



# Alkyloxy- and aryloxy-titanocenes: Synthesis, solid-state structure and cyclic voltammetric studies

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## ARTICLE INFO

### Article history:

Received 15 May 2008

Received in revised form 10 July 2008

Accepted 14 July 2008

Available online 22 July 2008

Dedicated to Professor Dr. Ch. Elschenbroich on the occasion of his 70th birthday.

### Keywords:

Titanocene

Alkyloxy

Aryloxy

Cyclic voltammetry

Hammett parameter

## ABSTRACT

Alkyloxy- and aryloxy-functionalized titanocenes of type  $[\text{Ti}](\text{Cl})(\text{OR})$  ( $\text{R} = \text{Me}$  (**2**),  $\text{CH}_2\text{PPh}_2$  (**3**),  $\text{CH}_2\text{Fc}$  (**4**),  $\text{C}_6\text{H}_5$  (**5**),  $\text{C}_6\text{H}_4\text{-4-C}\equiv\text{N}$  (**6**),  $\text{C}_6\text{H}_4\text{-4-NO}_2$  (**7**),  $\text{C}_6\text{H}_4\text{-4-Me}$  (**8**),  $\text{C}_6\text{H}_4\text{-4-OMe}$  (**9**),  $\text{C}_6\text{H}_4\text{-4-C(O)Me}$  (**10**),  $\text{C}_6\text{H}_4\text{-4-CO}_2\text{Me}$  (**11**),  $\text{C}_6\text{H}_4\text{-3-NO}_2$  (**12**);  $[\text{Ti}] = (\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}$ ;  $\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$ ) were synthesized by the reaction of  $[\text{Ti}]\text{Cl}_2$  (**1**) with ROH in a 1:1 molar ratio and in presence of  $\text{Et}_2\text{NH}$ . Diaryloxy-titanocenes (e.g.,  $[\text{Ti}](\text{OC}_6\text{H}_4\text{-4-NO}_2)_2$  (**13**)) are accessible, when the ratio of **1** and ROH is changed to 1:2. This synthesis methodology also allowed the preparation of dinuclear complexes of composition  $([\text{Ti}](\text{Cl}))_2(\mu\text{-OC}_6\text{H}_4\text{O})$  (**14**) and  $([\text{Ti}](\text{Cl}))_2(\mu\text{-OC}_6\text{H}_4\text{-4})_2$  (**15**) by the reaction of **1** with hydroquinone or 1,1'-dihydroxybiphenyl in a 2:1 stoichiometry.

Cyclic voltammetric studies show the characteristic  $[\text{Ti}(\text{IV})/\text{Ti}(\text{III})]$  reductions. It was found that the potentials of the alkyloxy titanocenes **2–4** do not differ, while for the aryloxy-titanocenes **5–15** the reduction potentials correlate linearly with the  $\sigma_{p/m}$  Hammett substituent constants showing a strong influence of the substituents on the electron density at titanium.

The structures of titanocenes **4**, **5**, **9**, and **11–13** in the solid state are reported. Typical for these organometallic sandwich compounds is a distorted tetrahedral coordination geometry around titanium with  $\text{D1-Ti-D2}$  angles ( $\text{D1}$ ,  $\text{D2}$  = centroids of the cyclopentadienyl ligands) of ca.  $130^\circ$ . In comparison to  $\text{FcCH}_2\text{O}$ -functionalized **4**, for the aryloxy-titanocenes **5**, **9**, and **11–13** a significant larger  $\text{Ti-O-C}$  angle was found confirming electronic interactions between the titanium atom and the appropriate aryl group.

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## 1. Introduction

Titanium compounds play an important role in industrial processes including homogeneous catalysis, for example, polymerization of  $\alpha$ -olefins [1], hydroboration [2], oxidation [3], and carbonyl coupling reactions. [4,5]. For the development and optimization of homogeneous catalysts it is necessary to fine-tune the electronic properties of the active metal atom by appropriately functionalized ligands, whereby an electronic interaction between the substituent(s) via the ligand(s) with the metal center is essential [6].

Although bis(cyclopentadienyl)titanium-oxo compounds are known for quite some years, the primary focus has been directed on their preparation [8–15]. However, only less is known about the electrochemical behavior of alkyloxy- and aryloxy-titanocenes [7]. In general, titanium–oxygen bonds are with ca.  $1.85 \text{ \AA}$  [8,9] unusual short, and the  $\text{Ti-O-Ti}$  bond angles are with  $\approx 170^\circ$  almost linear [10]. These data suggest a partial  $\text{Ti-O}$   $\pi$ -bond which should facilitate an electronic interaction between titanium and the respective terminal groups R with their diverse functionalities [9].

We here report on the synthesis, characterization, structural features and electrochemical behavior of the mononuclear bent

sandwich complexes  $[\text{Ti}](\text{Cl})(\text{OR})$  ( $\text{R} = \text{Me}$ ,  $\text{CH}_2\text{PPh}_2$ ,  $\text{CH}_2\text{Fc}$ ,  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4\text{-4-C}\equiv\text{N}$ ,  $\text{C}_6\text{H}_4\text{-4-NO}_2$ ,  $\text{C}_6\text{H}_4\text{-4-Me}$ ,  $\text{C}_6\text{H}_4\text{-4-OMe}$ ,  $\text{C}_6\text{H}_4\text{-4-C(O)Me}$ ,  $\text{C}_6\text{H}_4\text{-4-CO}_2\text{Me}$ ,  $\text{C}_6\text{H}_4\text{-3-NO}_2$ ;  $[\text{Ti}] = (\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}$ ;  $\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$ ) and  $[\text{Ti}](\text{OC}_6\text{H}_4\text{-4-NO}_2)_2$  as well as the homobimetallic titanocenes  $([\text{Ti}](\text{Cl}))_2(\mu\text{-OC}_6\text{H}_4\text{O})$  and  $([\text{Ti}](\text{Cl}))_2(\mu\text{-OC}_6\text{H}_4\text{-4})_2$ , respectively. In the latter molecules two  $[\text{Ti}]\text{Cl}$  moieties are connected by either a  $\text{OC}_6\text{H}_4\text{O}$  or a  $\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{O}$  bridging unit.

## 2. Results and discussion

### 2.1. Synthesis and spectroscopy

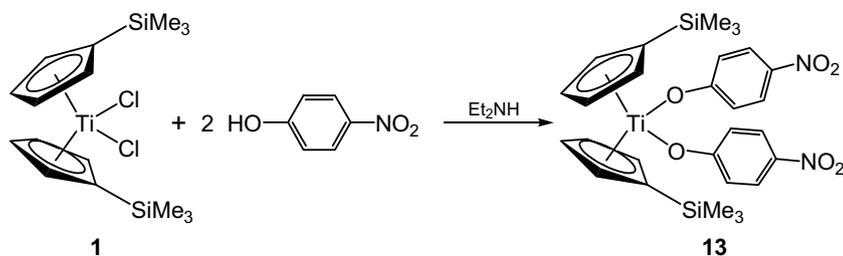
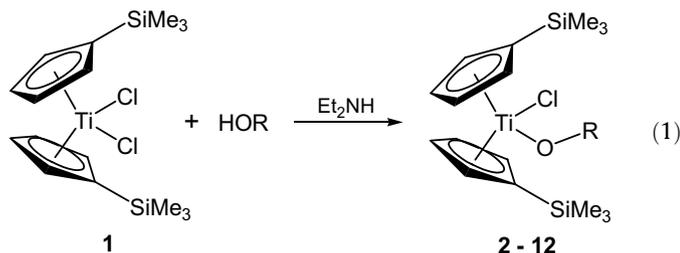
General synthetic methodologies for the preparation of alkyloxy- and aryloxy-functionalized titanocenes of type  $(\eta^5\text{-C}_5\text{H}_5)_2\text{-Ti}(\text{Cl})_{2-n}(\text{OR})_n$  ( $\text{R} = \text{alkyl, aryl}$ ;  $n = 1, 2$ ) include the reaction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  with acidic compounds such as alcohols or carboxylic acids in presence of a base [8, 11]. Care must be taken since from  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  one of the cyclopentadienyl annulenes can be replaced by a RO ligand to give the half-sandwich complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{Cl})_{3-n}(\text{OR})_n$  ( $n = 1, 2, 3$ ) depending on the reaction conditions applied [12]. As suitable base most commonly  $\text{Et}_3\text{N}$  is used but inorganic bases like  $\text{NaHCO}_3$  and  $\text{NaNH}_2$  can also be

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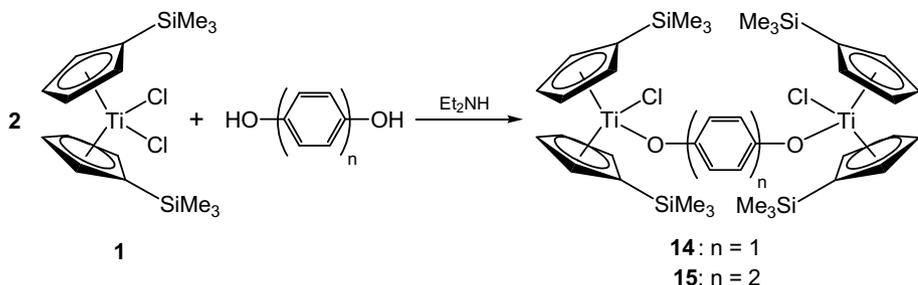
E-mail address: [heinrich.lang@chemie.tu-chemnitz.de](mailto:heinrich.lang@chemie.tu-chemnitz.de) (H. Lang).

considered [8–12]. Another straightforward access to alkyloxy- and aryloxy-titanocenes is given by the reaction of methyl-titanocene chlorides or dimethyl-titanocenes with alcohols or carboxylic acids, whereby methane is evolved as only further product [13,14]. The formation of quinonide bridged homodinuclear titanocenes can be realized by the reaction of titanium(III) precursors such as  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiCl}$  with benzoquinone as reported by Roesky and coworkers [15].

Following the first synthesis approach we prepared a series of different alkyloxy- and aryloxy-titanocene chlorides of type  $[\text{Ti}](\text{Cl})(\text{OR})$  ( $\text{R} = \text{Me}$  (**2**),  $\text{CH}_2\text{PPh}_2$  (**3**),  $\text{CH}_2\text{Fc}$  (**4**),  $\text{C}_6\text{H}_5$  (**5**),  $\text{C}_6\text{H}_4\text{-4-C}\equiv\text{N}$  (**6**),  $\text{C}_6\text{H}_4\text{-4-NO}_2$  (**7**),  $\text{C}_6\text{H}_4\text{-4-Me}$  (**8**),  $\text{C}_6\text{H}_4\text{-4-OMe}$  (**9**),  $\text{C}_6\text{H}_4\text{-4-C(O)Me}$  (**10**),  $\text{C}_6\text{H}_4\text{-4-CO}_2\text{Me}$  (**11**),  $\text{C}_6\text{H}_4\text{-3-NO}_2$  (**12**));  $[\text{Ti}] = (\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}$ ;  $\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$ ) by treatment of  $[\text{Ti}]\text{Cl}_2$  (**1**) with alcohols ROH ( $\text{R} = \text{Me}$ ,  $\text{CH}_2\text{PPh}_2$ ,  $\text{CH}_2\text{Fc}$ ,  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4\text{-4-C}\equiv\text{N}$ ,  $\text{C}_6\text{H}_4\text{-4-NO}_2$ ,  $\text{C}_6\text{H}_4\text{-4-Me}$ ,  $\text{C}_6\text{H}_4\text{-4-OMe}$ ,  $\text{C}_6\text{H}_4\text{-4-C(O)Me}$ ,  $\text{C}_6\text{H}_4\text{-4-CO}_2\text{Me}$ ,  $\text{C}_6\text{H}_4\text{-3-NO}_2$ ) in a 1:1 molar ratio in diethyl ether at room temperature (Table 1, Reaction 1). Instead of  $\text{NEt}_3$  more basic  $\text{HNEt}_2$  was chosen because this secondary amine allowed shorter reaction times, resulted in higher yields of titanocenes **2–12**, and due to the formation of the less soluble ammonium salt  $[\text{Et}_2\text{NH}_2]\text{Cl}$  a more efficient purification is permitted (Section 4).



After appropriate work-up, titanocene chlorides **2–12** could be isolated as orange (**4**, **10–12**), red (**2**, **3**, **5–8**) or purple (**9**) solids in very good to excellent yield (Table 1). They dissolve in polar organic solvents including diethyl ether, tetrahydrofuran and dichloromethane. These compounds are fairly stable to air and oxygen but sensitive toward acids.



**Table 1**  
Synthesis of **2–12** from **1** and ROH

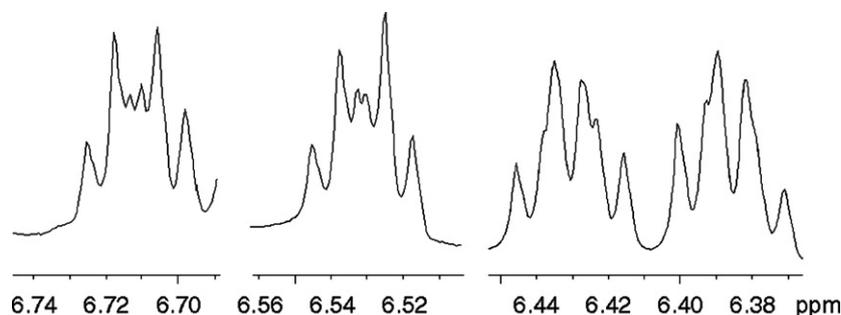
Compound	R	Yield <sup>a</sup> (%)
<b>2</b>	Me	95
<b>3</b>	$\text{CH}_2\text{PPh}_2$	74
<b>4</b>	$\text{CH}_2\text{Fc}^b$	89
<b>5</b>	$\text{C}_6\text{H}_5$	87
<b>6</b>	$\text{C}_6\text{H}_4\text{-4-C}\equiv\text{N}$	96
<b>7</b>	$\text{C}_6\text{H}_4\text{-4-NO}_2$	84
<b>8</b>	$\text{C}_6\text{H}_4\text{-4-Me}$	95
<b>9</b>	$\text{C}_6\text{H}_4\text{-4-OMe}$	94
<b>10</b>	$\text{C}_6\text{H}_4\text{-4-COMe}$	95
<b>11</b>	$\text{C}_6\text{H}_4\text{-4-CO}_2\text{Me}$	98
<b>12</b>	$\text{C}_6\text{H}_4\text{-3-NO}_2$	91

<sup>a</sup> Based on **1**.

<sup>b</sup>  $\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)\text{Fe}$ .

In the synthesis of  $[\text{Ti}](\text{Cl})(\text{OC}_6\text{H}_4\text{-4-NO}_2)$  (**7**) always reaction mixtures were obtained consisting the mono-aryloxy-titanocene chloride **7** and traces of the appropriate bis(aryloxy) titanium complex  $[\text{Ti}](\text{OC}_6\text{H}_4\text{-4-NO}_2)_2$  (**13**) (Section 4). This is inexplicable because in all other cases (vide supra) even by using an excess of the alcohol component the formation of mono-alkyloxy- and -aryloxy-titanocenes was favored over the dialcoholate species. Pure **7** could only be isolated, when a slight excess of **1** was used, which could easily be separated from **7** by fractional crystallization at low temperature. The bis(aryloxy) titanocene **13** could be prepared in a more straightforward way by treatment of **1** with 4-nitrophenol in a 1:2.1 molar ratio and using  $\text{Et}_2\text{NH}$  as base (Reaction 2). After appropriate work-up, organometallic **13** could be isolated as an orange solid in 84% yield.

The  $\text{Et}_2\text{NH}$ /diethyl ether reaction media could also successfully be applied for the synthesis of homodinuclear titanium compounds as outlined in Reaction 3. In the thus formed compounds ( $[\text{Ti}]\text{Cl}_2(\mu\text{-OC}_6\text{H}_4\text{O})$  (**14**) and ( $[\text{Ti}](\text{Cl})(\mu\text{-OC}_6\text{H}_4\text{-4})_2$  (**15**) two  $[\text{Ti}]\text{Cl}$  units are connected by a  $\text{OC}_6\text{H}_4\text{O}$  or a  $\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{O}$  bridging moiety. These molecules could be isolated in excellent yield as dark purple (**14**) or red (**15**) solid materials (Section 4).



**Fig. 1.** Resonance signals of the cyclopentadienyl ring protons in the  $^1\text{H}$  NMR spectrum of **6** ( $\text{CDCl}_3$ , 250.12 MHz, rel.  $\text{SiMe}_4$ :  $\delta = 0.00$  ppm,  $\text{CDCl}_3$  solvent reference signal:  $\delta = 7.26$  ppm,  $25^\circ\text{C}$ ).

The  $^1\text{H}$  NMR spectra of **2–15** show the expected resonance signals and coupling patterns [8]. Noteworthy is that in the  $^1\text{H}$  NMR spectra of **2**, **3**, **5–12** and **15** the cyclopentadienyl ring protons split into two pairs of duplets-of-triplets, which differs from the spectrum of **1**, where two pseudo-triplets are characteristic (6.56 and 6.78 ppm; AA'XX' spin system,  $J_{\text{HH}} = 1.8$  Hz). [16] This can be explained by a lower symmetry, when going from **1** with a distorted tetrahedral  $\text{A}_2\text{X}_2$  substituent pattern at Ti to an ABCD pattern for **2–12**, **14** and **15**. Exemplary, the chemical shift window of the cyclopentadienyl part of the  $^1\text{H}$  NMR of **6** is depicted in Fig. 1. The resonances at 6.53 and 6.71 ppm can be assigned to the  $\alpha$ -positioned cyclopentadienyl ring protons with coupling constants of  $^3J_{\text{HH}} = 3$  Hz and  $^4J_{\text{HH}} = 1.9$  Hz, respectively, while at 6.39 and 6.43 ppm the resonance signals for the  $\beta$ -positioned protons are found. A similar behavior is observed for the cyclopentadienyl ring carbon atoms in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **2–15** (e.g.,  $\text{C}_\alpha$ : 127.5 and 128.9,  $\text{C}_\beta$ : 115.0 and 119.0, *ipso*-C: 130.3 ppm).

The successful formation of organometallic **2–15** could additionally be monitored by  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy. The quaternary Ti–O–C carbon atoms, for example, upon formation of **6**, is shifted by ca. 12 ppm to lower field as compared to the starting material 4-hydroxybenzotrile and is found at 173.4 ppm.

In the IR spectrum of **10** a  $\nu_{\text{CO}}$  absorption band is observed at  $1673\text{ cm}^{-1}$  (for comparison, the  $\nu_{\text{CO}}$  of 4'-methoxyacetophenone absorbs at  $1668\text{ cm}^{-1}$ ) [17]. This is also characteristic for **11** ( $1712\text{ cm}^{-1}$ ; for comparison, methyl anisate absorbs at  $1714\text{ cm}^{-1}$ ). The cyano group in **6** shows its  $\nu_{\text{C}\equiv\text{N}}$  frequency at  $2220\text{ cm}^{-1}$  (e.g., *para*-methoxybenzotrile  $\nu_{\text{C}\equiv\text{N}} = 2219\text{ cm}^{-1}$ ) [17]. The nitro group present in **7**, **12** and **13** consists of two identical N–O bonds for which symmetrically and asymmetrically vibrations are characteristic, for example, the asymmetric band is found as strong absorption between  $1500$  and  $1530\text{ cm}^{-1}$  for nitrobenzene [18]. In **12**, where the  $\text{NO}_2$  functionality is *meta*-positioned, the asymmetric  $\nu_{\text{NO}}$  vibration was observed at  $1526\text{ cm}^{-1}$ . However, for **7** and **13**, which feature *para*-nitrobenzene units, the appropriate  $\nu_{\text{NO}}$  is shifted to higher wavenumbers (**7**:  $1582\text{ cm}^{-1}$ , **13**:  $1581$  and  $1587\text{ cm}^{-1}$ ) explainable by benzenes substituted with strong electron-withdrawing groups [18b]. The occurrence of two asymmetric  $\nu_{\text{NO}}$  bands for **13** is in accordance with its structure in the solid state. Other characteristic vibrations for **2–15** are observed in the expected ranges (Section 4) [18b].

## 2.2. Cyclic voltammetry

To study the effect of electron-withdrawing and electron-donating substituents at the benzene groups as well as the consequence of continuous and discontinuous  $\pi$ -conjugation the series of prepared alkyloxy- and aryloxy-titanocenes **2–15** (*vide supra*) were subjected to cyclic voltammetric measurements in tetrahydrofuran at  $25^\circ\text{C}$ . The introduction of diverse substituents in *para*

and *meta*-position at the benzene core should allow to carry out comparative studies of the electronic properties on the titanium atoms.

In general, titanium(IV) compounds show reversible [Ti(IV)/Ti(III)] redox couples [19,20]. However, this could only be observed for organometallics **1–3**, while **4–15** possess irreversible reductions as summarized in Table 2.

The introduction of an alkyloxy substituent in **2–4** results in a shift of the [Ti(IV)/Ti(III)] potential by about 0.10 V to more positive values as compared to **1**, which can be explained by the somewhat stronger electron-withdrawing properties of the RO groups ( $\text{R} = \text{Me}$ ,  $\text{CH}_2\text{PPh}_2$ ,  $\text{CH}_2\text{Fc}$ ) (Table 2). Since these potentials occur at practically the same value ( $-1.42$ ,  $-1.44$  V) it can be concluded that there is no electronic influence of the alkyloxy groups R onto the titanium(IV) ion. Additionally, for **3** an irreversible oxidation wave was found at  $+0.43$  V which most likely can be assigned to the oxidation of the phosphorus atom. Similar observations were made for phosphane-functionalized ferrocenes and, for example,  $\text{iPr}_3\text{P}$ . [21] The heterobimetallic molecule **4** shows next to the reduction potential at  $-1.44$  V ([Ti(IV)/Ti(III)]) a reversible one-electron [Fe(II)/Fe(III)] oxidation at  $-0.03$  V ( $\Delta E = 0.17$  V) which can be assigned to the ferrocene unit [22]. This potential is thereby not shifted, when compared to hydroxymethylferrocene, which is in accordance with the [Ti(IV)/Ti(III)] couple [23].

**Table 2**  
Electrochemical data of **1–15**<sup>a</sup>

Compound.	$E_{\text{red(Ti)}}$ (V)	$E_{1/2\text{red}}$ (V) ( $\Delta E_p$ (V))	$E_{\text{red}}$ (V)	$E_{\text{ox}}$ (V)	$E_{1/2\text{ox}}$ (V) ( $\Delta E_p$ (mV))
<b>1</b>	$-1.50^b$	$-1.45$ (0.10)			
<b>2</b>	$-1.42^b$	$-1.33$ (0.18)	$-2.02$ , $-2.60$		
<b>3</b>	$-1.44^b$	$-1.34$ (0.20)	$-2.53$ , $-3.07$	$+0.43$	
<b>4</b>	$-1.44$		$-2.03$		$-0.03$ (0.17)
<b>5</b>	$-1.80$		$-2.38$ , $-2.81$		
<b>6</b>	$-1.61$		$-2.06$		
<b>7</b>	$-1.65$		$-2.24$ , $-2.74$		
<b>8</b>	$-1.80$		$-2.40$		
<b>9</b>	$-1.86$		$-2.44$		$+0.53$ (0.26)
<b>10</b>	$-1.57$		$-1.90$ , $-2.12$		
<b>11</b>	$-1.60$		$-2.64$		
<b>12</b>	$-1.81$		$-1.99$ , $-2.22$		
<b>13</b>	$-1.64$		$-2.69$		
<b>14</b>	$-1.37$		$-1.87$ , $-2.92$	$+0.76$	$+0.28$ (0.20)
<b>15</b>	$-1.49$		$-2.17$		$+0.50$ (0.29)

<sup>a</sup>  $10^{-3}$  M solutions in tetrahydrofuran at  $25^\circ\text{C}$ ,  $[\text{n-Bu}_4\text{N}]\text{PF}_6$  supporting electrolyte (0.1 M), argon, scan rate =  $0.2\text{ V s}^{-1}$ . All potentials are referenced to the FcH/FcH<sup>+</sup> redox couple ( $\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$ ) with  $E_{1/2} = 0.00$  V.  $E_{\text{red(Ti)}}$  = wave maxima of the 1st titanium reduction.  $E_{1/2\text{red}}$  = potential of the [Ti(IV)/Ti(III)] couple with peak-to-peak separation  $\Delta E_p$ .  $E_{\text{red}}$  = wave maxima of the 2nd and 3rd irreversible titanium reduction.  $E_{\text{ox}}$  = wave maxima of the irreversible oxidation.  $E_{1/2\text{ox}}$  = potential of the anodic redox couple with peak-to-peak separation  $\Delta E_p$ .

<sup>b</sup> Although the [Ti(IV)/Ti(III)] redox couple is reversible, for comparative reasons the potential of the reduction wave is additionally listed.

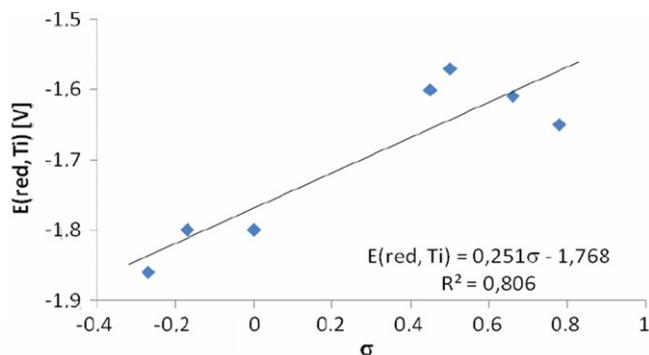


Fig. 2. Correlation between the [Ti(IV)/Ti(III)] reduction potentials and the  $\sigma$  Hammett substituent constants.

For the aryloxy-substituted titanocenes **5–15** the [Ti(IV)/Ti(III)] reductions vary in a 500 mV window (Table 2). To study the influence of the substituents of **5–13** vs. the 1st titanium-centered reduction, these values were plotted against the  $\sigma_{p/m}$  Hammett substituent constants reported by Taft (Fig. 2) [24].

As it can be seen from Fig. 2 the [Ti(IV)/Ti(III)] reductions of **5–13** show a modest correlation with the  $\sigma_{p/m}$  Hammett constants. A similar dependence of the reduction potentials was reported by Langmaier et al. for methyl-substituted titanocene dichlorides of type  $(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)_2\text{TiCl}_2$  ( $n = 0\text{--}5$ ) showing an average shift of the 1st reduction per one methyl group of 0.095 V [25]. It must be noted that the titanium-centered reductions of **5–15** originate from irreversible reductions which cannot be measured and compared as accurately as fully reversible electrochemical processes. With this uncertainty in mind we propose a direct dependence of the nature of the aryl-substituent on the [Ti(IV)/Ti(III)] reduction via the phenolic oxygen atom. Hence, the electronic configuration of the titanium ion can be predicted by selecting appropriately substituted phenols.

In addition to the titanium-centered reduction for **9**, **14** and **15** (vide supra) a oxidation wave was observed at 0.53 V ( $\Delta E = 0.26$  V) for **9**, 0.28 V ( $\Delta E = 0.20$  V) for **14**, and 0.50 V ( $\Delta E = 0.29$  V) for **15** which can be assigned to an oxidation of the hydroquinone (**9**, **14**) and 1,1'-dihydroxybiphenyl (**15**) moieties [26,27]. Remarkably, these compounds can be easier oxidized than related 1,4-dimethoxybenzene and 1,1'-dimethoxybiphenyl [26]. In the series of  $([\text{Ti}]\text{Cl})_n(\mu\text{-OC}_6\text{H}_4\text{O-1,4})\text{Me}_{2-n}$  ( $n = 0\text{--}2$ ), 1,4-dimethoxybenzene ( $n = 0$ ) shows a reversible oxidation at +0.90 V ( $\Delta E = 0.07$  V) [26, 28]. Exchange of one methyl group by a [Ti]Cl unit (**9**,  $n = 1$ ) shifts the oxidation potential by 0.37 V to more negative values. A second replacement (**14**,  $n = 2$ ) leads to a further shift of 0.25 V. The magnitude of the shift is very notable since, for example, in  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_2\text{SiMe}_3)(\text{C}\equiv\text{Cfc})$  the ferrocene oxidation is only facilitated by 0.080 V as compared to  $\text{HC}\equiv\text{Cfc}$  [29]. Therefore, it can be concluded that in **9**, **14** and **15** an effective resonance stabilization of the oxidized species (radical cation) takes place.

The 2nd irreversible oxidation wave found for **14** at 0.76 V can be assigned to the further oxidation of the hydroquinone radical to a dication as reported by Parker et al. for 1,4-dimethoxybenzene [26a]. However, this 2nd oxidation was not observed for **9** and **15**, most probably due to the electrochemical window of tetrahydrofuran used as solvent during the studies.

### 2.3. Structures of **4**, **5**, **9**, and **11–13** in the solid state

Single crystals of **4**, **5**, **9**, and **11–13** suitable for X-ray structure analysis were obtained by slow evaporation of diethyl ether solutions containing the corresponding compounds at  $-30$  °C. The molecular structures are shown in Figs. 3–8. Geometric details are

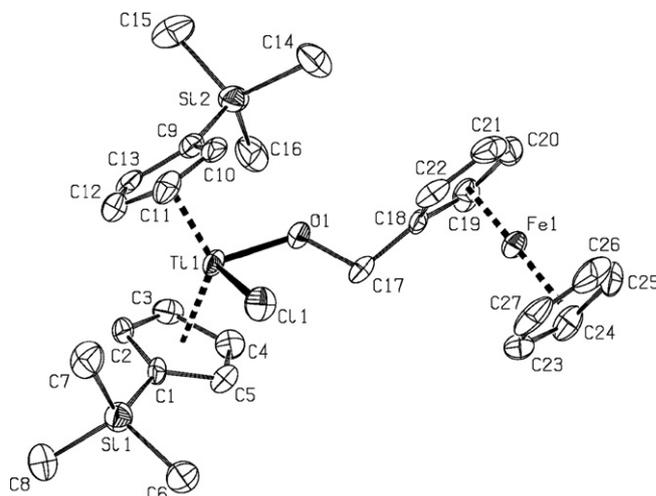


Fig. 3. Displacement ellipsoid plot (50% probability level) of the molecular structure of **4** with the atom numbering scheme (the hydrogen atoms are omitted for clarity). Selected bond distances (Å), angles (°), and torsion angles (°): Ti1–Cl1, 2.395(3); Ti1–O1, 1.849(4); O1–C17, 1.415(5); D1–Ti1, 2.070(4); D2–Ti1, 2.064(3); D3–Fe1, 1.637(3); Ti1–O1–C17, 132.5(3); C11–Ti1–O1, 90.9(1); D1–Ti1–D2, 129.7(1); D3–Fe1–D4, 178.4(2); Ti1–O1–C17–C18, 146.6(3). D1, D2: centroids of the titanocene cyclopentadienyl ligands (D1 = C1 – C5, D2 = C9–C13). D3, D4: centroids of the ferrocene cyclopentadienyl ligands (D3 = C18–C22, D4 = C23–C27).

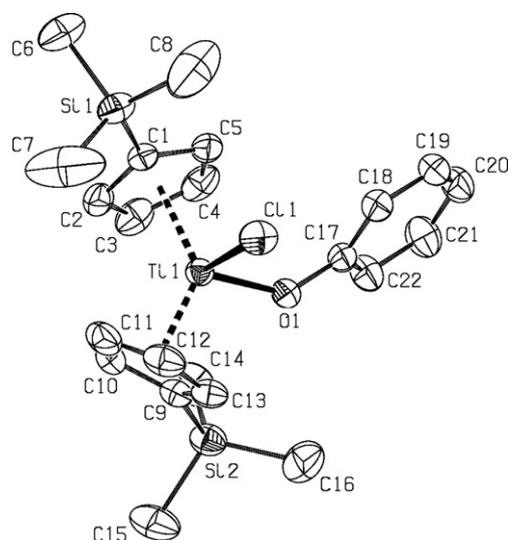
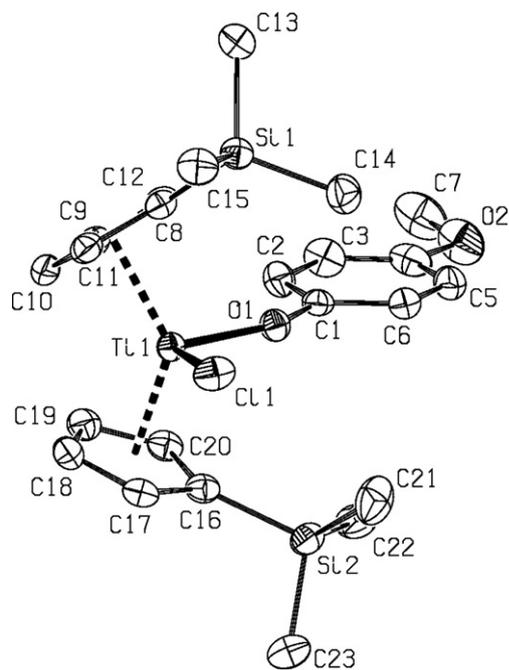


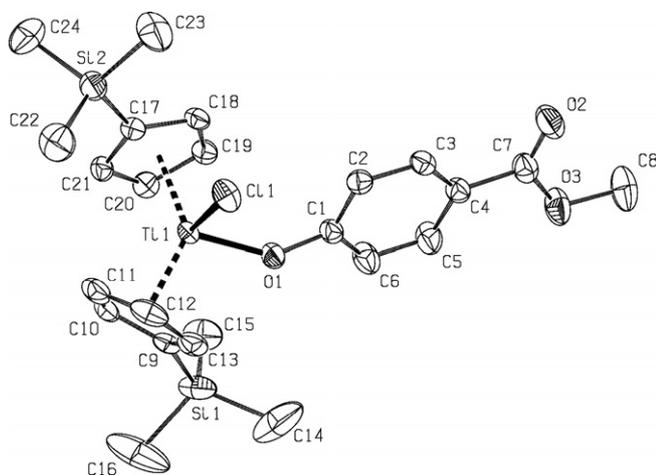
Fig. 4. Displacement ellipsoid plot (50% probability level) of the molecular structure of **5** with the atom numbering scheme (the hydrogen atoms are omitted for clarity). Selected bond distances (Å), angles (°), and torsion angles (°): Ti1–Cl1, 2.3964(6); Ti1–O1, 1.896(1); O1–C17, 1.355(2); D1–Ti1, 2.082(1); D2–Ti1, 2.085(1); Ti1–O1–C17, 137.5(1); C11–Ti1–O1, 93.06(4); D1–Ti1–D2, 130.3(1); Ti1–O1–C17–C18,  $-49.9(3)$ . D1, D2: centroids of the titanocene cyclopentadienyl ligands (D1 = C1–C5, D2 = C9–C13).

given in the legends of these figures, the respective crystal and intensity collection data are summarized in Table 3 (Section 4).

Molecules **4**, **5**, **9**, and **11–13** show a distorted tetrahedral coordination geometry at titanium set-up by two  $\text{C}_5\text{H}_4\text{SiMe}_3$  groups, a chloride and an oxygen atom (**4**, **5**, **9**, **11** and **12**) or two oxygen atoms (**13**). As characteristic for other titanocene complexes the Ti1–D1 and Ti1–D2 separations (D1, D2 = centroids of the cyclopentadienyl ligands) are found between 2.064(3) (D2–Ti1 in **4**) and 2.093(1) Å (D1–Ti1 in **12**), and the D1–Ti1–D2 angles are ranging from 129.7(1)° (**4**) to 131.2(1)° (**12**) [30]. The relative positions of the  $\text{SiMe}_3$  groups toward each other differ to a great extent. An



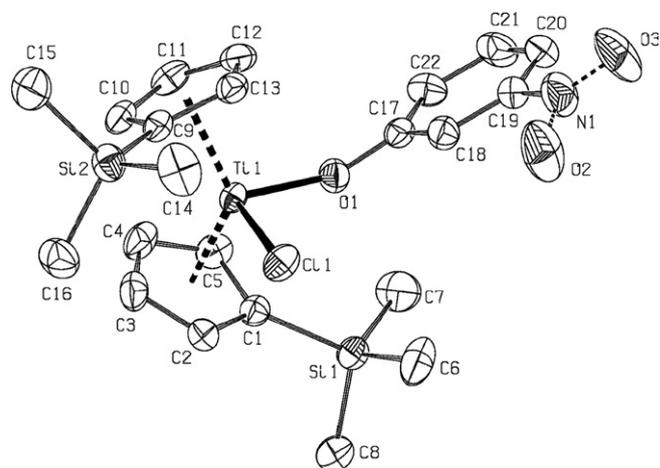
**Fig. 5.** Displacement ellipsoid plot (50% probability level) of the molecular structure of **9** with the atom numbering scheme (the hydrogen atoms are omitted for clarity). Selected bond distances (Å), angles (°), and torsion angles (°): Ti1–C1, 2.3854(8); Ti1–O1, 1.880(2); O1–C1, 1.346(3); O2–C4, 1.376(3); D1–Ti1, 2.092(1); D2–Ti1, 2.091(1); Ti1–O1–C1, 147.4(2); C1–Ti1–O1, 98.9(5); D1–Ti1–D2, 130.2(1); Ti1–O1–C1–C2, 3.7(4); C3–C4–O2–C7, 1.6(4). D1, D2: centroids of the titanocene cyclopentadienyl ligands (D1 = C8–C12, D2 = C16–C20).



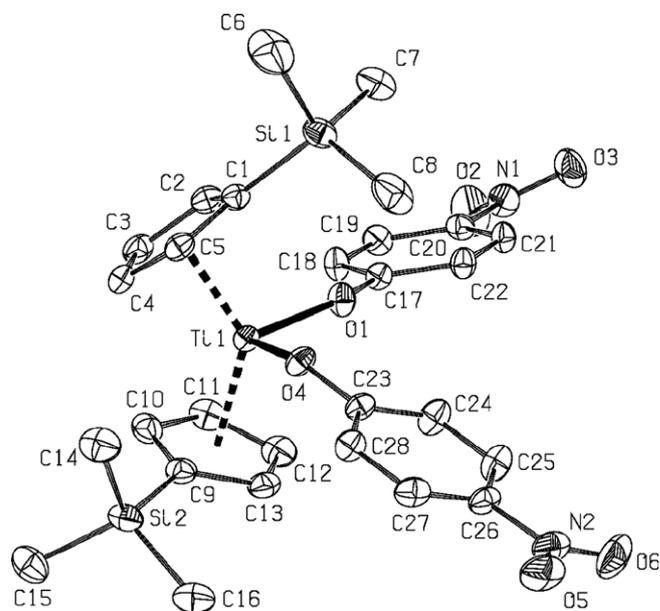
**Fig. 6.** Displacement ellipsoid plot (50% probability level) of the molecular structure of **11** with the atom numbering scheme (the hydrogen atoms are omitted for clarity). Selected bond distances (Å), angles (°), and torsion angles (°): Ti1–C1, 2.3683(9); Ti1–O1, 1.909(2); O1–C1, 1.326(2); D1–Ti1, 2.063(1); D2–Ti1, 2.085(1); Ti1–O1–C1, 143.3(1); C1–Ti1–O1, 94.10(5); D1–Ti1–D2, 130.3(1); Ti1–O1–C1–C2, 37.1(3); C3–C4–C7–O3, 168.0(2); C4–C7–O3–C8, –178.5(2). D1, D2: centroids of the titanocene cyclopentadienyl ligands (D1 = C9–C13, D2 = C17–C21).

almost eclipsed conformation is found in **9**, while for **4**, **5** and **11** completely staggered and for **12** and **13** partially staggered conformations are typical.

The O1–Ti1–O4 bite angle in **13** is 95.5(1)°, while the O–Ti–Cl one in **4**, **5**, **9**, **11** and **12** is found between 90.9(1)° (**4**) and 98.9(5)° (**9**). This shows that there is no significant steric effect on the titanium atom resulting from the substituents RO vs. Cl.



**Fig. 7.** Displacement ellipsoid plot (30% probability level) of the molecular structure of **12** with the atom numbering scheme. The nitro group is disordered and has been refined to split occupancies of 0.42/0.58 (the hydrogen atoms and one disordered nitro group are omitted for clarity). Selected bond distances (Å), angles (°), and torsion angles (°): Ti1–C1, 2.3780(8); Ti1–O1, 1.895(2); O1–C17, 1.336(3); N1–C19, 1.473(4); D1–Ti1, 2.093(1); D2–Ti1, 2.077(1); Ti1–O1–C17, 145.9(2); C11–Ti1–O1, 95.2(6); D1–Ti1–D2, 131.2(1); Ti1–O1–C17–C18, 56.4(4); C18–C19–N1–O2, 20.7(2); C18–C19–N1–O2', –19.2(2). D1, D2: centroids of the titanocene cyclopentadienyl ligands (D1 = C1–C5, D2 = C9–C13).



**Fig. 8.** Displacement ellipsoid plot (50% probability level) of the molecular structure of **13** with the atom numbering scheme (the hydrogen atoms are omitted for clarity). Selected bond distances (Å), angles (°), and torsion angles (°): Ti1–O1, 1.913(2); Ti1–O2, 1.918(2); O1–C17, 1.324(3); O4–C23, 1.327(3); N1–C20, 1.451(3); N2–C26, 1.459(4); D1–Ti1, 2.087(2); D2–Ti1, 2.085(2); Ti1–O1–C17, 150.3(2); Ti1–O4–C23, 140.4(2); O1–Ti1–O4, 95.5(1); D1–Ti1–D2, 130.9(1); Ti1–O1–C17–C18, 9.3(5); Ti1–O4–C23–C24, 42.4(4); C19–C20–N1–O3, 160.7(3); C25–C26–N2–O5, 173.2(3). D1, D2: centroids of the titanocene cyclopentadienyl ligands (D1 = C1–C5, D2 = C9–C13).

The Ti–O distances are located between 1.880(2) Å for **9** and 1.918(2) Å for **13**. Compared with previously reported  $d_{\text{Ti-O}}$  values of 1.855(2) Å for  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OEt})(\text{Cl})$  [**30a**], 1.835(2) Å for  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OMe})(\text{C}\equiv\text{N})$  [**30b**], or 1.860(5) Å for  $(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\mu\text{-OC}_6\text{H}_3\text{-2-PPh}_2\text{-6-}^t\text{Bu})\text{Cl}_2$  [**32b**] the Ti–O bonds appear to be slightly elongated, which is consistent with the presence of a somewhat lower Ti–O  $\pi$ -donation and a decreased bond order in **4**, **5**, **9**, and **11–13** [**31,32**].

**Table 3**  
Crystal and intensity collection data for **4**, **5**, **9**, and **11–13**

	<b>4</b>	<b>5</b>	<b>9</b>	<b>11</b>	<b>12</b>	<b>13</b>
Empirical formula	C <sub>27</sub> H <sub>37</sub> ClFeOSi <sub>2</sub> Ti	C <sub>22</sub> H <sub>31</sub> ClOSi <sub>2</sub> Ti	C <sub>23</sub> H <sub>33</sub> ClO <sub>2</sub> Si <sub>2</sub> Ti	C <sub>24</sub> H <sub>33</sub> ClO <sub>3</sub> Si <sub>2</sub> Ti	C <sub>22</sub> H <sub>30</sub> ClNO <sub>3</sub> Si <sub>2</sub> Ti	C <sub>28</sub> H <sub>34</sub> N <sub>2</sub> O <sub>6</sub> Si <sub>2</sub> Ti
Chemical formula	C <sub>27</sub> H <sub>37</sub> ClFeOSi <sub>2</sub> Ti	C <sub>22</sub> H <sub>31</sub> ClOSi <sub>2</sub> Ti	C <sub>23</sub> H <sub>33</sub> ClO <sub>2</sub> Si <sub>2</sub> Ti	C <sub>24</sub> H <sub>33</sub> ClO <sub>3</sub> Si <sub>2</sub> Ti	C <sub>22</sub> H <sub>30</sub> ClNO <sub>3</sub> Si <sub>2</sub> Ti	C <sub>28</sub> H <sub>34</sub> N <sub>2</sub> O <sub>6</sub> Si <sub>2</sub> Ti
Formula weight	572.95	451	481.02	509.03	496	598.65
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /c	Pna2 <sub>1</sub>	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c	C2/c	P2 <sub>1</sub> /n
a (Å)	7.508(9)	14.173(2)	7.4986(13)	7.262(3)	30.910(3)	8.980(7)
b (Å)	24.22(3)	18.183(3)	16.046(3)	23.759(6)	7.5901(7)	15.412(10)
c (Å)	15.598(19)	9.1832(15)	20.854(4)	15.145(4)	21.854(2)	21.849(16)
V (Å <sup>3</sup> )	2822(6)	2366.7(7)	2485.2(8)	2608.1(13)	5124.5(8)	3011(4)
β (°)	95.74(2)	90	97.920(4)	93.55(2)	91.871(2)	95.37(6)
ρ <sub>scale</sub> (g cm <sup>-3</sup> )	1.348	1.266	1.286	1.296	1.286	1.321
F(000)	1200	952	1016	1072	2080	1256
Z	4	4	4	4	8	4
Crystal dimensions (mm)	0.96 × 0.16 × 0.04	0.9 × 0.4 × 0.2	0.50 × 0.40 × 0.04	0.9 × 0.2 × 0.2	0.3 × 0.1 × 0.1	0.30 × 0.30 × 0.06
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
Absorption correction	Empirical	Empirical	Empirical	Empirical	Empirical	Empirical
Maximum, minimum transmission	0.9613, 0.4487	0.99999, 0.92560	0.9778, 0.7655	0.8989, 0.6399	0.99999, 0.58251	0.99999, 0.957143
Absorption coefficient (μ, mm <sup>-1</sup> )	0.994	0.585	0.565	0.545	0.554	0.406
Temperature (K)	173	293	293	173	298	223
Scan range (°)	1.56 ≤ θ ≤ 26.00	1.82 ≤ θ ≤ 25.99	1.61 ≤ θ ≤ 26.00	1.71 ≤ θ ≤ 25.99	1.86 ≤ θ ≤ 26.41	1.62 ≤ θ ≤ 26.00
Index ranges	-2 ≤ h ≤ 9 -17 ≤ k ≤ 29 -19 ≤ l ≤ 19	-17 ≤ h ≤ 17 -22 ≤ k ≤ 22 -11 ≤ l ≤ 11	-9 ≤ h ≤ 8 -13 ≤ k ≤ 19 -25 ≤ l ≤ 25	-2 ≤ h ≤ 8 -29 ≤ k ≤ 29 -14 ≤ l ≤ 18	-38 ≤ h ≤ 38 0 ≤ k ≤ 9 0 ≤ l ≤ 27	-11 ≤ h ≤ 11 -19 ≤ k ≤ 19 -26 ≤ l ≤ 26
Total reflections	10618	24064	14549	9848	22399	31186
Unique reflections	5527	4661	4880	4241	5252	5889
Observed reflections [I ≥ 2σ(I)]	2380	4446	3375	3431	3428	3714
Refined parameters	304	244	262	280	296	352
Restraints	0	1	0	0	13	0
Completeness to θ <sub>max</sub> (%)	99.70	99.90	99.90	82.70	99.70	99.90
R <sub>1</sub> , wR <sub>2</sub> [I ≥ 2σ(I)] <sup>a</sup>	0.0577, 0.0683 <sup>b</sup>	0.0238, 0.0603 <sup>c</sup>	0.0395, 0.0811 <sup>d</sup>	0.0333, 0.0874 <sup>e</sup>	0.0438, 0.0955 <sup>f</sup>	0.0453, 0.0970 <sup>g</sup>
R <sub>1</sub> , wR <sub>2</sub> (all data) <sup>a</sup>	0.1859, 0.0838 <sup>b</sup>	0.0258, 0.0611 <sup>c</sup>	0.0733, 0.0887 <sup>d</sup>	0.0454, 0.0914 <sup>e</sup>	0.0810, 0.1083 <sup>f</sup>	0.0923, 0.1084 <sup>g</sup>
R <sub>int</sub> , S	0.1200, 0.807	0.0322, 1.027	0.0521, 0.976	0.0299, 1.050	0.0546, 1.015	0.0835, 0.964
Maximum, minimum peaks in final Fourier map (e Å <sup>-3</sup> )	0.525, -0.573	0.202, -0.189	0.322, -0.272	0.273, -0.235	0.236, -0.212	0.282, -0.259

<sup>a</sup>  $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$  where  $P = [F_o^2 + 2F_c^2]/3$ .

<sup>b</sup>  $x = 0.012, y = 0$ .

<sup>c</sup>  $x = 0.0365, y = 0.1959$ .

<sup>d</sup>  $x = 0.0415, y = 0$ .

<sup>e</sup>  $x = 0.053, y = 0.2563$ .

<sup>f</sup>  $x = 0.0468, y = 2.4271$ .

<sup>g</sup>  $x = 0.0539, y = 0$ .

The aryloxy-titanocenes **9**, and **11–13** possess functional groups such as MeO, MeO<sub>2</sub>C, and NO<sub>2</sub> at the phenoxy entity. For all compounds the electron-donating (**9**: 4-OMe) or electron-withdrawing moieties (**11**: 4-CO<sub>2</sub>Me, **12**: 3-NO<sub>2</sub>, **13**: 4-NO<sub>2</sub>) are almost coplanar to the plane spanned by the phenyl ring (for selected torsion angles see Fig. 4–8), thus assuring optimal electronic overlap between these units. This can further be confirmed by comparing the C<sub>aryl</sub>-N<sub>nitro</sub> bond distances in **12** and **13** (Figs. 7 and 8). The nitro group in **12** is in *meta*-position and shows a distance of  $d(N1-C19) = 1.473(4)$  Å, while in **13** the two carbon-nitrogen bonds are by 0.022 and 0.015 Å, respectively, shorter. This suggests an increased participation of a 1,4-benzoquinone-like resonance structure in **12** and **13**, and thus, an electronic interaction between the [Ti](Cl)- and *para*-NO<sub>2</sub> groups. An electronic interaction between titanium and the aryl group is further verified by an increased hybridization of the oxygen atom resulting in significantly larger Ti–O–C angles (Figs. 3–8) in **9**, and **11–13** (143.3(1)° to 150.3(2)°) as compared to **4** (132.5(3)°) and a higher bond order of one of the two C<sub>aryl</sub>-O σ-bonds in **9**, whereby the C1–O1 separation next to titanium is by 0.03 Å shorter than the C4–O2 one ( $d(C1-O1) = 1.346(3)$ ,  $d(C4-O2) = 1.376(3)$  Å).

In contrast to mononuclear **5**, **9**, and **11–13** in **4** a ferrocenyl moiety is present as a second organometallic unit. This entity shows geometric features that resemble to the structural data characteristic for ferrocenes [33].

### 3. Conclusion

Alkyloxy- and aryloxy-titanocene chlorides of type [Ti](Cl)(OR) (R = Me, CH<sub>2</sub>PPh<sub>2</sub>, CH<sub>2</sub>Fc, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>-4-C≡N, C<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub>, C<sub>6</sub>H<sub>4</sub>-4-Me, C<sub>6</sub>H<sub>4</sub>-4-OMe, C<sub>6</sub>H<sub>4</sub>-4-C(O)Me, C<sub>6</sub>H<sub>4</sub>-4-CO<sub>2</sub>Me, C<sub>6</sub>H<sub>4</sub>-3-NO<sub>2</sub>; [Ti] = (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>Ti; Fc = (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Fe) were synthesized in high yield by reacting [Ti]Cl<sub>2</sub> with the respective alcohols ROH in a 1:1 molar ratio and in presence of Et<sub>3</sub>NH. In addition, the synthesis of diaryloxy-titanocenes (for example, [Ti](OC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub>)<sub>2</sub>) is reported by changing the ratio of **1** and ROH to 1:2. This synthesis methodology also allows the preparation of dinuclear complexes of composition ([Ti](Cl))<sub>2</sub>(μ-OC<sub>6</sub>H<sub>4</sub>O) and ([Ti](Cl))(μ-OC<sub>6</sub>H<sub>4</sub>-4))<sub>2</sub>, respectively. Cyclic voltammetric studies showed no influence of the nature of the alkyloxy substituent on the electronic properties of the titanium(IV) ion. In contrast, for the phenol-substituted titanocenes a strong influence was observed and the [Ti(IV)/Ti(III)] reduction potentials could be correlated with the σ<sub>p/m</sub> Hammett substituent constants. Aryloxy-titanocenes, featuring a hydroquinone unit as given in [Ti](Cl)(OC<sub>6</sub>H<sub>4</sub>-4-OMe) or ([Ti](Cl))<sub>2</sub>(μ-OC<sub>6</sub>H<sub>4</sub>O), can be easier oxidized than the related dimethoxy ether- or 1,4-dimethoxybenzene-functionalized ones, which suggest an effective resonance stabilization of the oxidized species.

Cyclic voltammetric, IR and solid state data point to an electron transfer *via* the oxygen atom between the aryloxy group and the

Ti(IV) ion. Furthermore, it is possible to predict the electronic configuration at titanium by selecting appropriately substituted phenols.

## 4. Experimental

### 4.1. General methods

All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, benzene and *n*-hexane were purified by distillation from sodium/benzophenone ketyl. MeOH was purified by distillation from magnesium. Et<sub>2</sub>NH and Et<sub>3</sub>N were dried by distillation from KOH. NMR spectra were recorded with a Bruker Avance 250 spectrometer (<sup>1</sup>H NMR at 250.12 MHz, <sup>13</sup>C{<sup>1</sup>H} NMR at 62.86 MHz and <sup>31</sup>P{<sup>1</sup>H} NMR at 101.20 MHz) in the Fourier transform mode. Chemical shifts are reported in  $\delta$  units (parts per million) downfield from tetramethylsilane ( $\delta = 0.0$  ppm) with the solvent as the reference signal (CDCl<sub>3</sub>: <sup>1</sup>H NMR,  $\delta = 7.26$  ppm; <sup>13</sup>C{<sup>1</sup>H} NMR,  $\delta = 77.0$  ppm). <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded with P(OMe)<sub>3</sub> ( $\delta = 139.0$  ppm) as external reference rel. to H<sub>3</sub>PO<sub>4</sub> ( $\delta = 0.0$  ppm). Cyclic voltammograms were recorded in a dried cell purged with argon at 25 °C. Platinum wires served as working and as counter electrode. A saturated calomel electrode served as reference electrode. For ease of comparison, all electrode potentials are converted using the redox potential of the ferrocene-ferrocenium couple FcH/FcH<sup>+</sup> (FcH = ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe) as the reference ( $E_0 = 0.00$  V) [34]. Electrolyte solutions were prepared from [*n*-Bu<sub>4</sub>N]PF<sub>6</sub> (dried in oil-pump vacuum at 120 °C,  $c = 0.1$  M) and freshly distilled tetrahydrofuran. The respective organometallic complexes were added at  $c = 1$  mM. Cyclic voltammograms were recorded at a scan rate of 100 mV s<sup>-1</sup> using a Radiometer Copenhagen DEA 101 Digital Electrochemical Analyzer with an IMT 102 Electrochemical Interface. Melting points were determined using sealed nitrogen purged capillaries on a Gallenkamp melting point apparatus. Microanalyses were performed by the Department of Organic Chemistry at Chemnitz, Technical University.

### 4.2. General remarks

[Ti]Cl<sub>2</sub> (**1**) [35], HOCH<sub>2</sub>PPh<sub>2</sub> [36] and HOCH<sub>2</sub>Fc [37] were prepared following published procedures. All other chemicals were purchased from commercial sources and were used without any further purification.

#### 4.2.1. Synthesis of [Ti](Cl)(OMe) (**2**)

Five hundred milligrams (1.27 mmol) of [Ti]Cl<sub>2</sub> (**1**) and 41 mg (1.28 mmol) of methanol were dissolved in 150 mL of diethyl ether and 0.20 mL of Et<sub>2</sub>NH were added in a single portion. The reaction solution was stirred for 4 h at 25 °C. Filtration through a pad of Celite and evaporation of the eluate under reduced pressure gave 470 mg (1.21 mmol, 95% based on **1**) of the title compound as a red solid.

M.p.: [°C] 156 (dec.). <sup>1</sup>H NMR (CDCl<sub>3</sub>): [ $\delta$ ] 0.21 (s, 18H, SiMe<sub>3</sub>), 4.17 (s, OCH<sub>3</sub>), 6.34 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.37 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.47 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.58 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [ $\delta$ ] -0.3 (SiMe<sub>3</sub>), 70.4 (OCH<sub>3</sub>), 116.8 (CH/C<sub>5</sub>H<sub>4</sub>), 117.1 (CH/C<sub>5</sub>H<sub>4</sub>), 123.1 (CH/C<sub>5</sub>H<sub>4</sub>), 126.1 (CH/C<sub>5</sub>H<sub>4</sub>), 128.8 (<sup>i</sup>C/C<sub>5</sub>H<sub>4</sub>). Anal. Calc. for C<sub>17</sub>H<sub>29</sub>ClOSi<sub>2</sub>Ti (388.90): C, 52.50; H, 7.52. Found: C, 52.20; H, 7.24%.

#### 4.2.2. Synthesis of [Ti](Cl)(OCH<sub>2</sub>PPh<sub>2</sub>) (**3**)

To 1.71 g (4.35 mmol) of [Ti]Cl<sub>2</sub> (**1**) and 940 mg (4.35 mmol) of HOCH<sub>2</sub>PPh<sub>2</sub> dissolved in 300 mL of diethyl ether were added in a

single portion 0.60 mL of Et<sub>2</sub>NH. This reaction solution was stirred for 5 h at 25 °C. Filtration through a pad of Celite and evaporation of all volatile materials in oil-pump vacuum gave 1.85 g (3.23 mmol, 74% based on **1**) of **3** in form of a red-brown solid.

M.p.: [°C] 142 (dec.). <sup>1</sup>H NMR (CDCl<sub>3</sub>): [ $\delta$ ] 0.26 (s, 18H, SiMe<sub>3</sub>), 5.26 (d, <sup>2</sup>J<sub>PH</sub> = 7.11 Hz, 2H, CH<sub>2</sub>), 6.22 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.42 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.47 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.54 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 7.3–7.6 (m, 10H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [ $\delta$ ] -0.1 (SiMe<sub>3</sub>), 84.8 (CH<sub>2</sub>), 117.5 (CH/C<sub>5</sub>H<sub>4</sub>), 118.5 (CH/C<sub>5</sub>H<sub>4</sub>), 125.2 (CH/C<sub>6</sub>H<sub>5</sub>), 125.8 (CH/C<sub>5</sub>H<sub>4</sub>), 127.3 (<sup>i</sup>C/C<sub>5</sub>H<sub>4</sub>), 128.2 (CH/C<sub>5</sub>H<sub>4</sub>), 128.4 (d, <sup>3</sup>J<sub>CP</sub> = 14.0 Hz, CH/C<sub>6</sub>H<sub>5</sub>), 133.2 (d, <sup>2</sup>J<sub>CP</sub> = 17.5 Hz, CH/C<sub>6</sub>H<sub>5</sub>), 136.9 (d, <sup>1</sup>J<sub>CP</sub> = 14.5 Hz, <sup>i</sup>C/C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): -10.6 (PPh<sub>2</sub>). Anal. Calc. for C<sub>29</sub>H<sub>38</sub>ClOSi<sub>2</sub>Ti (573.08): C, 60.78; H, 6.68. Found: C, 60.43; H, 6.40%.

#### 4.2.3. Synthesis of [Ti](Cl)(OCH<sub>2</sub>Fc) (**4**)

To a solution of 400 mg (1.02 mmol) of [Ti]Cl<sub>2</sub> (**1**) and 220 mg (1.02 mmol) of HOCH<sub>2</sub>Fc in 100 mL of diethyl ether were added 0.15 mL of Et<sub>2</sub>NH in a single portion. The reaction solution was stirred for 6 h at 25 °C and afterward it was worked-up as described above. Yield: 520 mg (0.91 mmol, 89% based on **1**) of **4**; orange-brown solid.

M.p.: [°C] 166 (dec.). <sup>1</sup>H NMR (CDCl<sub>3</sub>): [ $\delta$ ] 0.18 (s, 18H, SiMe<sub>3</sub>), 4.1 (m, 9H, Fc), 5.10 (s, 2H, CH<sub>2</sub>), 6.30 (pq, <sup>4</sup>J<sub>HH</sub> = 2.4 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.35 (pq, <sup>4</sup>J<sub>HH</sub> = 2.4 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.50 (pt, <sup>4</sup>J<sub>HH</sub> = 2.4 Hz, 4H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [ $\delta$ ] -0.1 (SiMe<sub>3</sub>), 68.0 (CH/Fc), 68.3 (CH/C<sub>5</sub>H<sub>5</sub>), 68.4 (<sup>i</sup>C/Fc), 69.1 (CH/Fc), 80.8 (CH<sub>2</sub>), 117.0 (CH/C<sub>5</sub>H<sub>4</sub>), 117.2 (CH/C<sub>5</sub>H<sub>4</sub>), 124.2 (CH/C<sub>5</sub>H<sub>4</sub>), 125.7 (CH/C<sub>5</sub>H<sub>4</sub>), 127.7 (<sup>i</sup>C/C<sub>5</sub>H<sub>4</sub>). Anal. Calc. for C<sub>27</sub>H<sub>37</sub>ClFeOSi<sub>2</sub>Ti (572.92): C, 56.60; H, 6.51. Found: C, 57.04; H, 6.64%.

#### 4.2.4. Synthesis of [Ti](Cl)(OPh) (**5**)

The synthesis and work-up procedures are identical with the one described for the preparation of **2** (500 mg (1.27 mmol) of [Ti]Cl<sub>2</sub> (**1**), 120 mg (1.28 mmol) of phenol, 150 mL of diethyl ether, and 0.3 mL of Et<sub>2</sub>NH). Yield: 500 mg (1.11 mmol, 87% based on **1**); red solid.

M.p.: [°C] 111. <sup>1</sup>H NMR (CDCl<sub>3</sub>): [ $\delta$ ] 0.24 (s, 18H, SiMe<sub>3</sub>), 6.33 (dt, <sup>4</sup>J<sub>HH</sub> = 1.9 Hz, <sup>3</sup>J<sub>HH</sub> = 3.0 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.43 (dt, <sup>4</sup>J<sub>HH</sub> = 1.9 Hz, <sup>3</sup>J<sub>HH</sub> = 3.0 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.56 (dt, <sup>3</sup>J<sub>HH</sub> = 3.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.9 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.65 (ddd, <sup>3</sup>J<sub>HH</sub> = 9.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, 2H, C<sub>6</sub>H<sub>5</sub>), 6.69 (dt, <sup>3</sup>J<sub>HH</sub> = 3.0 Hz, <sup>4</sup>J<sub>HH</sub> = 1.9 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.83 (tt, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, 1H, C<sub>6</sub>H<sub>5</sub>), 7.22 (ddd, <sup>3</sup>J<sub>HH</sub> = 9.0 Hz, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, <sup>4</sup>J<sub>HH</sub> = 3.2 Hz, 2H, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [ $\delta$ ] -0.2 (SiMe<sub>3</sub>), 114.4 (CH/C<sub>5</sub>H<sub>4</sub>), 116.8 (o-CH/C<sub>6</sub>H<sub>5</sub>), 118.2 (CH/C<sub>5</sub>H<sub>4</sub>), 119.9 (p-CH/C<sub>6</sub>H<sub>5</sub>), 126.5 (CH/C<sub>5</sub>H<sub>4</sub>), 128.8 (<sup>i</sup>C/C<sub>5</sub>H<sub>4</sub>), 128.9 (CH/C<sub>5</sub>H<sub>4</sub>), 129.0 (m-CH/C<sub>6</sub>H<sub>5</sub>), 170.9 (C=O). Anal. Calc. for C<sub>22</sub>H<sub>31</sub>ClOSi<sub>2</sub>Ti (450.97): C, 58.59; H, 6.93. Found: C, 58.87; H, 6.85%.

#### 4.2.5. Synthesis of [Ti](Cl)(OC<sub>6</sub>H<sub>4</sub>-4-C≡N) (**6**)

The synthesis and work-up procedures are identical with the one described for the preparation of **3** (787 mg (2.00 mmol) of [Ti]Cl<sub>2</sub> (**1**), 238 mg (2.00 mmol) of HOC<sub>6</sub>H<sub>4</sub>-4-C≡N, 200 mL of diethyl ether, and 0.3 mL of Et<sub>2</sub>NH). Yield: 915 mg (1.92 mmol, 96% based on **1**); orange solid.

M.p.: [°C] 123. IR (KBr): [cm<sup>-1</sup>] 2220 (s) [ $\nu_{\text{C}\equiv\text{N}}$ ]. <sup>1</sup>H NMR (CDCl<sub>3</sub>): [ $\delta$ ] 0.21 (s, 18H, SiMe<sub>3</sub>), 6.39 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.43 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.53 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.67 (dd, <sup>3</sup>J<sub>HH</sub> = 6.79 Hz, <sup>4</sup>J<sub>HH</sub> = 2.05 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 6.71 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 7.50 (dd, <sup>3</sup>J<sub>HH</sub> = 6.79 Hz, <sup>4</sup>J<sub>HH</sub> = 2.05 Hz, 2H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [ $\delta$ ] -0.5 (SiMe<sub>3</sub>), 101.1 (C≡N), 115.0 (CH/C<sub>5</sub>H<sub>4</sub>), 117.9 (CH/C<sub>6</sub>H<sub>5</sub>), 119.0 (CH/C<sub>5</sub>H<sub>4</sub>), 119.9 (C≡N), 127.0 (CH/C<sub>5</sub>H<sub>4</sub>), 128.9 (CH/C<sub>5</sub>H<sub>4</sub>), 130.3 (<sup>i</sup>C/C<sub>5</sub>H<sub>4</sub>), 133.5 (CH/C<sub>6</sub>H<sub>5</sub>),

173.4 (C–OTi). Anal. Calc. for  $C_{23}H_{30}ClNO_3Si_2Ti$  (476.01): C, 58.04; H, 6.35; N, 2.94. Found: C, 58.07; H, 6.79; N, 3.34%.

#### 4.2.6. Synthesis of [Ti](Cl)(OC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub>) (7)

The synthesis is identical with the one described for the preparation of **3** (393 mg (1.00 mmol) of [Ti]Cl<sub>2</sub> (**1**), 139 mg (1.00 mmol) of HOC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub>, 100 mL of diethyl ether, and 0.15 mL of Et<sub>2</sub>NH). Traces of **1** can be removed by fractional crystallization from a solution of **1** and **7** in 20 mL of diethyl ether at -30 °C. Yield: 415 mg (0.84 mmol, 84% based on **1**); red-brown solid.

M.p.: [°C] 131 (dec.). IR (KBr): [cm<sup>-1</sup>] 1336 [ $\nu_{N-O, sym}$ ], 1489 (m) [ $\nu_{C-C, str}$ ], 1582 (s) [ $\nu_{N-O, asym}$ ]. <sup>1</sup>H NMR (CDCl<sub>3</sub>): [δ] 0.21 (s, 18H, SiMe<sub>3</sub>), 6.42 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.46 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.55 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.66 (dd, <sup>3</sup>J<sub>HH</sub> = 9.2 Hz, <sup>4</sup>J<sub>HH</sub> = 2.2 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 6.73 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 8.13 (dd, <sup>3</sup>J<sub>HH</sub> = 9.2 Hz, <sup>4</sup>J<sub>HH</sub> = 2.2 Hz, 2H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] -0.3 (SiMe<sub>3</sub>), 115.1 (CH/C<sub>5</sub>H<sub>4</sub>), 117.2 (CH/C<sub>6</sub>H<sub>4</sub>), 119.2 (CH/C<sub>5</sub>H<sub>4</sub>), 125.9 (CH/C<sub>6</sub>H<sub>4</sub>), 127.4 (CH/C<sub>5</sub>H<sub>4</sub>), 129.2 (CH/C<sub>5</sub>H<sub>4</sub>), 130.8 (<sup>1</sup>C/C<sub>5</sub>H<sub>4</sub>), 139.9 (<sup>1</sup>C/C<sub>6</sub>H<sub>4</sub>), 175.6 (C–OTi). Anal. Calc. for  $C_{22}H_{30}ClNO_3Si_2Ti$  (495.97): C, 53.28; H, 6.10; N, 2.82. Found: C, 52.90; H, 6.18; N, 2.82%.

#### 4.2.7. Synthesis of [Ti](Cl)(OC<sub>6</sub>H<sub>4</sub>-4-Me) (8)

The synthesis and work-up procedures are identical with the one described for the preparation of **2** (393 mg (1.00 mmol) of [Ti]Cl<sub>2</sub> (**1**), 108 mg (1.00 mmol) of HOC<sub>6</sub>H<sub>4</sub>-4-CH<sub>3</sub>, 100 mL of diethyl ether, and 0.15 mL of Et<sub>2</sub>NH). Yield: 445 mg (0.95 mmol, 95% based on **1**); red solid.

M.p.: [°C] 142. <sup>1</sup>H NMR (CDCl<sub>3</sub>): [δ] 0.24 (s, 18H, SiMe<sub>3</sub>), 2.29 (s, 3H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 6.32 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.42 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.55 (m, 4H, C<sub>5</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>4</sub>), 6.69 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 7.02 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] -0.2 (SiMe<sub>3</sub>), 20.6 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 114.3 (CH/C<sub>5</sub>H<sub>4</sub>), 116.4 (CH/C<sub>6</sub>H<sub>4</sub>), 118.4 (CH/C<sub>5</sub>H<sub>4</sub>), 126.2 (CH/C<sub>5</sub>H<sub>4</sub>), 129.1 (CH/C<sub>5</sub>H<sub>4</sub>), 129.4 (CH/C<sub>6</sub>H<sub>4</sub>), 128.4 (<sup>1</sup>C/C<sub>5</sub>H<sub>4</sub>), 128.8 (<sup>1</sup>C/C<sub>6</sub>H<sub>4</sub>), 169.1 (C–OTi). Anal. Calc. for  $C_{23}H_{33}ClO_3Si_2Ti$  (465.00): C, 59.41; H, 7.15. Found: C, 59.20; H, 6.90%.

#### 4.2.8. Synthesis of [Ti](Cl)(OC<sub>6</sub>H<sub>4</sub>-4-OMe) (9)

The synthesis and work-up procedures are identical with the one described for the preparation of **2** (200 mg (0.51 mmol) of [Ti]Cl<sub>2</sub> (**1**), 63 mg (0.51 mmol) of HOC<sub>6</sub>H<sub>4</sub>-4-OMe, 50 mL of diethyl ether, and 0.10 mL of Et<sub>2</sub>NH). Yield: 230 mg (0.48 mmol, 94% based on **1**); purple solid.

M.p.: [°C] 146. <sup>1</sup>H NMR (CDCl<sub>3</sub>): [δ] 0.22 (s, 18H, SiMe<sub>3</sub>), 3.81 (s, 3H, OCH<sub>3</sub>), 6.31 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.39 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.52 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.61 (dd, <sup>3</sup>J<sub>HH</sub> = 9.3 Hz, <sup>4</sup>J<sub>HH</sub> = 3.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 6.67 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.77 (dd, <sup>3</sup>J<sub>HH</sub> = 9.3 Hz, <sup>4</sup>J<sub>HH</sub> = 3.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] -0.2 (SiMe<sub>3</sub>), 55.6 (OCH<sub>3</sub>), 113.9 (CH/C<sub>6</sub>H<sub>4</sub>), 114.5 (CH/C<sub>5</sub>H<sub>4</sub>), 117.1 (CH/C<sub>6</sub>H<sub>4</sub>), 118.4 (CH/C<sub>5</sub>H<sub>4</sub>), 125.9 (CH/C<sub>5</sub>H<sub>4</sub>), 128.3 (<sup>1</sup>C/C<sub>5</sub>H<sub>4</sub>), 129.1 (CH/C<sub>5</sub>H<sub>4</sub>), 153.0 (<sup>1</sup>C/C<sub>6</sub>H<sub>4</sub>), 165.9 (C–OTi). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] -5.74 (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>). Anal. Calc. for  $C_{23}H_{33}ClO_3Si_2Ti$  (467.01): C, 57.43; H, 6.92. Found: C, 57.54; H, 6.94%.

#### 4.2.9. Synthesis of [Ti](Cl)(OC<sub>6</sub>H<sub>4</sub>-4-C(O)Me) (10)

The synthesis and work-up procedures are identical with the one described for the preparation of **2** (393 mg (1.00 mmol) of [Ti]Cl<sub>2</sub> (**1**), 136 mg (1.00 mmol) of HOC<sub>6</sub>H<sub>4</sub>-4-C(O)Me, 100 mL of diethyl ether, and 0.15 mL of Et<sub>2</sub>NH). Yield: 460 mg (0.95 mmol, 95% based on **1**); orange-red solid.

M.p.: [°C] 117. IR (KBr): [cm<sup>-1</sup>] 1673 (s) [ $\nu_{C=O}$ ]. <sup>1</sup>H NMR (CDCl<sub>3</sub>): [δ] 0.21 (s, 18H, SiMe<sub>3</sub>), 2.55 (s, C(=O)CH<sub>3</sub>), 6.37 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.44 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.55 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.64 (dd, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 6.70 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 7.78 (dd, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] -0.3 (SiMe<sub>3</sub>), 26.2 (C(=O)CH<sub>3</sub>), 114.7 (CH/C<sub>5</sub>H<sub>4</sub>), 116.9 (CH/C<sub>6</sub>H<sub>4</sub>), 118.8 (CH/C<sub>5</sub>H<sub>4</sub>), 127.1 (CH/C<sub>5</sub>H<sub>4</sub>), 128.8 (<sup>1</sup>C/C<sub>6</sub>H<sub>4</sub>), 129.2 (CH/C<sub>5</sub>H<sub>4</sub>), 130.0 (<sup>1</sup>C/C<sub>5</sub>H<sub>4</sub>), 130.5 (CH/C<sub>6</sub>H<sub>4</sub>), 174.7 (C–OTi), 197.0 (C=O). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] -5.53 (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>). Anal. Calc. for  $C_{24}H_{33}ClO_2Si_2Ti$  (493.01): C, 58.47; H, 6.75. Found: C, 58.07; H, 6.98%.

#### 4.2.10. Synthesis of [Ti](Cl)(OC<sub>6</sub>H<sub>4</sub>-4-CO<sub>2</sub>Me) (11)

The synthesis and work-up procedures are identical with the one described for the preparation of **2** (393 mg (1.00 mmol) of [Ti]Cl<sub>2</sub> (**1**), 152 mg (1.00 mmol) of HOC<sub>6</sub>H<sub>4</sub>-4-CO<sub>2</sub>CH<sub>3</sub>, and 100 mL of diethyl ether, 0.15 mL Et<sub>2</sub>NH). Yield: 500 mg (0.98 mmol, 98% based on **1**); orange solid.

M.p.: [°C] 119. IR (KBr): [cm<sup>-1</sup>] 1712 (s) [ $\nu_{C=O}$ ]. <sup>1</sup>H NMR (CDCl<sub>3</sub>): [δ] 0.21 (s, 18H, SiMe<sub>3</sub>), 4.16 (s, 3H, OCH<sub>3</sub>), 6.36 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.44 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.54 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.63 (dd, <sup>3</sup>J<sub>HH</sub> = 6.79 Hz, <sup>4</sup>J<sub>HH</sub> = 2.05 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 6.70 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 7.98 (dd, <sup>3</sup>J<sub>HH</sub> = 6.79 Hz, <sup>4</sup>J<sub>HH</sub> = 2.05 Hz, 2H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] -0.2 (SiMe<sub>3</sub>), 51.7 (OCH<sub>3</sub>), 114.7 (CH/C<sub>5</sub>H<sub>4</sub>), 121.0 (<sup>1</sup>C/C<sub>6</sub>H<sub>4</sub>), 116.8 (CH/C<sub>6</sub>H<sub>4</sub>), 118.7 (CH/C<sub>5</sub>H<sub>4</sub>), 127.0 (CH/C<sub>5</sub>H<sub>4</sub>), 129.2 (CH/C<sub>5</sub>H<sub>4</sub>), 129.9 (<sup>1</sup>C/C<sub>5</sub>H<sub>4</sub>), 131.4 (CH/C<sub>6</sub>H<sub>4</sub>), 167.3 (C=O), 174.4 (C–OTi). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] -5.48 (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>). Anal. Calc. for  $C_{24}H_{33}ClO_3Si_2Ti$  (509.11): C, 56.63; H, 6.54. Found: C, 56.39; H, 6.52%.

#### 4.2.11. Synthesis of [Ti](Cl)(OC<sub>6</sub>H<sub>4</sub>-3-NO<sub>2</sub>) (12)

The synthesis and work-up procedures are identical with the one described for the preparation of **3** (393 mg (1.00 mmol) of [Ti]Cl<sub>2</sub> (**1**), 139 mg (1.00 mmol) of HOC<sub>6</sub>H<sub>4</sub>-3-NO<sub>2</sub>, 100 mL of diethyl ether, and 0.15 mL of Et<sub>2</sub>NH). Yield: 450 mg (0.91 mmol, 91% based on **1**); orange solid.

M.p.: [°C] 96 (dec.). IR (KBr): [cm<sup>-1</sup>] 1350 [ $\nu_{N-O, sym}$ ], 1473 (m) [ $\nu_{C-C, str}$ ], 1526 (s) [ $\nu_{N-O, asym}$ ]. <sup>1</sup>H NMR (CDCl<sub>3</sub>): [δ] 0.22 (s, 18H, SiMe<sub>3</sub>), 6.40 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.44 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.55 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.72 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 7.05 (ddd, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, <sup>4</sup>J<sub>HH</sub> = 2.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, 1H, C<sub>6</sub>H<sub>4</sub>-4), 7.34 (t, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 1H, C<sub>6</sub>H<sub>4</sub>-5), 7.37 (t, <sup>4</sup>J<sub>HH</sub> = 2.3 Hz, 1H, C<sub>6</sub>H<sub>4</sub>-2), 7.67 (ddd, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, <sup>4</sup>J<sub>HH</sub> = 2.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.0 Hz, 1H, C<sub>6</sub>H<sub>4</sub>-6). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] -0.3 (SiMe<sub>3</sub>), 111.5 (C<sup>2</sup>H/C<sub>6</sub>H<sub>4</sub>), 114.0 (C<sup>6</sup>H/C<sub>6</sub>H<sub>4</sub>), 115.0 (CH/C<sub>5</sub>H<sub>4</sub>), 119.1 (CH/C<sub>5</sub>H<sub>4</sub>), 123.8 (C<sup>4</sup>H/C<sub>6</sub>H<sub>4</sub>), 127.2 (CH/C<sub>5</sub>H<sub>4</sub>), 128.9 (CH/C<sub>5</sub>H<sub>4</sub>), 129.4 (<sup>1</sup>C/C<sub>5</sub>H<sub>4</sub>), 130.4 (C<sup>5</sup>H/C<sub>6</sub>H<sub>4</sub>), 149.0 (<sup>1</sup>C<sup>3</sup>H/C<sub>6</sub>H<sub>4</sub>), 170.2 (C–OTi). <sup>29</sup>Si{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] -5.37 (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>). Anal. Calc. for  $C_{22}H_{30}ClNO_3Si_2Ti$  (495.97): C, 53.28; H, 6.10; N, 2.82. Found: C, 52.96; H, 6.23; N, 2.90%.

#### 4.2.12. Synthesis of [Ti](OC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub>)<sub>2</sub> (13)

The synthesis and work-up procedures are identical with the one described for the preparation of **3** (393 mg (1.00 mmol) of [Ti]Cl<sub>2</sub> (**1**), 290 mg (2.1 mmol) of HOC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub>, 100 mL of diethyl ether, and 0.30 mL of Et<sub>2</sub>NH). Yield: 415 mg (0.84 mmol, 84% based on **1**); orange solid.

M.p.: [°C] 134 (dec.). IR (KBr): [cm<sup>-1</sup>] 1341 [ $\nu_{N-O, sym}$ ], 1487 (m) [ $\nu_{C-C, str}$ ], 1491 (m) [ $\nu_{C-C, str}$ ], 1581 (s) [ $\nu_{N-O, asym}$ ], 1587 (s) [ $\nu_{N-O, asym}$ ]. <sup>1</sup>H NMR (CDCl<sub>3</sub>): [δ] 0.15 (s, 18H, SiMe<sub>3</sub>), 6.45 (pt, <sup>3</sup>J<sub>HH</sub> = 2.3 Hz, 4H, C<sub>5</sub>H<sub>4</sub>), 6.59 (dd, <sup>3</sup>J<sub>HH</sub> = 9.1 Hz, <sup>4</sup>J<sub>HH</sub> = 2.5 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 6.63 (pt, <sup>3</sup>J<sub>HH</sub> = 2.3 Hz, 4H, C<sub>5</sub>H<sub>4</sub>), 8.19 (dd, <sup>3</sup>J<sub>HH</sub> = 9.1 Hz, <sup>4</sup>J<sub>HH</sub> = 2.5 Hz, 4H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] -0.5 (SiMe<sub>3</sub>),

115.8 (CH/C<sub>5</sub>H<sub>4</sub>), 117.8 (CH/C<sub>6</sub>H<sub>4</sub>), 126.1 (CH/C<sub>6</sub>H<sub>4</sub>), 126.8 (CH/C<sub>5</sub>H<sub>4</sub>), 131.2 (<sup>13</sup>C/C<sub>5</sub>H<sub>4</sub>), 139.4 (<sup>13</sup>C/C<sub>6</sub>H<sub>4</sub>), 174.8 (C–OTi). Anal. Calc. for C<sub>28</sub>H<sub>34</sub>N<sub>2</sub>O<sub>6</sub>Si<sub>2</sub>Ti (598.62): C, 56.18; H, 5.72; N, 4.68. Found: C, 56.43; H, 5.71; N, 4.38%.

#### 4.2.13. Synthesis of ([Ti]Cl)<sub>2</sub>(μ-OC<sub>6</sub>H<sub>4</sub>O) (14)

The synthesis and work-up procedures are identical with the one described for the preparation of **2** (393 mg (1.00 mmol) of [Ti]Cl<sub>2</sub> (**1**), 55 mg (0.50 mmol) of C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>-1,4, 150 mL of diethyl ether, and 0.20 mL of Et<sub>2</sub>NH). Yield: 390 mg (0.47 mmol, 95% based on **1**); purple solid.

M.p.: [°C] 96 (dec.). <sup>1</sup>H NMR (CDCl<sub>3</sub>): [δ] 0.22 (s, 36H, SiMe<sub>3</sub>), 6.35 (pt, J<sub>HH</sub> = 2.4 Hz, 8H, C<sub>5</sub>H<sub>4</sub>), 6.54 (s, 4H, C<sub>6</sub>H<sub>4</sub>), 6.57 (pq, J<sub>HH</sub> = 2.1 Hz, 4H, C<sub>5</sub>H<sub>4</sub>), 6.65 (pq, J<sub>HH</sub> = 2.1 Hz, 4H, C<sub>5</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] –0.2 (SiMe<sub>3</sub>), 115.5 (CH/C<sub>5</sub>H<sub>4</sub>), 116.5 (CH/C<sub>6</sub>H<sub>4</sub>), 118.3 (CH/C<sub>5</sub>H<sub>4</sub>), 125.9 (CH/C<sub>5</sub>H<sub>4</sub>), 127.9 (<sup>13</sup>C/C<sub>5</sub>H<sub>4</sub>), 128.3 (CH/C<sub>5</sub>H<sub>4</sub>), 166.1 (C–OTi). Anal. Calc. for C<sub>38</sub>H<sub>56</sub>Cl<sub>2</sub>O<sub>2</sub>Si<sub>4</sub>Ti<sub>2</sub> (823.93): C, 55.40; H, 6.85. Found: C, 54.95; H, 7.10%.

#### 4.2.14. Synthesis of ([Ti](Cl)(μ-OC<sub>6</sub>H<sub>4</sub>-4))<sub>2</sub> (15)

The synthesis and work-up procedures are identical with the one described for the preparation of **2** (393 mg (1.00 mmol) of [Ti]Cl<sub>2</sub> (**1**), 93 mg (0.50 mmol) of HOC<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>OH, 150 mL of diethyl ether, and 0.20 mL of Et<sub>2</sub>NH). Yield: 430 mg (0.48 mmol, 96% based on **1**); red solid.

M.p.: [°C] 107 (dec.). <sup>1</sup>H NMR (CDCl<sub>3</sub>): [δ] 0.24 (s, 36H, SiMe<sub>3</sub>), 6.36 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 4H, C<sub>5</sub>H<sub>4</sub>), 6.44 (dt, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, 4H, C<sub>5</sub>H<sub>4</sub>), 6.56 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 4H, C<sub>5</sub>H<sub>4</sub>), 6.68 (dd, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 4H, C<sub>6</sub>H<sub>4</sub>), 6.69 (dt, <sup>3</sup>J<sub>HH</sub> = 3.00 Hz, <sup>4</sup>J<sub>HH</sub> = 1.90 Hz, 4H, C<sub>5</sub>H<sub>4</sub>), 7.45 (dd, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 4H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] –0.2 (SiMe<sub>3</sub>), 114.5 (CH/C<sub>5</sub>H<sub>4</sub>), 117.1 (CH/C<sub>6</sub>H<sub>4</sub>), 118.5 (CH/C<sub>5</sub>H<sub>4</sub>), 126.4 (CH/C<sub>5</sub>H<sub>4</sub>), 126.7 (CH/C<sub>6</sub>H<sub>4</sub>), 128.6 (<sup>13</sup>C/C<sub>5</sub>H<sub>4</sub>), 129.2 (CH/C<sub>5</sub>H<sub>4</sub>), 132.4 (<sup>13</sup>C/C<sub>6</sub>H<sub>4</sub>), 170.3 (C–OTi). Anal. Calc. for C<sub>44</sub>H<sub>60</sub>Cl<sub>2</sub>O<sub>2</sub>Si<sub>4</sub>Ti<sub>2</sub> (899.93): C, 58.72; H, 6.72. Found: C, 58.70; H, 6.98%.

#### 4.2.15. X-ray structure determination

X-ray structure measurements were performed with a Bruker Smart CCD equipment (Table 3) using Mo K $\alpha$  radiation. Reflections were collected in the  $\omega$ -scan mode. All data were corrected for absorption using SADABS [38]. The structures were solved by direct methods using SHELXS-97 [39] and refined by full-matrix least-square procedures on F<sup>2</sup> using SHELXL-97 [40]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms have been refined using ideal positions to their neighbored atoms (**4**, **12**, **13**) or were taken from the electron density difference map and refined freely in their positions (**5**, **9**, **11**). The nitro group in **12** is disordered and has been refined to split occupancies of 0.42/0.58 (O2–O3). The structure plots were performed with the PLATON program. [41] The figure(s) in parenthesis after each calculated value represents the standard deviation in units of the last significant digit.

### 5. Supplementary material

CCDC 686172, 686170, 686173, 686174, 686169 and 686171 contain the supplementary crystallographic data for **4**, **5**, **9**, **11**, **12** and **13**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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