

# Titanocene thiolates [Ti]Cl(SCHR-2-<sup>c</sup>C<sub>4</sub>H<sub>3</sub>S) and [Ti](SCHR-2-<sup>c</sup>C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub> (R = H, Me): Synthesis, properties and reaction chemistry

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## ABSTRACT

Titanocene dichloride, [Ti]Cl<sub>2</sub> (**1**) ([Ti] = Ti(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>), with one equiv. of the lithium thiolates LiSCHR-2-<sup>c</sup>C<sub>4</sub>H<sub>3</sub>S (**2a**, R = H; **2b**, R = Me) gave the appropriate [Ti](Cl)(SCHR-2-<sup>c</sup>C<sub>4</sub>H<sub>3</sub>S) compounds (**3a**, R = H; **3b**, R = Me) under mild reaction conditions. Further treatment of **3a,b** with another equiv. of thiolates **2a,b** produced the respective bis(thiolates) species [Ti](SCHR-2-<sup>c</sup>C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub> (**4a,b**). Titanocenes **4a,b** are also accessible, when **1** is reacted with **2a,b** in a 1:2 M ratio. The hydrolysis reaction of **4a,b** produced the titanoxane cluster **5**, consisting of a [Ti']<sub>6</sub>O<sub>9</sub> cage ([Ti'] = Ti(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)) with a silsesquioxane analog structure. The molecular structure of **5** in the solid state is the first example of a trigonal prismatic Ti<sub>6</sub>-polyhedron. Upon treatment of **4a,b** with MCl<sub>2</sub> (M = Pd, Pt), aiming to obtain heterobimetallic coordination complexes, however, either **1** or **3a,b** were formed, depending on the reaction conditions. All the compounds have been characterized by elemental analysis, IR, NMR (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}) spectroscopy and mass-spectrometry.

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## 1. Introduction

Titanocene thiolates have been known since the early work of Köpf [1]. Since then, quite a number of metallocene chalcogenide complexes have been reported, including mono- and dinuclear species [2], as well as coordination polymers [3]. Their application as anti-cancer drugs, as synthons for the preparation of bimetallic and heteromultinuclear coordination complexes [4], and, for example, as homogeneous catalysts in, e.g., hydroboration [5], α-olefin polymerization [6], carbonyl coupling [7] and oxidation reactions [8,9] are reported. Fine-tuning of the electronic properties of the active metal atom to improve and optimize the activity and productivity of the homogeneous catalysts can be achieved through the functionalization of the respective thiolate ligands. Also, titanocene thiolates have been examined with the view to understanding the mechanisms of the remarkable number and variety of reactions catalyzed by such compounds [10]. In addition, titanocene thiolates can be used as SR transfer reagents [11]. Very recently, titanocene-thiolates, -oxonates and -oxo clusters have become of interest, since they can be used as preceramic materials

[12] to produce titanium sulfide or titanium oxides, respectively, at relatively low temperatures [11,13]. Also, titanium oxo clusters have been applied in twin polymerizations to obtain highly porous hybrid materials based on carbon or silicon dioxide [14].

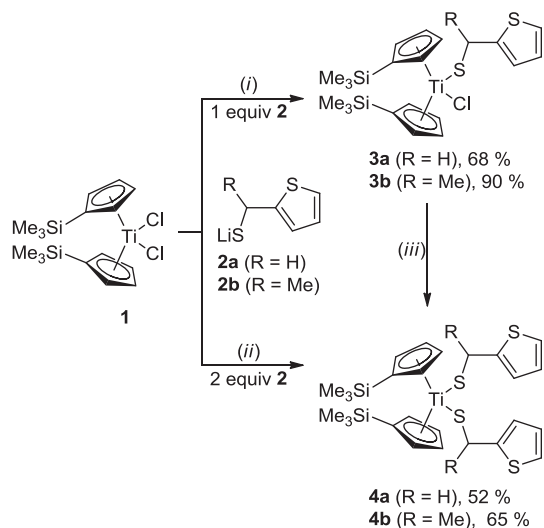
We here report on the synthesis, characterization and chemical and physical properties of mononuclear titanocene thiolates of the type [Ti](Cl)(SCHR-2-<sup>c</sup>C<sub>4</sub>H<sub>3</sub>S) and [Ti](SCHR-2-<sup>c</sup>C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub> (R = H, Me; [Ti] = Ti(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>). Their reaction behavior towards metal dichlorides MCl<sub>2</sub> (M = Pd, Pt) and against moisture is discussed as well.

## 2. Results and discussion

Treatment of [Ti]Cl<sub>2</sub> (**1**) ([Ti] = Ti(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>) with one equiv. of Li(SCH<sub>2</sub>-2-<sup>c</sup>C<sub>4</sub>H<sub>3</sub>S) (**2a**) afforded [Ti](Cl)(SCH<sub>2</sub>-2-<sup>c</sup>C<sub>4</sub>H<sub>3</sub>S) (**3a**) along with a minor amount of [Ti](SCH<sub>2</sub>-2-<sup>c</sup>C<sub>4</sub>H<sub>3</sub>S)<sub>2</sub> (**4a**) in diethyl ether as the solvent at -78 °C (Scheme 1). Both column chromatography over Celite and crystallization allowed the separation of the compounds (see Section 4). However, if instead of Celite, silica gel is used as the stationary phase, then decomposition of **3** and **4** occurred. When a methyl group is present on the methylene thiolate unit, as given in Li(SCHMe-2-<sup>c</sup>C<sub>4</sub>H<sub>3</sub>S) (**2b**), the reaction needs higher temperatures (-25 °C) to obtain the cor-

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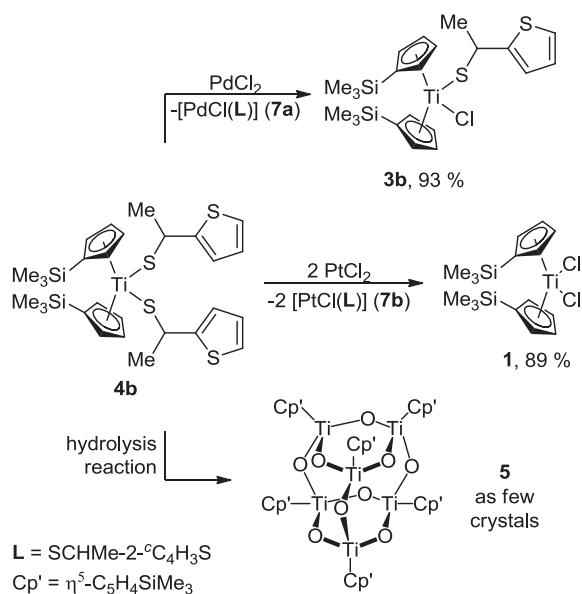
E-mail address: [d.taher@ju.edu.jo](mailto:d.taher@ju.edu.jo) (D. Taher).



**Scheme 1.** Synthesis of compounds **3a,b** and **4a,b** from **1** and **2a,b**. ((i) diethyl ether, 1 equiv. of  $\text{LiSCHR-2-}^{\text{C}}\text{C}_4\text{H}_3\text{S}$  (ii) diethyl ether, 2 equiv. of  $\text{LiSCHR-2-}^{\text{C}}\text{C}_4\text{H}_3\text{S}$ ,  $-30^\circ\text{C}$ ; Yields are based on **2a,b**; (iii) diethyl ether, 1 equiv. of  $\text{LiSCHR-2-}^{\text{C}}\text{C}_4\text{H}_3\text{S}$ .

responding mono-thiolate  $[\text{Ti}](\text{Cl})(\text{SCHMe-2-}^{\text{C}}\text{C}_4\text{H}_3\text{S})$  (**3b**) (Scheme 1). In contrast, when this reaction was carried out at ambient temperature, then next to **3b** also  $[\text{Ti}](\text{SCHMe-2-}^{\text{C}}\text{C}_4\text{H}_3\text{S})_2$  (**4b**) was formed. Changing the solvent from diethyl ether to tetrahydrofuran resulted in the formation of bis(thiolate) titanocenes **4a,b** in high yields, while **3a,b** were produced in minor amounts. After the appropriate work-up, the titanocenes **3a,b** could be isolated as wine-red solids and compounds **4a,b** as red crystals. Titanocene thiolates **4a,b** were also accessible by treatment of **1** with two equiv. of **2a,b** at  $-30^\circ\text{C}$  in good yields (Scheme 1).

Complexes **3** and **4** contain thiolate ligands and hence could act as chelating ligands towards diverse transition metal complexes to produce heterobimetallic Ti–M species. Hence, **3b** and **4b** were reacted with the metal salts  $\text{MCl}_2$  ( $\text{M} = \text{Pt}, \text{Pd}$ ) in both 1:1 and 1:2 molar ratios in diethyl ether at  $-30^\circ\text{C}$  (Scheme 2, Section 4). The reaction of **3b** with one equiv. of  $\text{MCl}_2$  resulted in the



**Scheme 2.** Reaction of **4b** with  $\text{MCl}_2$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) in 1:1 and 1:2 M ratios to give **3b** and **7a,b**, and the hydrolysis reaction of **4b** to produce cluster **5**.

formation of  $[\text{MCl}(\text{SCHMe-2-}^{\text{C}}\text{C}_4\text{H}_3\text{S})]$  (**7a**,  $\text{M} = \text{Pd}$ ; **7b**,  $\text{M} = \text{Pt}$ ) and the respective titanocene dichloride  $[\text{Ti}]\text{Cl}_2$  (**1**). On the other hand, when **4b** was reacted with  $\text{PdCl}_2$  in a 1:1 ratio, a ligand transfer of  $\text{SCHMe-2-}^{\text{C}}\text{C}_4\text{H}_3\text{S}$  from **4b** to  $\text{Pd}$  to form **7a** and the mono-thiolate **3b** was observed. Moreover, the reaction of **4b** with  $\text{PtCl}_2$  in a 2:1 ratio, induced a  $\text{SCHMe-2-}^{\text{C}}\text{C}_4\text{H}_3\text{S}$  transfer to  $\text{Pt}$  to give **7b** and titanocene dichloride  $[\text{Ti}]\text{Cl}_2$  (**1**) (Scheme 2). Thiolate transfer reactions from the bis(thiolate)titanocenes  $[\text{Ti}](\text{SET})_2$  or  $[\text{Ti}](\text{S-}^i\text{Pr})_2$  to  $[\text{PtCl}_2(\text{cod})_2]$  ( $\text{cod} = \eta^2, \eta^2\text{-1,5-cyclooctadiene}$ ) were reported [15]. Moreover, intermolecular ligand migration occurred between the titanocene complexes  $[\text{Ti}](\text{SAr})_2$  or  $[\text{Ti}]\text{Cl}(\text{SAr})$  to  $\text{PtCl}(\text{Me})(\text{cod})$  [16].

Compounds **3a,b** and **4a,b** were purified by column chromatography over Celite with diethyl ether, while **7a,b** were isolated by extraction methods. Red to wine-red solids of these species could be obtained by layering diethyl ether solutions containing either **3a,b** or **4a,b** with *n*-hexane at  $-20^\circ\text{C}$ . Complexes **3a,b**, **4a,b** and **7a,b** dissolve in polar organic solvents, including diethyl ether, tetrahydrofuran and dichloromethane, however, in hydrocarbons they are insoluble. Compounds **3a,b** and **4a,b** are stable to air and oxygen in the solid state, while in solution hydrolysis reactions to the titano-oxo cluster **5** occurred. Coordination complexes **7a,b** are stable against moisture and air, both in the solid state and in solution.

Compounds **3a,b**, **4a,b** and **7a,b** have been identified by NMR ( $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$ ) and IR spectroscopy, ESI mass-spectrometry and elemental analysis. In the IR spectra of **3**, **4** and **7** the anticipated absorptions could be observed. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **3**, **4** and **7** show the expected signal patterns in the predicted chemical shift ranges. Characteristic signals for the  $\text{CH}_2$  and  $\text{CHMe}$  protons are found between  $\delta$  4.3 and 5.3 ppm ( $\text{CH}$ ,  $\text{CH}_2$ ) and at ca.  $\delta$  1.5 ppm ( $\text{Me}$ ). The thiophene ring protons appear at  $\delta$  6.8–7.3 ppm [17], while the cyclopentadienyl hydrogen atoms are observed between  $\delta$  5.9 and 6.8 ppm as multiplets [11,18]. In addition, at ca.  $\delta$  0.2 ppm a signal for the  $\text{SiMe}_3$  groups is found.

Distinctive resonance signals of **3**, **4** and **7** in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra are seen for the CHR entities at  $\delta$  31.9 (**3a**), 43.1 (**4a**), 51.1 (**3b**), 49.6 (**4b**), 62.5 (**7a**) and 62.9 ppm (**7b**) and at ca.  $\delta$  140 (**3a**, **4a**) and 154 (**3b**, **4b**, **7a**, **7b**) ppm for the carbon atoms directly attached to the thiophene sulfur atom. The respective signals for the cyclopentadienyl and the thiophene carbons resonate between  $\delta$  111 and 139 ppm.

In the case of compound **3b**, the two diastereotopic  $\text{Cp}'$  groups result in two sets of  $\text{SiMe}_3$  and  $\text{C}_5\text{H}_4$  signals in the  $^1\text{H}$  and  $\{^1\text{H}\}^{13}\text{C}$  NMR spectra. In contrast, only one set of signals is observed for complex **4b**, indicating that one of the two possible sets of diastereomers has been formed.

Hydrolysis of either **4a** or **4b** in dichloromethane solutions afforded a few crystals of the titano-oxo cluster  $[\text{Ti}']_6\text{O}_9$  ( $[\text{Ti}'] = \text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)$ ) (**5**) (Scheme 2). The structure of **5** in the solid state was determined by single X-ray structure analysis at 173(2) K. The molecular structure of **5** is depicted in Figs. 1 and 2. Selected bond distances ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and torsion angles ( $^\circ$ ) are summarized in Table 1.

Titanoxane cage **5** consists of two planar, 6-membered  $\text{Ti}_3\text{O}_3$  rings. Both units are connected by three oxygen atoms, forming a  $\text{Ti}_6\text{O}_9$  silsequioxane analog cage with an  $\text{ABA}'$  layer structure ( $\text{A}, \text{A}' = \text{Ti}_3\text{O}_3$ ;  $\text{B} = \text{O}_3$ ). The A and A' layers are separated by 3.3785 (15)  $\text{\AA}$ , differing in their planarity (A, rmsd = 0.0076; A', rmsd = 0.0135) and are coplanar towards each other. The cage is generated by a  $\text{C}_3$  axis (Fig. 2, right), present through the midpoints of the 6-membered  $\text{Ti}_3\text{O}_3$  rings from the asymmetric unit. The Ti atoms of the 6-membered rings and the oxygen atoms, respectively, form a trigonal-prismatic coordination polyhedron, due to the eclipsed-type conformation of both rings (Fig. 2, right), which is a unique example for titanoxane clusters. Usually, 6-membered

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