



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

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ABSTRACT

Alkyloxy- and aryloxy-functionalized titanocenes of type $[\text{Ti}](\text{Cl})(\text{OR})$ ($\text{R} = \text{Me}$ (**2**), CH_2PPh_2 (**3**), CH_2Fc (**4**), C_6H_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 Et_2NH . 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 $([\text{Ti}](\text{Cl}))_2(\mu\text{-OC}_6\text{H}_4\text{-4})$ (**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 D1-Ti-D2 angles (D1 , D2 = centroids of the cyclopentadienyl ligands) of ca. 130° . In comparison to FcCH_2O -functionalized **4**, for the aryloxy-titanocenes **5**, **9**, and **11–13** a significant larger 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 α -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 \AA [8,9] unusual short, and the Ti-O-Ti bond angles are with $\approx 170^\circ$ almost linear [10]. These data suggest a partial Ti-O π -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 $[\text{Ti}](\text{Cl})(\text{OR})$ ($\text{R} = \text{Me}$, CH_2PPh_2 , CH_2Fc , C_6H_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

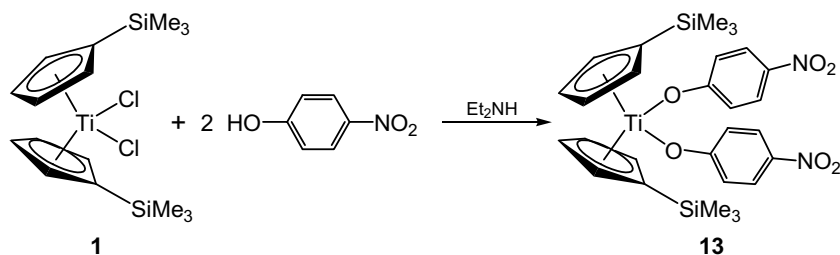
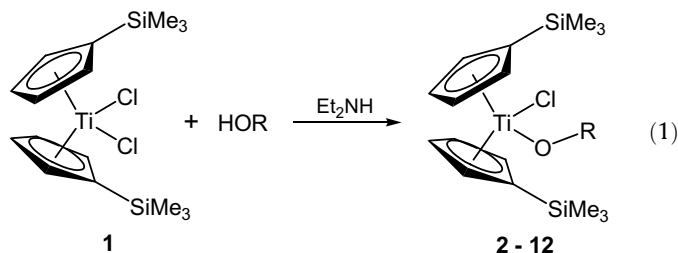
General synthetic methodologies for the preparation of alkyloxy- and aryloxy-functionalized titanocenes of type $(\eta^5\text{-C}_5\text{H}_5)_2\text{-Ti}(\text{Cl})_{2-n}(\text{OR})_n$ ($\text{R} = \text{alkyl, aryl}$; $n = 1, 2$) include the reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ 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 Et_3N is used but inorganic bases like NaHCO_3 and NaNH_2 can also be

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considered [8–12]. Another straightforward access to alkoxy- 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 alkoxy- and aryloxy-titanocene chlorides of type $[\text{Ti}](\text{Cl})(\text{OR})$ ($\text{R} = \text{Me}$ (**2**), CH_2PPh_2 (**3**), CH_2Fc (**4**), C_6H_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 ($\text{R} = \text{Me}$, CH_2PPh_2 , CH_2Fc , C_6H_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 NEt_3 more basic 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.

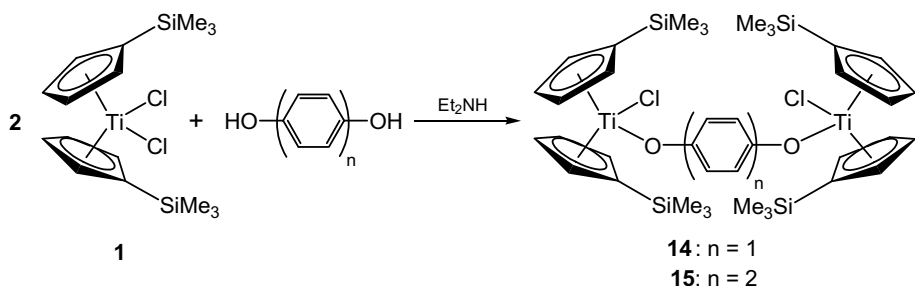


Table 1
Synthesis of **2–12** from **1** and ROH

Compound	R	Yield ^a (%)
2	Me	95
3	CH_2PPh_2	74
4	CH_2Fc^b	89
5	C_6H_5	87
6	$\text{C}_6\text{H}_4\text{-4-C}\equiv\text{N}$	96
7	$\text{C}_6\text{H}_4\text{-4-NO}_2$	84
8	$\text{C}_6\text{H}_4\text{-4-Me}$	95
9	$\text{C}_6\text{H}_4\text{-4-OMe}$	94
10	$\text{C}_6\text{H}_4\text{-4-COMe}$	95
11	$\text{C}_6\text{H}_4\text{-4-CO}_2\text{Me}$	98
12	$\text{C}_6\text{H}_4\text{-3-NO}_2$	91

^a Based on **1**.

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

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-alkoxy- 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 Et_2NH as base (Reaction 2). After appropriate work-up, organometallic **13** could be isolated as an orange solid in 84% yield.

The Et_2NH /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).

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