

# Sterically Shielded Titanocene Enolates – Synthesis, Structure and Their Exceptional Stability towards Hydrolysis

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The reaction of various sterically congested sodium enolates, generated by quantitative deprotonation of stable enols (of diphenylacetaldehyde in the case of **5**), with dichlorotitanocene afforded a series of novel titanium enolates **1–5**. The crystal structure of **1** could be determined. Due to the considerable steric shielding of the  $\beta,\beta$ -diaryl moiety, all the titanium enolates exhibit an outstanding stability towards hydrolysis, which increases with the higher steric demand of the

substituents at the C–C double bond. The kinetics of the hydrolysis, which is pseudo-first-order in THF/water (1 : 1) and acetonitrile/water (1 : 1), was investigated by UV spectroscopy. The pseudo-first-order rate constants measured in these solvent mixtures are in the range  $6.4 \cdot 10^{-4} \text{ s}^{-1} < k_1 < 1.1 \cdot 10^{-3} \text{ s}^{-1}$ . For comparison, the hydrolysis of **6**, which should exhibit the usual sensitivity of titanium enolates towards hydrolysis, is about 1000 times faster.

Metal enolates constitute a most valuable class of organometallic compounds in modern organic synthesis because of their extensive use in synthetically useful C–C bond forming reactions. In the early 1980's titanium enolates were introduced to organic synthesis<sup>[1]</sup>. Since then the importance of these versatile nucleophiles<sup>[2]</sup> has steadily increased, in particular because of their usefulness in stereoselective aldol condensations<sup>[3]</sup> and Michael reactions<sup>[4]</sup>. The main advantages of titanium enolates over simple lithium enolates are the enhanced stereochemical control in C–C bond forming reactions and the possibility of incorporating chiral ligands at the titanium metal center, a strategy which has led to enantioselective aldol reactions with excellent *e.e.* values<sup>[5]</sup>. In addition, titanium enolates have been used in oxidation reactions with remarkable diastereoselectivities<sup>[6]</sup>.

Surprisingly, the knowledge about structural and spectroscopic data of titanium enolates is rather limited, in spite of their importance in organic synthesis. This is understandable due to the fact that these reactive compounds are generally very sensitive towards hydrolysis. As a consequence they are generated in situ and converted without isolation in synthetic applications. The isolation of these compounds as well as their spectroscopic and structural characterization has been reported only in a few cases<sup>[7]</sup>.

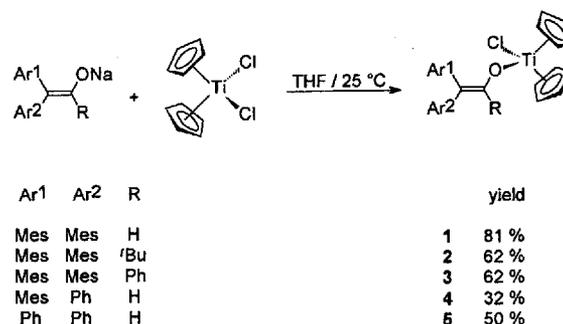
## Results and Discussion

In order to gain more information about the structure, spectroscopic data and chemical properties of titanium enolates, it was our intention to prepare a series of stable titanium enolates with exceptional stability towards hydrolysis. We reasoned that titanium enolates derived from stable

$\beta,\beta$ -diarylenols (with the exception of titanium enolate **5**, which is derived from diphenylacetaldehyde) should exhibit an increased stability due to the electronic stabilization and steric shielding by the two aryl units in the  $\beta$ -position, as compared to those generated from simple carbonyl compounds.

The high acidity of these enols led to quantitative deprotonation with sodium hydride within one hour in THF at room temperature. The corresponding enolates were reacted with equimolar amounts of dichlorotitanocene also at room temperature, affording the desired titanium enolates. After removal of sodium chloride by filtration they could be isolated as dark red-brown solids after precipitation through addition of a nonpolar solvent. Crystals of **1** suitable for X-ray structure analysis were obtained after crystallization from boiling *n*-hexane.

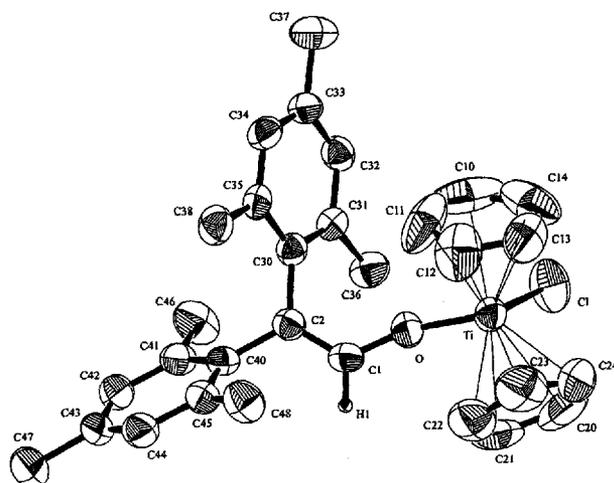
Scheme 1. Synthesis of the titanium enolates **1–5**



The <sup>1</sup>H-NMR spectra of all  $\beta,\beta$ -dimesityl titanium enolates show coalescence phenomena for the mesityl methyl

groups as well as for the mesityl protons, indicating that the rotational motion of the two bulky mesityl rings is restricted. This effect has been previously observed in the corresponding enols<sup>[8]</sup> and their derivatives<sup>[9]</sup>. As anticipated, our X-ray analysis leads to a structure that indicates that the mesityl rings of **1** are not coplanar with the central C–C double bond, but form dihedral angles of 57.7(3)° and 59.8(4)°, resulting in an almost perpendicular [83.1(2)°] arrangement of the two mesityl groups. The dihedral angles are slightly larger than those in 2,2-dimesitylethenol, which indicates that the titanocene unit has almost no effect on the position of the two mesityl rings. The bond lengths C1–C2 [1.336(5) Å] and C1–O [1.328(5) Å] are typical for the enolato moiety. A similar C1–C2 bond distance can be found in the corresponding dimesitylethenol [1.33(1) Å]<sup>[10]</sup> as well as in a corresponding enol ester<sup>[11]</sup> [1.339(9) Å]. The geometry about the titanocene unit is undisturbed, with even the O–Ti–Cl angle [96.5(1)°] being within the usual range observed for TiCp<sub>2</sub>X<sub>2</sub> structures<sup>[7a]</sup>. Thus, the high steric congestion about the enolato moiety does not convey a compression and deformation of the TiCp<sub>2</sub>Cl subunit. The large Ti–O–C1 angle in combination with the Ti–O bond length suggests a comparatively high Ti–O multiple bond order<sup>[7a]</sup>. The subject of oxygen to metal  $\pi$ -bonding has been discussed in detail by Caulton<sup>[12]</sup>, who also finds large Ti–O–C angles in cyclopentadienyltitanium alkoxides. The dihedral angle Ti–O–C1–C2 [129.9(5)°] attests a rather poor interaction between the p-orbitals of the oxygen and the  $\pi$ -orbitals of the C–C double bond. For comparison, in the corresponding enol both the C–C double bond and the OH-unit lie in one plane thus maximizing  $\pi$ -orbital overlap<sup>[10]</sup>.

Figure 1. ORTEP view of titanium enolate **1** (50% probability ellipsoids)



The novel titanium enolates **1–5** distinguish themselves by an outstanding stability towards hydrolysis, which surpassed our expectations. While titanium enolates derived from simple carbonyl compounds can be handled only under rigorous exclusion of water, **1** could be exposed to atmospheric water and oxygen over a period of at least three months without any significant decomposition. Even the

Table 1. Selected bond distances and angles for titanium enolate **1**

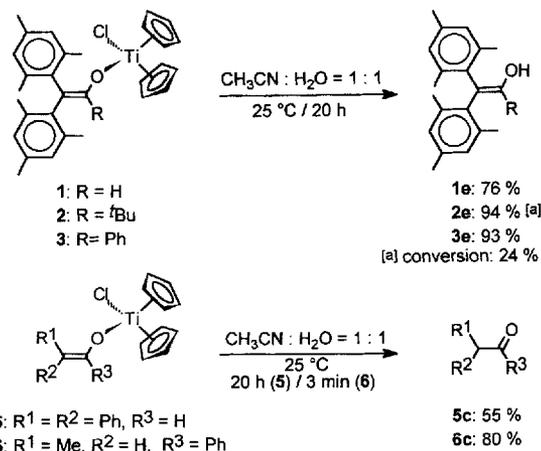
Atoms	Bond Distance [Å]	Atoms	Angle [deg]
Ti–O	1.852(4)	C2–C1–O	124.9(4)
C1–O	1.328(5)	Ti–O–C1	153.1(3)
C1–C2	1.336(5)	O–Ti–Cl	96.5(1)
Ti–Cl	2.385(3)	Cp1–Ti–Cp2	130.0(1)
C2–C30	1.494(5)	Cp1–Ti–O	105.8(1)
C2–C40	1.491(5)	Cp2–Ti–O	107.6(1)
Ti–Cp1 <sup>[a]</sup>	2.069(1)	Cp1–Ti–Cl	104.5(1)
Ti–Cp2 <sup>[b]</sup>	2.070(1)	Cp2–Ti–Cl	107.5(1)
		C30–C2–C1	119.9(4)
		C40–C2–C1	119.6(3)
		C30–C2–C40	120.5(3)

[a] Cp1: C10–C11–C12–C13–C14. – [b] Cp2: C20–C21–C22–C23–C24.

sterically less shielded compounds **4** and **5** could be handled under atmospheric conditions. For example, this enormous insensitivity allows purification of **2** by column chromatography on silica gel under usual conditions (no anhydrous solvents and nitrogen atmosphere are necessary), whereas conventional titanium enolates will decompose during this operation.

In the following we take a closer look at this outstanding resistance towards hydrolysis and investigate the kinetics of hydrolysis of various titanium enolates in the presence of rather high concentrations of water, as our experience suggested that comparatively drastic conditions would be necessary to speed up the hydrolysis. For comparison, we also examine this reaction with the titanium enolate **6** derived from propiophenone<sup>[6a]</sup> as an example of a sterically unshielded system with the usual sensitivity towards moisture.

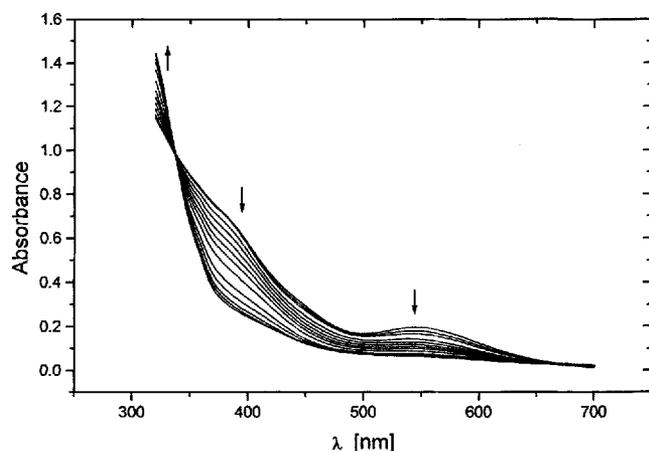
Scheme 2. Preparative scale hydrolysis of titanium enolates



At first, we carried out preparative scale hydrolyses with all the titanium enolates except **4** (insufficient substrate was available) in an acetonitrile/water (1:1) mixture in order to identify the products. The hydrolysis to the corresponding enols (diphenylacetaldehyde in the case of **5** and propiophenone in the case of **6**) was quantitative after 20 h at room temperature, except in the case of **2**, conversion of

which was only 24% complete because of limited solubility. The yields of the isolated enols and carbonyl compounds are given in Scheme 2. The final titanium product of this hydrolysis reaction has yet to be firmly identified, however we suppose that in a first step the corresponding hydroxytitanocene is formed, which undergoes further follow-up reactions such as condensation to  $\mu$ -O-bridged titanium complexes<sup>[13]</sup> or polymerization to biscyclopentadienyl titanoxane polymers<sup>[14]</sup>. These compounds can split off cyclopentadienyl rings under aqueous conditions, finally forming titanium dioxide. In all preparative scale hydrolyses we found solid precipitates containing unidentified titanium compounds. The IR spectra of these solids showed no significant C–H valences, and therefore we believe that titanium dioxide is formed under our conditions.

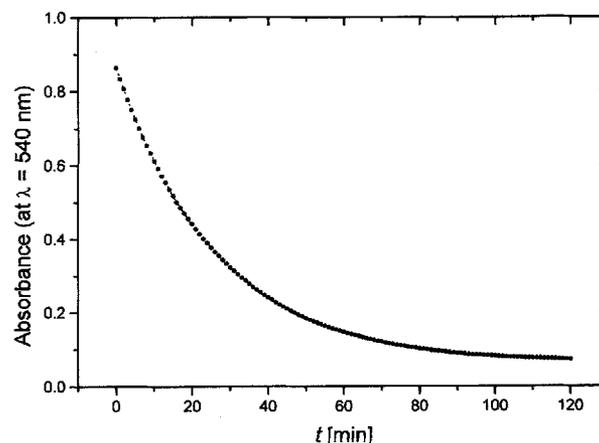
Figure 2. UV spectra of **3** in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1) at different times



UV spectroscopy was selected as the most convenient method to follow the kinetics of the hydrolysis. We recorded the UV spectrum of **3** in acetonitrile and found two maxima at 217 nm and 252 nm, a shoulder at around 390 nm and a weak, broad maximum at around 540 nm. UV spectra of **3** recorded at intervals in an acetonitrile/water (1:1) mixture exhibited an isosbestic point at 337 nm, indicative of a clean conversion of the titanium enolate into a follow-up product. In order to measure the kinetics of this reaction we followed the decrease of the absorption at  $\lambda = 540$  nm at 32 °C. The evaluation of the kinetics from the exponential decay provided a pseudo-first-order rate constant of  $k_1 = 6.4 \cdot 10^{-4} \text{ s}^{-1}$  ( $t_{1/2} = 18$  min) and a second-order rate constant  $k_2 = 2.3 \cdot 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ . Kinetic NMR studies, although in a mixture of THF/water (1:1), confirmed this result.

The kinetics of the hydrolysis could also be measured for titanium enolates **1** and **5** by UV spectroscopy in THF/water (1:1). The pseudo-first-order rate constant for compound **5** was determined as  $k_1 = 1.2 \cdot 10^{-3} \text{ s}^{-1}$  ( $t_{1/2} = 10$  min), furnishing a second-order rate constant  $k_2 = 4.3 \cdot 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ . For titanium enolate **1**, the rate constants  $k_1 = 7.2 \cdot 10^{-4} \text{ s}^{-1}$  ( $t_{1/2} = 16$  min) and  $k_2 = 2.6 \cdot 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  were obtained. Obviously, there is a rough relationship between the steric congestion of these titanium enolates and the kinetics of their hydrolysis, with  $k_2$  (**5**) >  $k_2$  (**1**). For comparison we followed the hydrolysis of **6** by <sup>1</sup>H-NMR

Figure 3. UV investigation of the hydrolysis of **3** in CH<sub>3</sub>CN/H<sub>2</sub>O (1:1) at 32 °C



spectroscopy in [D<sub>8</sub>]THF/D<sub>2</sub>O (25:1) at 22 °C. Because of the very fast reaction, only an estimate of the second-order rate constant could be made ( $k_2 = 1 \cdot 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ ). With a correction for the different temperatures used, this result indicates that the hydrolysis of **6** is faster than that of the sterically shielded titanium enolate **3** roughly by a factor of  $10^3$ .

In conclusion, we have synthesized the novel, sterically shielded titanium enolates **1–5**, which exhibit an unprecedented resistance towards hydrolysis. Importantly, the one-electron oxidation of such stable titanium enolates led to the first characterization of their radical cations in solution<sup>[15]</sup>, the details and reactions of which will be reported in due course.

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## Experimental Section

<sup>1</sup>H and <sup>13</sup>C NMR: Bruker AM 200 (200 MHz) and AM 250 (250 MHz); chemical shifts refer to tetramethylsilane; owing to the nature of the  $\beta,\beta$ -dimesityl moiety, signals in the <sup>13</sup>C-NMR spectra are often superimposed. – IR: Perkin-Elmer FT-IR 1605. – Mass spectra: Finnigan MAT90; electron ionization (EI) at 70 eV. – Microanalyses: Carlo Erba Elemental Analyzer 1106. – Melting points were determined by using a differential scanning calorimeter Dupont 910. – UV: Hitachi U-3200 Spectrophotometer. – All solvents were purified by standard literature methods and distilled directly from their drying agents under nitrogen: THF/potassium, diethyl ether/sodium, *n*-pentane/potassium, *n*-hexane/potassium, dichloromethane/P<sub>4</sub>O<sub>10</sub>. – Dichlorotitanocene<sup>[16]</sup>, 2,2-dimesityl-etheno<sup>[17]</sup>, *Z*-2-mesityl-2-phenyletheno<sup>[18]</sup>, 2,2-dimesityl-1-phenyletheno<sup>[19]</sup>, 1,1-dimesityl-3,3-dimethylbuten-2-ol<sup>[20]</sup> and chloro-dihydro-cyclopentadienyl-[(1-phenyl-1-propenyl)oxy]titanium<sup>[6a]</sup> (**6**) were prepared according to literature procedures. – All reactions were carried out under an atmosphere of dry argon by using standard Schlenk techniques.

*Chloro-dihydro-cyclopentadienyl*[2,2-dimesitylethenoxy]titanium (**1**): To a suspension of sodium hydride (237 mg, 9.88 mmol) in 30 ml of THF, solid 2,2-dimesitylethanol (561 mg, 2.00 mmol) was added

in small portions at room temperature. The mixture was stirred for 1 h and the surplus sodium hydride was removed by filtration. The filtrate was added slowly to a solution of dichlorotitanocene (498 mg, 2.00 mmol) in 50 ml of THF at room temperature. After stirring the dark-red mixture for 12 h the solvent was removed in vacuo. The residue was stirred with 100 ml of *n*-hexane for 1 h and after filtration the solvent was removed from the filtrate in vacuo. The yield was 795 mg (81%) of dark-red **1**. – M.p. 172°C. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 1.77 (br. s, 3H, *p*-Mes-CH<sub>3</sub>), 2.03 (s, 6H, *o*-Mes-CH<sub>3</sub>), 2.24 (s, 6H, *o*-Mes-CH<sub>3</sub>), 2.63 (br. s, 3H, *p*-Mes-CH<sub>3</sub>), 6.21 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 6.80 (br. s, 4H, Mes-H), 7.34 (s, 1H, C=CH). – <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>): δ = 20.5 (Mes-CH<sub>3</sub>), 20.7 (Mes-CH<sub>3</sub>), 20.9 (Mes-CH<sub>3</sub>), 21.1 (Mes-CH<sub>3</sub>), 112.9 (C2), 117.2 (C<sub>5</sub>H<sub>5</sub>), 128.5 (Mes), 129.6 (Mes), 134.8 (Mes), 135.2 (Mes), 135.4 (Mes), 135.5 (Mes), 137.6 (Mes), 161.0 (C1). – IR (KBr):  $\tilde{\nu}$  = 3096 cm<sup>-1</sup>, 2916, 2861, 1608, 1557, 1444, 1373, 1220, 1173, 1091, 1019, 904, 850, 814, 634, 495. – C<sub>30</sub>H<sub>33</sub>ClOTi (492.9): calcd. C 73.10, H 6.75; found C 73.39, H 7.03.

*Chlorodi-η<sup>5</sup>-cyclopentadienyl[1,1-dimesityl-3,3-dimethyl-1-buten-2-oxyl]titanium (2)*: To a suspension of sodium hydride (734 mg, 30.6 mmol) in 30 ml of THF, solid 1,1-dimesityl-3,3-dimethyl-1-buten-2-ol (678 mg, 2.01 mmol) was added in small portions at room temperature. The mixture was stirred for 1 h and the excess NaH was filtered off. The filtrate was added slowly to a solution of dichlorotitanocene (499 mg, 2.00 mmol) in 50 ml of THF and stirred for 12 h. The solvent was then removed in vacuo and the residue extracted with 100 ml of diethyl ether. The residue was filtered off and extracted again with 20 ml of dichloromethane. The extracts were combined and concentrated to about 10 ml. After addition of *n*-hexane (90 ml) a yellow, unidentified precipitate formed, which was removed by filtration. After storing the filtrate at -40°C, 685 mg (62%) of **2** was obtained as black crystals. – M.p. 185°C (decomp.). – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 1.04 (s, 9H, *t*Bu-CH<sub>3</sub>), 2.0–2.4 (coalescence, 12H, *o*-Mes-CH<sub>3</sub>), 2.20 (s, 3H, *p*-Mes-CH<sub>3</sub>), 2.28 (s, 3H, *p*-Mes-CH<sub>3</sub>), 6.17 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 6.73 (br. s, 2H, Mes-H), 6.81 (br. s, 2H, Mes-H). – <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>): δ = 20.7 (Mes-CH<sub>3</sub>), 20.8 (Mes-CH<sub>3</sub>), 29.7 (*t*Bu-CH<sub>3</sub>), 42.5 (C3), 109.4 (C1), 117.3 (C<sub>5</sub>H<sub>5</sub>), 135.0 (Mes), 135.2 (Mes), 137.4 (Mes), 138.3 (Mes), 138.8 (Mes), 176.0 (C2). – IR (KBr):  $\tilde{\nu}$  = 2997 cm<sup>-1</sup>, 2955, 2916, 2861, 1608, 1528, 1478, 1455, 1393, 1374, 1262, 1230, 1196, 1151, 1096, 1029, 967, 935, 912, 853, 822, 808, 733, 672, 485. – C<sub>34</sub>H<sub>41</sub>ClOTi (549.0): calcd. C 74.38, H 7.53; found C 74.10, H 7.79.

*Chlorodi-η<sup>5</sup>-cyclopentadienyl[2,2-dimesityl-1-phenylethenoxy]titanium (3)*: 2,2-Dimesityl-1-phenylethanol (713 mg, 2.00 mmol) was added in small portions at room temperature to a suspension of sodium hydride (314 mg, 13.1 mmol) in 30 ml of THF. After stirring for 1 h the excess NaH was filtered off and the filtrate was added slowly to a solution of dichlorotitanocene (498 mg, 2.00 mmol) in 50 ml of THF at room temperature. The mixture was stirred overnight and then the solvent was evaporated in vacuo. The dark residue was extracted with 100 ml of diethyl ether for 3 h and then the extract was filtered. The filtrate was concentrated to about 10 ml and 90 ml of *n*-hexane was added. The mixture was kept for 3 days at -40°C. After removing the precipitate the solvents were distilled off in vacuo, affording 708 mg (62%) of **3** as a brown powder. – M.p. 144°C (decomp.). – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.01 (br. s, 6H, *o*-Mes-CH<sub>3</sub>), 2.10 (br. s, 3H, *p*-Mes-CH<sub>3</sub>), 2.15 (br. s, 6H, *o*-Mes-CH<sub>3</sub>), 2.24 (br. s, 3H, *p*-Mes-CH<sub>3</sub>), 6.01 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 6.56 (br. s, 2H, Mes-H), 6.82 (br. s, 2H, Mes-H), 7.1–7.2 (m, 3H, *m/p*-Ph-H), 7.3–7.4 (m, 2H, *o*-Ph-H). – <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>): δ = 20.7 (Mes-CH<sub>3</sub>), 20.9 (Mes-CH<sub>3</sub>), 21.3 (Mes-CH<sub>3</sub>), 21.9 (Mes-CH<sub>3</sub>), 114.7 (C2), 117.6 (C<sub>5</sub>H<sub>5</sub>), 127.1

(Ar), 127.7 (Ar), 129.0 (Ar), 129.2 (Ar), 130.4 (Ar), 135.3 (Ar), 135.6 (Ar), 138.0 (Ar), 140.3 (Ar), 167.7 (C1). – IR (KBr):  $\tilde{\nu}$  = 2955 cm<sup>-1</sup>, 2917, 2855, 1609, 1522, 1489, 1440, 1373, 1277, 1242, 1202, 1155, 1077, 1027, 969, 910, 853, 815, 775, 749, 701, 668, 635, 597. – C<sub>36</sub>H<sub>37</sub>ClOTi (569.0): calcd. C 75.99, H 6.55; found C 76.35, H 6.81.

*Chlorodi-η<sup>5</sup>-cyclopentadienyl[(Z)-2-mesityl-2-phenylethenoxy]titanium (4)*: A suspension of sodium hydride (136 mg, 5.67 mmol) in 5 ml of THF was treated with a solution of *Z*-2-mesityl-2-phenylethanol (308 mg, 1.29 mmol) in 10 ml of THF. After stirring for 1 h at room temperature and removing the excess NaH, the enolate solution was slowly added to a solution of dichlorotitanocene (267 mg, 1.07 mmol) in 20 ml of THF at room temperature. The solvent was removed and the residue was stirred with 50 ml of diethyl ether for 12 h. The NaCl deposited was then filtered off and the filtrate concentrated as far as possible. Addition of *n*-pentane (40 ml) afforded 155 mg (32%) of **4** as a red-brown powder after 3 d at -40°C. – M.p. 177°C (decomp.). – <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 2.06 (s, 6H, *o*-Mes-CH<sub>3</sub>), 2.10 (s, 3H, *p*-Mes-CH<sub>3</sub>), 6.12 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 6.92 (s, 2H, Mes-H), 7.1–7.3 (m, 5H, Ph-H), 8.04 (s, 1H, C=CH). – <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>): δ = 20.2 (*o*-Mes-CH<sub>3</sub>), 21.5 (*p*-Mes-CH<sub>3</sub>), 108.0 (C2), 117.3 (C<sub>5</sub>H<sub>5</sub>), 124.7 (*p*-Mes-CH<sub>3</sub>), 125.3 (*m*-Mes), 126.0 (*p*-Ph), 128.1 (Ph), 128.7 (Ph), 129.2 (*o*-Mes), 136.7 (Mes or Ph), 137.2 (Mes or Ph), 156.0 (C1). – IR (KBr):  $\tilde{\nu}$  = 3090 cm<sup>-1</sup>, 2970, 2908, 2841, 1581, 1560, 1492, 1443, 1374, 1280, 1230, 1170, 1106, 1074, 1021, 855, 815, 766, 685, 586, 530. – MS (70 eV), *m/z*: 452 (19), 451 (17), 450 (44) [M<sup>+</sup>], 415 (8), 350 (4), 320 (7), 385 (11), 238 (12), 220 (4), 214 (22), 213 (100), 212 (11), 211 (11), 191 (8), 179 (10), 178 (21), 150 (8), 148 (21), 115 (7). – C<sub>27</sub>H<sub>27</sub>ClOTi: calcd. 450.1230, found 450.1239 (HRMS).

*Chlorodi-η<sup>5</sup>-cyclopentadienyl[2,2-diphenylethenoxy]titanium (5)*: A suspension of sodium hydride (673 mg, 28.0 mmol) in 10 ml of THF was stirred with a solution of diphenylacetaldehyde (942 mg, 4.80 mmol) in 40 ml of THF at room temperature for 1 h. Excess NaH was then filtered off and the filtrate was added to a solution of dichlorotitanocene (1.20 g, 4.80 mmol) in 150 ml of THF at room temperature. After removal of the solvent, the residue was stirred with 200 ml of diethyl ether. The precipitated NaCl was filtered off and the filtrate was concentrated as far as possible. Following the addition of *n*-pentane (150 ml), 975 mg (50%) of **5** slowly crystallized at -40°C as a black-brown microcrystalline solid. – M.p. 136°C. – <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 6.28 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 7.2–7.4 (m, 10H, Ph-H), 7.65 (s, 1H, C=CH). – <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>): δ = 106.7 (C2), 117.7 (C<sub>5</sub>H<sub>5</sub>), 126.2 (Ph), 126.3 (Ph), 127.7 (Ph), 128.1 (Ph), 128.2 (Ph), 130.3 (Ph), 138.8 (Ph), 140.2 (Ph), 157.1 (C1). – IR (KBr):  $\tilde{\nu}$  = 3117 cm<sup>-1</sup>, 3060, 2966, 1648, 1584, 1560, 1495, 1441, 1375, 1224, 1122, 1073, 1028, 1013, 944, 813, 766, 732, 694, 686, 579, 553. – C<sub>24</sub>H<sub>21</sub>ClOTi (408.8): calcd. C 70.52, H 5.18; found C 70.60, H 5.02.

*General Procedure for the Preparative Scale Hydrolysis of Titanium Enolates*: 40 μmol of the titanium enolate was dissolved in a mixture of 20 ml of acetonitrile and 20 ml of water. The resulting solution was stirred at room temperature for 20 h (**1–5**), or 3 min in the case of (**6**), and then extracted with three 50 ml portions of dichloromethane. The combined organic layers were dried with MgSO<sub>4</sub> and the solvents were removed. The products were characterized by <sup>1</sup>H-NMR spectroscopy by comparison with authentic samples. The yields of the formed enols, or respective carbonyl compounds, were determined from the ratio of their NMR signal intensities to those of an internal standard (*m*-nitroacetophenone).

*General Procedure for the UV Investigations*: The UV spectra of the titanium enolates were recorded either in pure acetonitrile or

in pure THF. In order to study the kinetics of the hydrolysis reaction, the titanium enolates were dissolved in THF/water (1:1) or acetonitrile/water (1:1, v/v) and the absorption at  $\lambda = 540$  nm was monitored. Solutions were maintained at  $T = 32^\circ\text{C}$  by means of a thermostat.

**Determination of the X-ray Crystal Structure of 1:** Single crystals were grown from *n*-hexane. Crystal data (from 25 reflections,  $10^\circ < \Theta < 15^\circ$ ): monoclinic, space group  $P2_1/c$  (No. 14);  $a = 9.39(2)$ ,  $b = 17.34(2)$ ,  $c = 15.76(2)$  Å,  $\beta = 94.87(7)^\circ$ ,  $V = 2558(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calcd}} = 1.280$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.457$  mm<sup>-1</sup>; crystal size  $0.35 \times 0.20 \times 0.20$  mm; Enraf-Nonius CAD4 diffractometer, Mo-K $\alpha$  radiation (0.70930 Å), graphite monochromator, Zr filter (factor 15.4);  $T = 293(2)$  K;  $\omega/\Theta$  scan, max  $2\Theta = 46^\circ$ ; 3955 reflections measured, 3550 independent reflections [ $R(\text{int}) = 0.0183$ ], 2389 reflections with  $I > 2\sigma(I)$ , 3550 independent reflections included in data set. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares on  $F^2$  {308 parameters, weighting scheme applied in the last cycle:  $w = 1/[\sigma^2(F_o^2) + (0.0386 \cdot P)^2 + 2.2348 \cdot P]$  where  $P = (F_o^2 + 2F_c^2)/3$ , SHELXL-93}. The positions of all hydrogen atoms except the vinylic H1 were calculated according to ideal geometry and were refined by using the riding method. The position of H1 could be located in a final difference Fourier synthesis and refined isotropically. Conventional  $R = 0.0486$  [for 2389 reflections with  $I > 2\sigma(I)$ ] and weighted  $wR2 = 0.1185$  for all 3550 data reflections; reflex/parameter ratio 11.5; residual electron density  $+0.161/-0.237$  eÅ<sup>-3</sup>.

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405604 (1), the names of the authors and the journal citation.

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