



Chemical transformation of dithiolene ligands in heteroleptic and homoleptic complexes (M = Ti, Zn, Au)



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ABSTRACT

Heteroleptic and homoleptic dithiolene metal complexes such as $\text{Cp}_2\text{Ti}(\text{dithiolene})$, $[\text{Zn}(\text{dithiolene})_2]^{2-}$ and $[\text{Au}(\text{dithiolene})_2]^{-1}$ complexes have been synthesized from the 1-*tert*-butyl-1,3-thiazoline-2-thione-4,5-dithiolate (*t*Bu-thiazdt) dithiolene ligand. The reactivity of these complexes towards iodo-methane (MeI) has been examined. Both the titanocene and the gold complexes undergo a transformation of the *t*Bu-1,3-thiazoline-2-thione core to a 2-methylthio-1,3-thiazole one with elimination of the *t*Bu substituent. The reaction of MeI with the Zn complex leads to a tris(thiomethyl)-thiazole derivative due to the alkylation of the sulfur atoms and the decoordination together with the transformation into the thiazole core. Electrochemical, spectral and X-ray diffraction investigations carried out on these various complexes are also presented.

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1. Introduction

Numerous metal (1,2-dithiolene) complexes, either homoleptic or heteroleptic have been prepared for their highly unusual physical properties and their rich redox-chemistry but fewer studies were performed on the chemical reactivity of these complexes as quite often decomposition is observed [1,2]. For instance, alkylation reaction with alkyl halides might occur on the sulfur atoms of the metallacycle followed in some cases by the decoordination of the bis(alkylthio) derivative [3–5]. It has been shown also that the redox state of metal bis(1,2-dithiolene) complexes has an influence on the nucleophilicity of the sulfur atoms and thus on the reactivity. For example, the monoanion state of $[\text{M}(\text{mnt})_2]^-$ is less reactive towards alkyl halides than the corresponding dianion $[\text{M}(\text{mnt})_2]^{2-}$ [6]. Recently we have also evidenced an unprecedented transformation of *N-tert*-butyl-1,3-thiazoline-2-thione heterocycles in 2-alkylthiothiazole derivatives in the presence of electrophile such methyl iodide (Chart 1) [7].

Thus, we decided to explore the reactivity of homoleptic and heteroleptic dithiolene complexes bearing a *N-tert*-butyl-1,3-thiazoline-2-thione-4,5-dithiolate ligand towards methyl iodide. We choose methyl iodide as it is more reactive than most of the other

alkyl iodides in order to test the robustness of the metal-sulfur bond towards this electrophile while at the same time we wanted to induce the transformation of *N-tert*-butyl-1,3-thiazoline-2-thione into the 2-methylthio-1,3-thiazole. Concerning the heteroleptic complexes, we investigated the reactivity of the bis(cyclopentadienyl)/dithiolene Titanium complex formulated as $\text{Cp}_2\text{Ti}(\text{tBu-thiazdt})$. For the homoleptic complexes, we focused on bis(dithiolene) complexes of d^{10} and d^8 metal ions such as the tetrahedral dianionic zinc bis(dithiolene) complex $[\text{NET}_4]_2[\text{Zn}(\text{tBu-thiazdt})_2]$ and the square planar monanionic gold bis(dithiolene) complex, $[\text{PPh}_4][\text{Au}(\text{tBu-thiazdt})_2]$. Both the titanocene and the Zn complexes can be considered as protected form of the dithiolene ligands and these complexes have been widely used as starting material for the synthesis of various heterocycles [8,9]. Moreover, the titanocene and the Zn dithiolene complexes are also known for their ability to transfer the dithiolene ligand to softer metals. Herein we report the synthesis of three novel metal dithiolene complexes: the $\text{Cp}_2\text{Ti}(\text{tBu-thiazdt})$, the

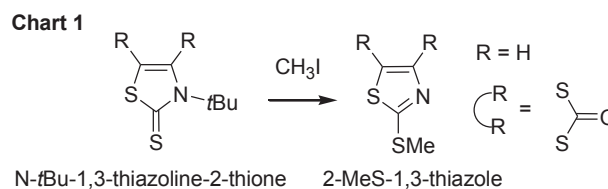


Chart 1. Reactivity of *N-tert* substituted thiazole derivatives.

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$[\text{NEt}_4]_2[\text{Zn}(\text{tBu-thiazdt})_2]$ and the $[\text{PPh}_4][\text{Au}(\text{tBu-thiazdt})_2]$ (**Chart 2**) together with their reactivity towards MeI. The transformation of the thiazoline-2-thione core into the 2-methylthio-1,3-thiazole occurs with the Ti and Au complexes without destruction of the metal dithiolene complex. Contrariwise, for the Zn complex, a transformation of the heterocycle occurs concomitantly with the alkylation of the sulfur atoms of the metallacycle, followed by the decoordination of the bis(methylthio) derivative. The spectroscopic and redox properties of the various complexes obtained as well as their X-Ray crystal structures have been compared with those of their precursors and discussed.

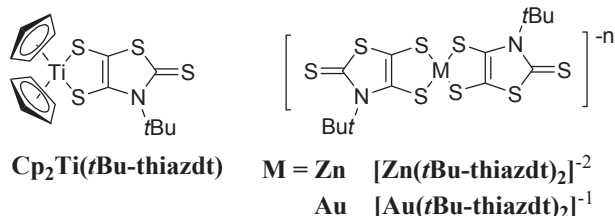
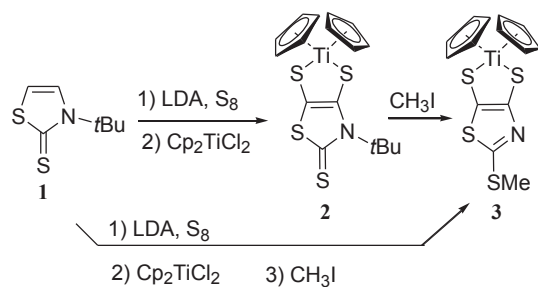


Chart 2. Investigated metal dithiolene complexes.

2. Results and discussion

2.1. Titanocene complexes

The mixed cyclopentadienyl/dithiolene target complex **2** was prepared from *N*-*t*Bu-1,3-thiazoline-2-thione **1** according to the chemical route described in **Scheme 1**. Sequential metalation of the thiazole core **1** followed by the addition of sulfur leads to the formation of the dithiolate which reacts *in situ* with Cp_2TiCl_2 . The corresponding $\text{Cp}_2\text{Ti}(\text{tBu-thiazdt})$ **2** was isolated as blue green crystals in 68% yield after purification (**Scheme 1**). Reaction of



Scheme 1.

$\text{Cp}_2\text{Ti}(\text{tBu-thiazdt})$ **2** with MeI in refluxing CH_2Cl_2 afforded the corresponding 2-methylthio-1,3-thiazole derivative, $\text{Cp}_2\text{Ti}(\text{MeS-tzdt})$ **3**, in 90% yield. In this reaction of MeI with a 1,3-thiazoline-2-thione derivative, the nucleophilic attack of the exocyclic sulfur atom on the electrophile generates the 2-methylthio-1,3-thiazolium salt [10] which evolves rapidly, in the case of the *N*-*t*Bu-derivative, to the thiazole core through the loss of *t*BuI. It is worth mentioning that the formation of $\text{Cp}_2\text{Ti}(\text{MeS-tzdt})$ **3**, can also be realized in one step by adding in the medium where **2** was formed, after the addition of LDA, successively sulfur, Cp_2TiCl_2 , and MeI. Using that strategy, the $\text{Cp}_2\text{Ti}(\text{MeS-tzdt})$ **3** was formed at room temperature in 56% yield in one step from **1**.

Crystals of the complexes $\text{Cp}_2\text{Ti}(\text{tBu-thiazdt})$ **2**, and $\text{Cp}_2\text{Ti}(\text{MeS-tzdt})$ **3** suitable for an X-ray diffraction study were obtained by slow concentration of a dichloromethane solution. They crystallize in the triclinic system, space group P-1 and the monoclinic system, space group C2/c for **2** and **3** respectively. The molecular structures are given in **Fig. 1**.

These complexes adopt a distorted tetrahedral geometry around the titanium atom with fully planar thiazoline-2-thione and thiazole cores and a non-planar metallacycle folded along the S...S axis by a θ angle (**Chart 3**). Selected bond lengths and folding angles are listed in **Table 1** together with the *N*-methyl thiazole analogue, $\text{Cp}_2\text{Ti}(\text{Me-thiazdt})$ [11], for comparison. The bond lengths, Ti–S and S–C, and bond angles, S–Ti–S and θ , in the metallacycles for all these compounds are in the same range indicating that the nature of the heterocycle, 2-methylthio-1,3-thiazole or *N*-methyl-1,3-

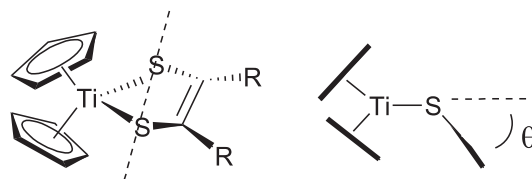


Chart 3. Folding angle θ along the S...S axis of the metallacycle.

Table 1

Significant bond lengths [Å] and angles [°], of titanocenes **2**, **3** and $\text{Cp}_2\text{Ti}(\text{Me-thiazdt})$.

Compound	Ti–S (Å)	S–C (Å)	C=C (Å)	S–Ti–S (°)	θ (°)
$\text{Cp}_2\text{Ti}(\text{tBu-thiazdt})$ 2	Ti(1): 2.4225(14)	1.723(5)	1.379(6)	83.67(5)	48.63 (2)
	2.4244(16)	1.718(5)			
	Ti(2): 2.4226(15)	1.730(5)	1.383(6)	83.24(5)	48.59(2)
	2.4306(16)	1.716(5)			
$\text{Cp}_2\text{Ti}(\text{MeS-tzdt})$ 3	2.4157(6)	1.717(2)	1.383(3)	85.48(2)	47.78(5)
	2.4588(6)	1.740(2)			
	$\text{Cp}_2\text{Ti}(\text{Me-thiazdt})$ [11]	2.4336(10)	1.714(4)	1.386(5)	85.30(4)
	2.4516(10)	1.722(3)			

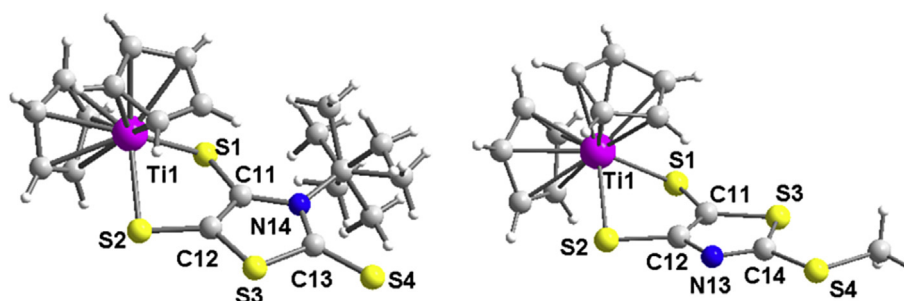


Fig. 1. Molecular structure of $\text{Cp}_2\text{Ti}(\text{tBu-thiazdt})$ **2** (left) $\text{Cp}_2\text{Ti}(\text{MeS-tzdt})$ **3** (right).

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