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Synthesis, structure, and sunlight photolysis of benzyl- and *tert*-butyl-substituted octamethyltitanocene dihydrosulfides

Michal Horáček [a], Ivana Císařová [b], Róbert Gyepes [c], Jiří Kubišta [a], Jiří Pinkas [a], Martin Lamač [a], Karel Mach [a,*]

[a] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic
[b] Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic
[c] Faculty of Education, J. Selye University, Bratislavská cesta 3322, 945 01 Komárno, Slovak Republic

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ABSTRACT

New titanocene dihydrosulfide compounds $[(C_5Me_4CH_2Ph)_2Ti(SH)_2]$ (**6**) and $[(C_5Me_4t\text{-}Bu)_2Ti(SH)_2]$ (**7**) were obtained by addition of hydrogen sulfide to the corresponding doubly tucked-in titanocenes, and titanocene hydrosulfide compounds $[(C_5Me_4CH_2Ph)_2TiSH]$ (**8**) and $[(C_5Me_4t\text{-}Bu)_2TiSH]$ (**9**) by H_2S-induced protonolysis of σ-Ti–C bonds in $[(\eta^5\text{-}C_5Me_4CH_2Ph)Ti(III)(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2\text{-}o\text{-}C_6H_4)]$ and $[(C_5Me_4t\text{-}Bu)Ti(III)(\eta^5{:}\eta^1\text{-}C_5Me_4CMe_2CH_2)]$, respectively. The crystal structures of **6**, **8**, and **9** and electronic absorption spectra of **6**–**9** in hexane solution highly resemble those of corresponding $[Cp^*_2Ti(SH)_2]$ (**1**) and $[Cp^*_2TiSH]$ (**2**), however, compounds **6** and **7** strongly differ in their sensitivity to sunlight mutually and with respect to **1**. The sunlight photolysis of **6** in toluene proceeded similarly to the process described previously for **1** except that about three times longer exposition (300 h) was required to obtain the cyclopentadienyltitanium sulfide cage cluster $[\{(C_5Me_4CH_2Ph)Ti\}_4S_6]$ (**10**) in 48% yield. In contrast, compound **7** photo-decomposed very efficiently to give compound **9** as the only isolated titanium-containing product in 87% yield. The formation of **10** can be accounted for the redox elimination of the cyclopentadiene followed by elimination of hydrogen sulfide in intramolecular condensation reaction whereas the formation of **9** requires the dissociation of SH radicals. Both the processes were recognized by Rosenthal and Beweries to concur in photodecomposition of $[Cp^*_2Ti(OH)_2]$.

1. Introduction

In contrast to biological systems where the photosynthesis is the driving force, the synthetic exploration of sunlight is still rather seldom in chemistry although it can be instrumental in a sustainable development. An example of the latter in sulfur chemistry is a photolysis-driven coupling of thiols into disulfides catalyzed by transition metal complexes. Particularly on manganese complexes the coupling is accompanied by elimination of hydrogen (Eq. (1)) [1].

$$2R{-}SH \xrightarrow{CpMn(CO)_3,h\nu} R{-}S{-}S{-}R + H_2 \qquad (1)$$

Suitable for a broadband photolysis are various titanocene (Ti(IV)) derivatives yielding products that depend on the particular ligand-to-metal excitation. Thus, titanocene dimethyls were shown to cleave the Ti–Me bond [2] whereas titanocene dihalides eliminated the Cp radical [3] except Cp_2TiI_2, where elimination of I_2 was proved [4]. The titanocene pentasulfide Cp_2TiS_5 was shown to form a transient with one Ti–S bond cleaved, however, the compound was surprisingly low-susceptible to photolysis due to an efficient recombination process [5].

Recently a zero-waste synthetic access has been used to prepare decamethyltitanocene dihydrosulfide $[Cp^*_2Ti(SH)_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (**1**) and monohydrosulfide $[Cp^*_2Ti(SH)]$ (**2**) from the doubly tucked-in titanocene $[Cp^*Ti(C_5Me_3(CH_2)_2)]$ and the singly tucked-in titanocene $[Cp^*Ti(C_5Me_4CH_2)]$, respectively, by reacting them with H_2S. Both compounds **1** and **2** appeared to be sensitive to sunlight in toluene solution; compound **1** liberating the cyclopentadiene Cp^*H and H_2S in comparable amount, and compound **2** releasing mainly Cp^*H [6]. Subsequent investigation of solid products of photolysis of **1** in toluene revealed that new cage clusters $[(Cp^*Ti)_4S_6]\cdot$toluene (**3**) and $[(Cp^*Ti)_6S_8]\cdot$toluene (**4**) can thus be obtained in 50% and 3% yield, respectively. A trace amount of another complex, $[(Cp^*Ti)_3S_4]$ (**5**) was isolated from the sunlight photolysis of **1** in hexane solution. Compound **5** was suggested to photo-dimerize to **4** (Chart 1) [7]. A tentative mechanism of the

* Corresponding author.
E-mail addresses: mach@jh-inst.cas.cz, karel.mach@jh-inst.cas.cz (K. Mach).

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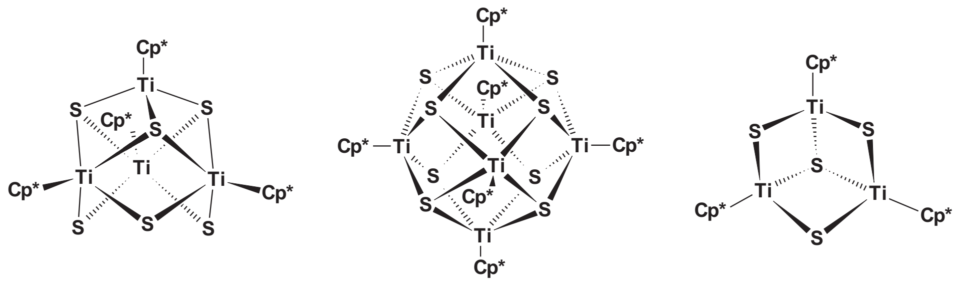


3 4 5

Chart 1. Sunlight photolysis products of $[Cp^*_2Ti(SH)_2]$.

photolytic formation of **3** and **5** was assumed to follow the reactions established for the photodecomposition of $[Cp^*_2Ti(OH)_2]$ by Rosenthal et al. [8] and Beweries [9].

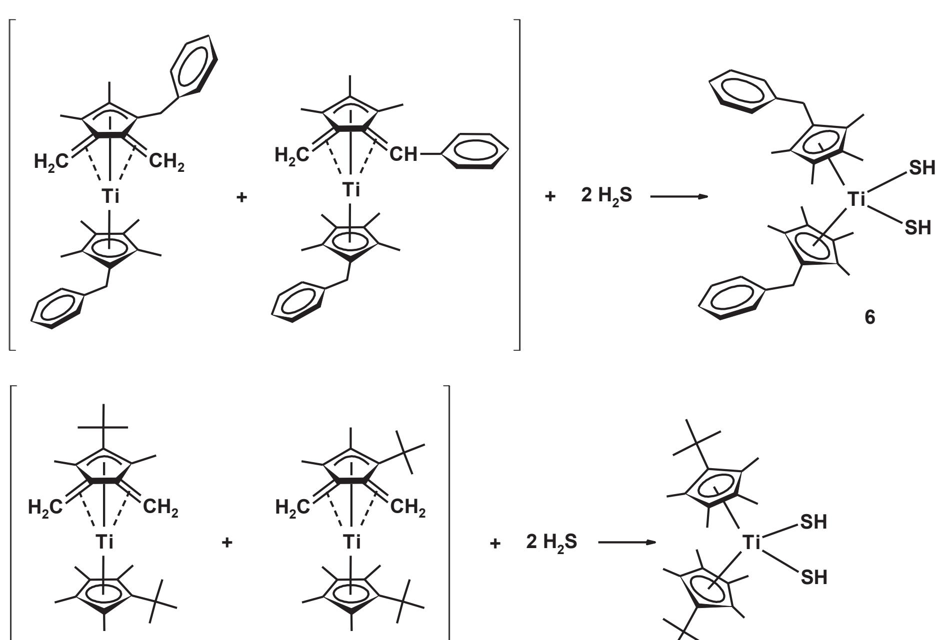
Here we report the synthesis of titanocene dihydrosulfides and monohydrosulfides containing one bulkier group R on otherwise methylated cyclopentadienyl ligands using zero-waste synthetic methods. The compounds $[(C_5Me_4R)_2Ti(SH)_2]$ (R = benzyl (**6**) and *tert*-butyl (**7**)) and $[(C_5Me_4R)_2Ti(SH)]$ (R = benzyl (**8**) and *tert*-butyl (**9**)) were investigated by the single crystal X-ray diffraction analysis, and compounds **6** and **7** were examined for their photodecomposition upon exposure to sunlight in an effort to obtain new titanium-sulfide cage compounds relevant to **3**–**5**.

2. Results and discussion

2.1. Synthesis and properties of 6–9

Compounds $[(C_5Me_4CH_2Ph)_2Ti(SH)_2]$ (**6**) and $[(C_5Me_4t\text{-}Bu)_2Ti(SH)_2]$ (**7**) were prepared from corresponding doubly tucked-in titanocenes which were obtained as mixtures of isomers from thermolyses of $[(C_5Me_4CH_2Ph)_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ [10] and $[(C_5Me_4t\text{-}Bu)_2Ti(\eta^2\text{-}C_2H_4)]$ [11] (Scheme 1).

Blue-colored doubly tucked-in titanocenes were reacted with an excess of hydrogen sulfide in toluene solution until the color of the solution turned clean red. Then, excessive hydrogen sulfide and toluene were distilled to an attached ampule cooled by liquid nitrogen. Red residues were purified by crystallization from hexane, that of **6** in semidarkness, that of **7** in darkness. Solutions of the both compounds in hexane, toluene or toluene C_7D_8 were stored in total darkness except for their photolysis by exposition to sunlight. The ^1H and ^{13}C NMR spectra of **6** and **7** displayed a similar spectral pattern consistent with the C_{2v} molecular symmetry. The signals of thiol groups were observed as singlets at 2.93 ppm for **6** and 3.12 ppm for **7**. The methyl groups on cyclopentadienyl rings appeared as two singlets (**6**: δ_H 1.81, 1.92 ppm, δ_C 12.88, 13.58 ppm; **7**: δ_H 1.61, 2.19 ppm, δ_C 12.52, 17.46 ppm). The ^1H and ^{13}C NMR resonances of the benzyl group in **6** (CH_2Ph: δ_H/δ_C 3.90/34.25 ppm) and the *tert*-butyl group in **7** (CMe_3: δ_H/δ_C 1.57/32.45 ppm) were found close to the data for the respective titanocene dichlorides $[(C_5Me_4CH_2Ph)_2TiCl_2]$ [12] and $[(C_5Me_4t\text{-}Bu)_2TiCl_2]$ [13]. Infrared spectra of KBr pellets registered ν(S–H) vibrations at 2597 cm^{-1} for



Scheme 1.