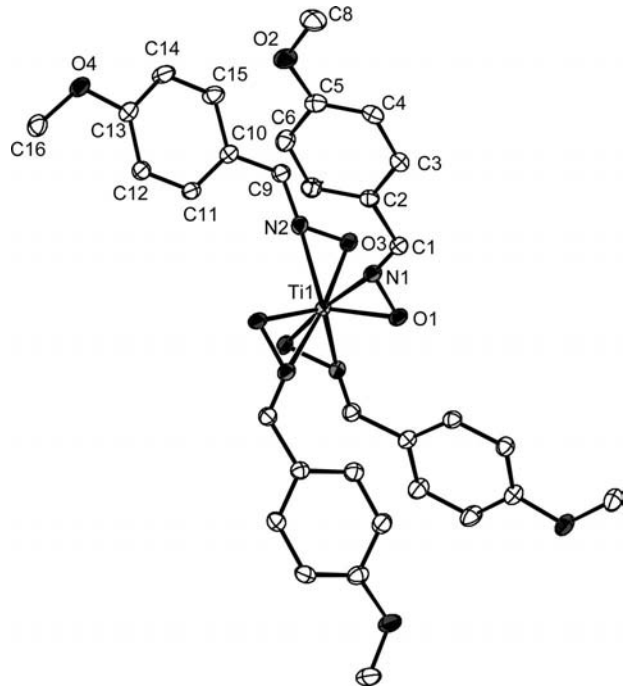

Figure 9. Molecular structure of Ti(*p*-anisaldoximate)$_4$ (**6**). The two molecules in the asymmetric unit of **5** have approximately the same geometry. Ti1–O1 195.98(8), Ti1–O3 197.95(8), Ti1–N1 208.34(10), Ti1–N2 205.61(10) pm; N1–Ti1–N1* 93.59(5), N2–Ti1–N2* 120.97(5), N1–Ti1–N2 89.13(4), N1–Ti1–N2* 133.60(4)°.

Because of the low solubility of the tetrasubstituted compound **6** in common solvents at room temperature, the compound was dissolved in [D_6]DMSO at elevated temperatures. Surprisingly, in the NMR spectra of the [D_6]DMSO solution (δ = 147.5 ppm for the carbon bearing the oximate group) signals corresponding to the deoximation product anisaldehyde and *p*-methoxybenzonitrile (Figure 10) were observed in addition to the expected signals of the coordinated oximate ligands; for example, ^{13}C NMR resonances at δ = 191.1 ppm for the carbonyl carbon of the aldehyde and δ = 102.7 ppm for the nitrile carbon. The ratio of oxime/aldehyde/nitrile was 2:1:1, as indicated by the corresponding intensities in the ^{1}H NMR spectrum. This ratio resembles almost exactly that reported for the photooxidative deoximation products when *p*-anisaldehyde oxime was irradiated in the presence of quinone sensitizers.[14]

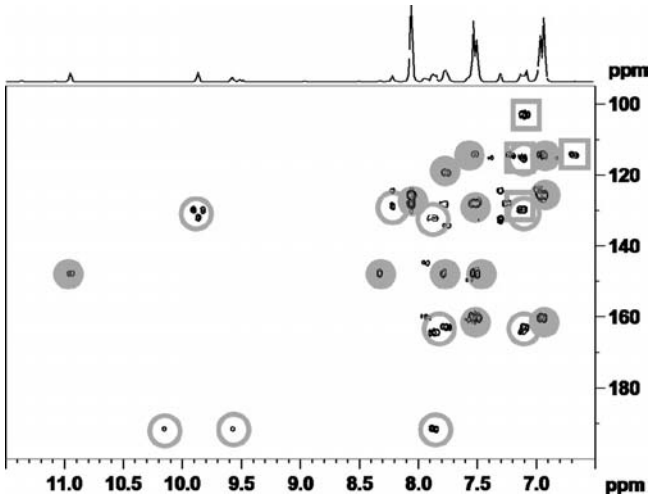

Figure 10. HMBC spectrum of the $[D]_6$DMSO solution of **6** heated to 100 °C. The signals referring to *p*-anisaldoxime are marked with full circles, those corresponding to the decomposition products are marked with open circles (*p*-anisaldehyde) and squares (4-methoxybenzonitrile).

One of the advantages of using oximes for the modification of metal alkoxides is that derivatives with functional groups are easily accessible. The latter are required for the preparation of inorganic–organic hybrid materials by sol–gel processing. As examples, Ti(O*i*Pr)$_4$ was treated with the oximes of two ligands bearing double bonds, viz. perillaldoxime and *trans*-cinnamaldoxime (Figure 2). Both [Ti(O*i*Pr)$_2$(perillaldoximate)$_2$]$_2$ (**7**) and [Ti(O*i*Pr)$_2$(*trans*-cinnamaldoximate)$_2$]$_2$ (**8**) were obtained as crystalline solids. The solid-state structures are of "isomer 2"-type for **7** and "isomer 1"-type for **8**.

Conclusions

The room-temperature reactions of Ti(O*i*Pr)$_4$ with different stereoisomers of benzaldoximes yielded dimeric complexes [Ti(O*i*Pr)$_2$(benzaldoximate)$_2$]$_2$. There is no apparent correlation between the formed isomer and the oxime. Solution NMR spectroscopy revealed ligand exchange, which can be explained by equilibration of the two isomeric forms.

Higher reaction temperatures led to the formation of more highly substituted titanium alkoxide derivatives, as investigated by using anisaldoximes for the modification. Products with substitution degrees ranging from 2 over 2.5 to 4 were obtained depending on the position of the methoxy group at the aromatic ring and on the applied temperature. Whereas solution NMR spectroscopy confirmed the results of X-ray structure analyses, deoximation products were also observed when the sparingly soluble Ti(*p*-anisaldoximate)$_4$ was heated in $[D_6]$DMSO.

Experimental Section

General Procedures: All operations were carried out under a moisture- and oxygen-free argon atmosphere by using Schlenk and glove box techniques. Ti(O*i*Pr)$_4$ (Acros, 98+%), (*Z*)-benzaldoxime (Aldrich, 97%), (*E*)-benzaldoxime (Aldrich, 97%), *o*-anisaldehyde (ABCR, 98%), *m*-anisaldehyde (Aldrich, 98%), *p*-anisaldehyde (Aldrich, 98%), *trans*-cinnamaldehyde (ABCR, 98%), and (*S*)-(–)-perillaldehyde (Aldrich, 92%) were used as received. All solvents were dried and purified by standard methods.[15] The solvents for NMR spectroscopy (Eurisotop) were degassed prior to use and stored over molecular sieves. ^{1}H and ^{13}C solution NMR spectra were recorded with 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}, 30.38 MHz {^{15}N}) 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), EXSY (exchange spectroscopy, t_{mix} = 1 s), HSQC (heteronuclear single quantum correlation), and HMBC (heteronuclear multiple-bond correlation). Solid-state ^{13}C and ^{15}N NMR spectra of **6** were recorded with a Bruker Avance 300 [75.40 MHz (^{13}C), 30.38 MHz (^{15}N), $\delta_N(NH_4Cl)$ = 0 ppm] equipped with a 4-mm broadband MAS probe head. ^{13}C NMR spectra were recorded with ramped CP/MAS spectra (cross-polarization and magic angle spinning) with a rotor spinning speed of 6–8 kHz. The numeric labels of the carbon atoms refer to the phenyl groups, where C^1 is the *ipso* carbon atom. Due to the tendency of the complexes to hydrolyze, reliable elemental analysis could not be obtained for **1**–**4**, **7**, and **8**.

Synthesis of the Anisaldoximes: Anisaldehyde oximes were synthesized as (*E*)-isomers from the corresponding aldehydes and hydroxylamine hydrochloride by modification of the procedure described by Bousquet.[16] In a typical synthesis, $NH_2OH{\cdot}HCl$ (7.14 g, 102.7 mmol) was dissolved in H_2O (12 mL) and cooled to 5 °C; *p*-anisaldehyde (10.0 mL, 82.2 mmol) was then added while stirring. A solution of Na_2CO_3 (5.44 g, 51.4 mmol) in deionized water (20 mL) was added dropwise while the reaction mixture was stirred in an ice/water mixture. After stirring overnight at room temperature, the product was extracted with several portions of $CHCl_3$. The combined $CHCl_3$ solutions were dried with Na_2SO_4. Evaporation of the solvent yielded *p*-anisaldoxime (11.2 g, 73.9 mmol, 90%).

[Ti(O*i*Pr)$_2${benzaldehyde-(*Z*)-oximate}$_2$]$_2$ (1): To a solution of benzaldehyde-(*Z*)-oxime (420 mg, 3.47 mmol) in CH_2Cl_2 (0.40 mL) at room temperature was dropwise added Ti(O*i*Pr)$_4$ (490 mg, 1.72 mmol). The reaction mixture was stirred for 10 min. Colorless crystals of **1** (535 mg, 81%) were obtained from the yellow solution after 2 h. They were recrystallized from CH_2Cl_2, washed with several portions of *n*-pentane at –20 °C, and dried in vacuo. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.18 [m, 6 H, CH(C*H*$_3$)$_2$], 3.96/4.51 (m, 1 H, C*H*Me$_2$), 7.28 (m, 3 H, C$^{3-5}$*H*), 7.54/7.70 (d, *J* = 6.7 Hz, 2 H, C^{2,6}*H*), 8.24 (s, 1 H, C*H*N) ppm. ^{13}C NMR (250 MHz, $CDCl_3$): δ = 26.1 [CH(*C*H$_3$)$_2$], 77.2 (*C*HMe$_2$), 127.1 (*C*^{2,6}), 128.8 (*C*^{3,5}), 129.8 (*C*^{4}), 132.0 (*C*^{1}), 141.4 (*C*=N) ppm.

[Ti(O*i*Pr)$_2${benzaldehyde-(*E*)-oximate}$_2$]$_2$ (2): To a solution of benzaldehyde-(*E*)-oxime (870 mg, 7.18 mmol) in CH_2Cl_2 (1.10 mL) at room temperature was dropwise added Ti(O*i*Pr)$_4$ (1.02 g 3.58 mmol). The reaction mixture was stirred for 1 min. Colorless crystals of **2** (1.39 g, 95%) were obtained from the yellow solution after 1 d. They were washed with several portions of *n*-pentane at –20 °C and dried in vacuo. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.14 [m, 6 H, CH(C*H*$_3$)$_2$], 3.97/4.49 [m, 1 H, C*H*(CH$_3$)$_2$], 7.26 (m, 3 H, C$^{3-5}$*H*), 7.53/7.69 (d, *J* = 6.7 Hz, 2 H, C^{2,6}*H*), 8.21 (s, 1 H, C*H*N) ppm. ^{13}C NMR (250 MHz, $CDCl_3$): δ = 25.8 [CH(*C*H$_3$)$_2$], 77.2 (*C*HMe$_2$), 127.1 (*C*^{2,6}), 128.8 (*C*^{3,5}), 129.8 (*C*^{4}), 132.0 (*C*^{1}), 141.4 (*C*=N) ppm.

[Ti(O*i*Pr)$_2$(*m*-anisaldoximate)$_2$]$_2$ (3): To solution of *m*-anisaldoxime (664 mg, 4.39 mmol) in CH_2Cl_2 (0.70 mL) at room temperature was dropwise added Ti(O*i*Pr)$_4$ (624 mg, 2.19 mmol). The reaction mixture was stirred for 1 min. Colorless crystals of **3** (866 mg, 83%) were obtained from the yellow solution after 3 d. They were washed with several portions of *n*-pentane at –20 °C and dried in vacuo. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.18 [d, J = 5.8 Hz, 6 H, CH(CH_3)$_2$], 3.74 (s, 3 H, OCH_3), 3.71/4.49 [m, 1 H, CH(CH$_3$)$_2$], 6.82 (d, J = 8.0 Hz, 1 H, C^4H), 7.07 (t, J = 7.9 Hz, 1 H, C^2H), 7.19 (m, 2 H, C$^{5,6}H$), 8.19 (s, 1 H, CHN) ppm. ^{13}C NMR (250 MHz, $CDCl_3$): δ = 26.0 [CH(CH_3)$_2$], 55.3 (OCH$_3$), 77.2 (CHMe$_2$), 111.0 (C^2), 116.5 (C^4), 120.1 (C^6), 129.7 (C^5), 133.4 (C^1), 141.5 (C=N), 159.9 (C^3) ppm.

Ti$_2$(O*i*Pr)$_3$(*o*-anisaldoximate)$_5$ (4): To solution of *o*-anisaldehyde oxime (736 mg, 4.87 mmol) in 1,2-dichloroethane (4.0 mL) at room temperature was dropwise added Ti(O*i*Pr)$_4$ (0.691 g, 2.43 mmol). The reaction mixture was heated at reflux for 5 min and then reduced to half of its volume in vacuo. Colorless crystals of **4** (1.25 g, 64%) were obtained from the yellow solution after 1 d at 30 °C. They were washed with several portions of *n*-pentane at –20 °C and dried in vacuo. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.14 [d, J = 6.2 Hz, 18 H, CH(CH_3)$_2$], 3.79 (s, 15 H, OCH_3), 3.66/3.96 [m, 3 H, CH(CH$_3$)$_2$], 6.88 (q, J = 7.7 Hz, 5 H, C^5H), 7.27 (d, J = 8.2 Hz, 5 H, C^3H), 7.51 (m, 5 H, C^4H), 7.64 (d, J = 7.6 Hz, 5 H, C^6H), 8.43/8.63 (s, 5 H, CHN) ppm. ^{13}C NMR (250 MHz, $CDCl_3$): δ = 25.3 [CH(CH$_3$)$_2$], 55.5 (OCH$_3$), 77.2 (CHMe$_2$), 111.1 (C^3), 120.6 (C^1), 120.8 (C^5), 126.8 (C^6), 131.2 (C^4), 146.7 (C=N), 159.9 (C^2) ppm.

Ti(*o*-anisaldoximate)$_4$ (5)

Method A: To solution of *o*-anisaldehyde oxime (748 mg, 4.95 mmol) in CH_2Cl_2 (2.0 mL) at room temperature was dropwise added Ti(O*i*Pr)$_4$ (701 mg, 2.47 mmol). A whitish solid precipitated from the yellow solution after 1 min of stirring at room temperature. Recrystallization from hot CH_2Cl_2 gave colorless crystals of **5** (482 mg, 30%) after 1 d. They were washed with several portions of *n*-pentane at –20 °C and dried in vacuo.

Method B: To solution of *o*-anisaldehyde oxime (1.65 g, 10.9 mmol) in 1,2-dichloroethane (9.0 mL) at room temperature was dropwise added Ti(O*i*Pr)$_4$ (1.54 g 5.40 mmol). The reaction mixture was heated at reflux for 5 min. Colorless crystals of **5** (1.21 g, 35%) were obtained from the yellow solution upon slow cooling to room temperature after 5 h. They were washed with several portions of *n*-pentane at –20 °C and dried in vacuo. $C_{32}H_{32}N_4O_8Ti$ (648.52): calcd. C 59.27, H 4.97, N 8.64; found C 57.70, H 4.90, N 8.25. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.70 (s, 3 H, OCH_3), 6.66 (t, J = 7.1 Hz, 1 H, C^5H), 6.78 (d, J = 7.6 Hz, 1 H, C^3H), 7.18 (m, 1 H, C^4H), 8.09 (d, J = 6.2 Hz, 1 H, C^6H), 8.62 (s, 1 H, CHN) ppm. ^{13}C NMR (250 MHz, $CDCl_3$): δ = 55.6 (OCH$_3$), 111.1 (C^3), 120.7 (C^1), 121.0 (C^5), 127.1 (C^6), 131.1 (C^4), 137.0 (C=N), 157.2 (C^2) ppm.

Ti(*p*-anisaldoximate)$_4$ (6): To solution of *p*-anisaldehyde oxime (532 mg, 3.52 mmol) in dichloromethane (2.00 mL) at room temperature was dropwise added Ti(O*i*Pr)$_4$ (499 mg 1.76 mmol). The reaction mixture was stirred for 1 min. Yellow crystals of **6** (34 mg, 5.4%) were obtained from the yellow solution after 1 h. They were washed with several portions of *n*-pentane at –20 °C and dried in vacuo. $C_{32}H_{32}N_4O_8Ti$ (648.52): calcd. C 59.27, H 4.97, N 8.64; found C 58.55, H 4.75, N 8.50. ^{13}C NMR (^{13}C CP/MAS, 75.40 MHz): δ = 153.1 (C^4), 130.2 (C=N), 116.5 (C^1), 109.1 ($C^{2,6}$), 102.3 ($C^{3,5}$), 46.3/47.9 (OCH$_3$) ppm. ^{15}N NMR (^{15}N MAS, 30.39 MHz): δ = 291.5, 286.9 (C=N) ppm. An amount of **6** (24 mg) was dissolved in [D]$_6$DMSO (0.60 mL) in a Young tube. The mixture was heated to 100 °C for 3 d. A yellow solution and a whitish precipitate were obtained. NMR spectra of the solution were recorded (*ox*, *ald*, and *nitr* refer to anisaldoxime, anisaldehyde, and 4-methoxybenzonitrile, respectively). ^{1}H NMR (250 MHz, [D]$_6$-DMSO): δ = 11.37 (s, 2 H, NOH), 11.08 (s, 1 H, CHO), 10.95 (s, 2 H, CHN), 7.87 (d, J = 8.9 Hz, 2 H, C$_{ald}^{2,6}H$), 7.77 (d, J = 8.7 Hz, 2 H, C$_{nitr}^{2,6}H$), 7.52 (d, J = 8.7 Hz, 4 H, C$_{ox}^{2,6}H$), 7.12 (d, J = 8.9 Hz, 2 H, C$_{ald}^{2,6}H$), 7.10 (d, J = 8.9 Hz, 2 H, C$_{nitr}^{3,5}H$), 6.96 (d, J = 8.7 Hz, 4 H, C$_{ox}^{3,5}H$), 3.86 (s, 3 H, C$_{ald}H_3$), 3.84 (s, 3 H, C$_{nitr}H_3$), 3.77 (s, 6 H, C$_{ox}H_3$) ppm. ^{13}C NMR (75.40 MHz, [D]$_6$-DMSO): δ = 191.1 (C_{ald}=O), 164.5 (C_{ald}^4), 164.5 (C_{nitr}^4), 160.4 (C_{ox}^4), 147.9 (C_{ox}=N), 134.6 ($C_{nitr}^{2,6}$), 132.2 ($C_{ald}^{2,6}$), 129.8 (C_{nitr}^1), 128.3 ($C_{ox}^{2,6}$), 125.8 (C_{ox}^1), 124.6 (C_{ald}^1), 115.3 ($C_{ald}^{3,5}$), 115.2 ($C_{nitr}^{3,5}$), 114.3 ($C_{ox}^{3,5}$), 102.7 (C_{nitr}≡N), 56.1 (OC_{ald}H$_3$), 56.1 (OC_{nitr}H$_3$), 55.6 (OC_{ox}H$_3$) ppm.

[Ti(O*i*Pr)$_2$(perillaldoximate)$_2$]$_2$ (7): To a solution of perillaldehyde oxime (429 mg, 2.60 mmol) in dichloromethane (0.42 mL) at room temperature was dropwise added titanium isopropoxide (365 mg, 1.28 mmol). The dark yellow reaction mixture was stirred for 5 min. Colorless crystals of **7** (178 mg, 30%) were obtained from the yellow solution after 10 d. The crystals were washed with several portions of *n*-pentane at –20 °C and dried in vacuo. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.84 (s, 1 H, CHN), 6.02 (s, 1 H, C^2H), 4.68 (s, 2 H, CMeCH_2), 4.49 (m, 1 H, CHMe$_2$), 2.63–2.09 (m, 5 H, C$^{3,5,6}H$), 1.82 (d, J = 6.0 Hz, 1 H, C^4H), 1.68 [s, 1 H, C(CH_3)CH$_2$], 1.42 (m, 1 H, C^5H), 1.18 [d, J = 5.4 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (^{13}C CP/MAS, 75.40 MHz): δ = 149.0 (C=N), 143.8 (C^6), 134.8 (CMeCH$_2$), 133.0 (C^1), 109.1 (CMeCH$_2$), 77.2 (CHMe$_2$), 40.8 (C^4), 31.4 (C^5), 26.9 (C^3), 26.8 [CH(CH$_3$)$_2$], 23.9 (C^2), 20.7 [C(CH$_3$)CH$_2$] ppm.

[Ti(O*i*Pr)$_2$(*trans*-cinnamaldoximate)$_2$]$_2$ (8): To a mixture of cinnamaldehyde oxime (231 mg, 1.57 mmol) in toluene (20 mL) at room temperature was dropwise added Ti(O*i*Pr)$_4$ (221 mg, 777 µmol), resulting in complete dissolution of the oxime and yellow discoloration. The reaction mixture was stirred for 5 min. The yellow solid foam obtained after removal of the solvent was recrystallized from CH_2Cl_2. Colorless crystals of **8** (122 mg, 34%) were obtained from the yellow solution after 12 d. The crystals were washed with several portions of *n*-pentane at –20 °C and dried in vacuo. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.95 (s, 1 H, CHN), 7.31–7.54 (m, 5 H, C^{2-6}H), 7.26 (s, 1 H, CH–CH–CH=N), 6.86 (s, 1 H, CH–CH–CH=N), 4.49/3.96 [q, J = 5.4 Hz, 1 H, CH(CH$_3$)$_2$], 1.14 [m, 6 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (^{13}C CP/MAS, 75.40 MHz): δ = 150.8 (CH–CH-CH=N), 142.9 (C=N), 132.0 (C^1), 130.9 (CH-CH=N), 128.9 ($C^{3,5}$), 128.8 (C^4), 128.7 ($C^{2,6}$), 77.2 [CH(CH$_3$)$_2$], 25.4 [CH(CH$_3$)$_2$] ppm.

X-ray Structure Analyses: Single-crystal X-ray diffraction measurements were performed with a Bruker AXS SMART and a Bruker-AXS KAPPA APEX II diffractometer with CCD area detectors and a crystal-to-detector distance of 5.5 cm by using graphite-monochromated Mo-K_α radiation (λ = 71.073 pm; Table 2). The data collection at 100 K in a stream of cold nitrogen covered at least a hemisphere of the reciprocal space by recording three or more sets of exposures, each of them exhibiting a different Φ angle. The times for each exposure were 5 to 20 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 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 **1** the whole molecule is disor-

Table 2. Crystallographic and structural parameters of **1**–**8**.

	1	**2**	**3**	**4**·2$C_2H_4Cl_2$
Empirical formula	$C_{40}H_{52}N_4O_8Ti_2$	$C_{40}H_{52}N_4O_8Ti_2$	$C_{44}H_{60}N_4O_{12}Ti_2$	$C_{53}H_{69}Cl_4N_5O_{13}Ti_2$
Formula weight	812.66	812.66	932.76	1221.73
Crystal system	orthorhombic	monoclinic	triclinic	triclinic
Space group	*P*bca	*C*2/*c*	$P\bar{1}$	$P\bar{1}$
a [pm]	1062.88(4)	2776.3(3)	999.78(12)	1366.5(3)
b [pm]	1851.29(7)	961.90(11)	1129.38(14)	1409.8(3)
c [pm]	2138.50(10)	2002.1(4)	1217.86(15)	1608.9(3)
α [°]			75.046(2)	78.646(3)
β [°]		130.692(1)	68.727(2)	89.398(3)
γ [°]			66.048(2)	76.148(3)
Volume [$\times 10^6$ pm^3]	4207.9(3)	4054.1(11)	1161.1(2)	2948.3(11)
Z	4	4	1	2
Calcd. density [g cm^{-3}]	1.283	1.331	1.334	1.376
μ [mm^{-1}]	0.433	0.449	0.408	0.516
Crystal size [mm]	0.30 × 0.30 × 0.25	0.57 × 0.43 × 0.34	0.57 × 0.43 × 0.34	0.42 × 0.32 × 0.17
Θ range [°]	2.40–28.29	2.33–28.34	2.86–24.99	2.14–25.00
Reflections coll./unique	30122/5219	25893/5043	6099/3967	15875/10296
Data/parameters	5219/488	5043/248	3967/286	10296/819
GOF on F^2	0.990	1.091	1.107	1.104
R [$I > 2\sigma(I)$]	0.071	0.039	0.040	0.064
wR_2	0.184	0.108	0.107	0.191
Largest diff. peak/hole [e Å^{-3}]	0.431/–0.295	0.621/–0.384	0.684/–0.330	1.036/–1.681
	5	**6**	**7**	**8**
Empirical formula	$C_{32}H_{32}N_4O_8Ti$	$C_{32}H_{32}N_4O_8Ti$	$C_{52}H_{80}N_4O_8Ti_2$	$C_{48}H_{60}N_4O_8Ti_2$
Formula weight	648.52	648.52	985.00	916.80
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	*C*2/*c*	$P\bar{1}$	*C*2/*c*
a [pm]	1500.3(3)	2162.48(14)	1028.2(3)	3641.1(3)
b [pm]	1602.0(3)	743.30(5)	1049.2(4)	1394.49(11)
c [pm]	1621.7(3)	1950.20(13)	1296.7(4)	1903.60(13)
α [°]	107.159(3)		85.293(5)	
β [°]	102.799(3)	97.912(1)	73.388(5)	99.326(2)
γ [°]	115.148(3)		89.671(5)	
Volume [$\times 10^6$ pm^3]	3088.2(11)	3104.9(4)	1335.7(8)	9537.7(12)
Z	4	4	1	8
Calcd. density [g cm^{-3}]	1.395	1.387	1.225	1.277
μ [mm^{-1}]	0.335	0.333	0.352	0.390
Crystal size [mm]	0.25 × 0.20 × 0.12	0.40 × 0.40 × 0.20	0.22 × 0.20 × 0.10	0.56 × 0.21 × 0.19
Θ range [°]	1.59–25.00	2.64–28.29	2.65–24.49	2.17–24.97
Reflections coll./unique	31593/10827	14737/3844	7233/4281	18660/6552
Data/parameters	10827/819	3844/206	4281/342	6552/567
GOF on F^2	1.068	1.031	1.065	1.010
R [$I > 2\sigma(I)$]	0.060	0.033	0.083	0.053
wR_2	0.171	0.089	0.216	0.120
Largest diff. peak/hole [e Å^{-3}]	0.823/–0.587	0.446/–0.321	0.893/–0.449	0.632/–0.393

dered, and in **4** the bridging oximate group and a dichloroethane solvent molecule are disordered.

CCDC-789194 (for **1**), -789195 (for **2**), -789196 (for **3**), -789197 (for **4**), -789198 (for **5**), -789199 (for **6**), -789200 (for **7**), and -789201 (for **8**) 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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