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Sulfur compounds

CXXXIII *. Synthesis and spectra of new titanocene complexes containing the chelating ligands $C_2S_4^{4-}$, $C_2S_5^{2-}$, and $C_2S_6^{2-}$

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Abstract

By analogy with the synthesis of $[(\eta^5\text{-}C_5H_5)_2Ti]_2C_2S_4$ (**1**) from $Cp_2Ti(CO)_2$ and CS_2, the compounds $[(MeC_5H_4)_2Ti]_2C_2S_4$ (**2**) and $[(Me_3SiC_5H_4)_2Ti]_2C_2S_4$ (**3**) were synthesized from the corresponding dicarbonyls ($Me = CH_3$). **1** and **2** react with SCl_2 in CH_2Cl_2 to give the corresponding mononuclear complexes $Cp'_2TiC_2S_5$ (**4**: $Cp' = C_5H_5$; **5**: $Cp' = MeC_5H_4$) containing the previously unknown $\eta^2\text{-}C_2S_5^{2-}$ ligand. Similarly, **1** and **2** react with S_2Cl_2 to give compounds of type $Cp'_2TiC_2S_6$ (**6**: $Cp' = C_5H_5$; **7**: $Cp' = MeC_5H_4$) containing the novel ligand $C_2S_6^{2-}$. UV-VIS, mass, and NMR (^1H and ^{13}C) spectra of the new compounds are reported. Compounds **1**–**7** can be separated by reversed-phase HPLC.

Introduction

Transition metal compounds containing the bridging tetrathiolene ligand, $C_2S_4^{4-}$, have been known for some time [2–7], but the corresponding titanocene derivative **1** was synthesized only recently (eq. 1) [8].

$$2\,Cp'_2Ti(CO)_2 + 2\,CS_2 \rightarrow (Cp'_2Ti)_2C_2S_4 + 4\,CO \qquad (1)$$

(**1**: $Cp' = C_5H_5$; **2**: $Cp' = MeC_5H_4$; **3**: $Cp' = Me_3SiC_5H_4$; $Me = CH_3$)

Complex **1** was characterized by infrared, mass, UV, and ^1H NMR spectroscopy [8]. An X-ray structural analysis of the dark purple (almost black) crystals of **1**

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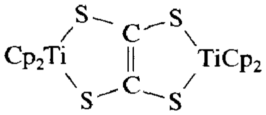
* For Part CXXXII see Ref. 1.

showed that the titanium atoms and the C_2S_4 ligand form a bicyclic, non-planar system of C_{2h} symmetry:



The C–C bond length is 141 pm [8], corresponding to a bond order of 2.

Mono- and dinuclear titanocene polysulfido complexes react with sulfur halides of type S_nCl_2 ($n = 1$–8) quantitatively to give the corresponding sulfur-ring species along with titanocene dichloride [9–12]. We therefore decided to study the analogous behaviour of **1** towards the sulfur compounds SCl_2 and S_2Cl_2.

Results and discussion

In an attempt to prepare new binary carbon sulfides **1** was treated with the sulfur chlorides SCl_2 and S_2Cl_2 (eq. 2) [13]:

$$Cp_4Ti_2C_2S_4 + 2\ S_nCl_2 \rightarrow C_2S_{4+2n} + 2\ Cp_2TiCl_2 \qquad (2)$$

$(n = 1, 2)$

Since the solubility of **1** is rather low it is difficult to carry out the reaction (eq. 2) under homogeneous conditions and to control the stoichiometric ratio of the reactants. Thus, we also prepared the previously unknown compounds **2** and **3** (eq. 1), which are more soluble, and treated these with S_nCl_2. Reaction shown in eq. 2 was found to proceed in two distinct steps, and the new compounds **4**–**7** were obtained pure by use of an ca. 1 : 1 molar ratio of the reactants (eq. 3):

$$Cp'_4Ti_2C_2S_4 + S_nCl_2 \rightarrow Cp'_2TiC_2S_{4+n} + Cp'_2TiCl_2 \qquad (3)$$

(**4**: $n = 1$, $Cp' = C_5H_5$; **5**: $n = 2$, $Cp' = C_5H_5$; **6**: $n = 1$, $Cp' = MeC_5H_4$; **7**: $n = 2$, $Cp' = MeC_5H_4$)

Compounds **2** and **3** are violet microcrystalline solids which gave satisfactory elemental analyses (C, H). Both compounds showed the molecular ion in the mass spectrum (EI, 70 eV). The ^{13}C NMR data support the proposed structures (with signals from doubly-bonded C atoms of C_2S_4 unit close to 170 ppm; see Experimental Section).

Reactions shown in eq. 3 were monitored by reversed-phase HPLC with methanol as an eluent and a UV absorption detection. Under identical conditions all seven titanocene complexes showed distinctly different retention times (t_R):

	1	**2**	**3**	**4**	**5**	**6**	**7**
t_R[min]	1.98	2.33	4.64	2.70	3.55	2.93	3.83

The increase in molecular size from **1** via **2** to **3** is reflected in the increasing retention time. Similarly, increase in the number of sulfur atoms in going from **4** to **5** and from **6** to **7** results in an enhanced retention time, as it does in homocyclic sulfur rings [14,15]. Under identical conditions the retention times of $(C_5H_5)_2TiCl_2$ and $(MeC_5H_4)_2TiCl_2$ were 1.75 and 1.82 min, respectively. The HPLC analysis of

Table 1

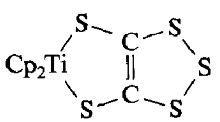
UV-VIS absorption spectra of the titanocene complexes **1**–**7** in methanol solution (values in nm; relative extinctions in parentheses).

$Cp_4Ti_2C_2S_4$	220	313	488	648	> 800
(**1**)	(10.0)	(4.2)	(0.5)	(0.2)	
$(MeCp)_4Ti_2C_2S_4$	232	310	492	636	> 800
(**2**)	(10.0)	(4.9)	(0.5)	(0.4)	
$(Me_3SiCp)_4Ti_2C_2S_4$	234	318	494	638	> 800
(**3**)	(10.0)	(4.4)	(0.7)	(0.4)	
$Cp_2TiC_2S_5$	224	294	483	670	
(**4**)	(10.0)	(2.9)	(0.5)	(1.1)	
$Cp_2TiC_2S_6$	231	300	473	645	
(**5**)	(10.0)	(3.1)	(0.4)	(1.1)	
$(MeCp)_2TiC_2S_5$	224	294	483	670	
(**6**)	(10.0)	(2.1)	(0.4)	(1.0)	
$(MeCp)_2TiC_2S_6$	231	300	473	645	
(**7**)	(10.0)	(2.3)	(0.4)	(1.0)	

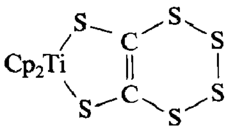
the mixtures from reactions shown in eq. 3 demonstrated that there were only two major products, one of which was identified as the corresponding titanocene dichloride from its retention time and ^1H NMR spectrum. The yield of **4**–**7** was highest when the molar ratio of the reactants (titanocene/S_nCl_2) was between 0.8 and 1.0.

By use of a diode-array detector the UV-VIS spectra of **1**–**7** were recorded at the time of their chromatographic separation (range; 200–800 nm; solvent: methanol). This technique does not allow the determination of extinction coefficients, and the relative intensities are given for the absorption bands (see Table 1). The spectra are quite similar, as would be expected from their rather similar molecular structures. The absorption at 670 nm of compounds **4** and **6** is responsible for the green colour of the solutions; **5** and **7** are blue in dichloromethane. Compound **1** shows an additional absorption near 840 nm [8], which is outside the range of our apparatus, and the same is to be expected for **2** and **3**. All three dinuclear complexes are violet in dichloromethane.

The mononuclear complexes **4**–**7** form air-stable but light-sensitive microcrystalline solids. Satisfactory single crystals could not be obtained. Satisfactory C–H analyses were obtained for **4**–**6**, but **7** has so far been characterized from its retention time and UV spectrum only. Solutions of **4**–**7** in CH_2Cl_2 slowly decompose at 20 °C. The mass spectra of **5** and **6** show the molecular ions and typical fragmentation patterns. The formation of **4**–**7** in reaction shown in eq. 3 and their spectroscopic properties indicate that these novel compounds have the following structures:

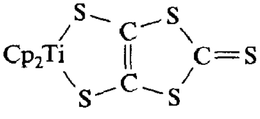


(**4** and **6**)



(**5** and **7**)

Complexes **4** and **6** resemble the recently prepared green-black $Cp_2TiC_3S_5$ [16]:



To the best of our knowledge the η^2-ligands $C_2S_5{}^{2-}$ (1,2,3-trithio-4-cyclopentene-4,5-dithiolate) and $C_2S_6{}^{2-}$ (1,2,3,4-tetrathio-5-cyclohexene-5,6-dithiolate) have not been prepared before. When **5** was treated with S_2Cl_2 at 0 °C in dilute methylene chloride Cp_2TiCl_2 was formed, and a new and strong HPLC peak indicated that reaction shown in eq. 4 had taken place:

$$(C_5H_5)_2TiC_2S_6 + S_2Cl_2 \rightarrow C_2S_8 + (C_5H_5)_2TiCl_2 \qquad (4)$$

The new peak ($t_R = 4.57$ min) was strongest at a molar ratio of $\mathbf{5}/S_2Cl_2 = 1{:}1.0$; the UV absorption spectrum of this product showed peaks at 245 and 385 nm in the range 200–800 nm, indicating that it is not a titanocene derivative. Attempts to isolate the C_2S_8 from the solution gave an orange-colored microcrystalline light-sensitive solid which was soluble in CS_2 and CH_2Cl_2 (from both of which it could be recovered unchanged), contained carbon (9.6%) and sulfur only and exhibited the ions CS^+, C_2S^+, CS_2^+, and S_n^+ ($n = 1$–8) in the EI mass spectrum (70 eV). The carbon content calculated for C_2S_8 is 8.6%. A more detailed investigation of this novel carbon sulfide is in progress.

Experimental

The following spectrometers were used: Varian MAT 311 A mass spectrometer (EI, 70 eV); Bruker WP 80 and Varian EM 390 NMR-spectrometers for ^1H and Bruker WM 270 for ^{13}C NMR spectra. Chemical shifts are given in ppm relative to internal $SiMe_4$ for ^1H and ^{13}C.

HPLC equipment: Varian 5000 pump (microprocessor controlled) with Rheodyne loop injector (10 μl), Waters Radial Pak 10C18 reversed-phase column (length 10 cm, inner diameter 8 mm) contained in a compression module, UV absorbance detector operating at 254 nm, Waters 990 diode-array detector with NEC APC III computer (512 diodes, range 190–800 nm). Freshly distilled and degassed methanol was used as eluent.

Preparations

All manipulations were carried out with exclusion of air and moisture. Solvents were carefully dried and distilled. Complex **1** was made as described by Harris et al. [8] (involving reaction of titanocene dicarbonyl with an excess of CS_2), and **2** and **3** were prepared analogously. The three titanocene dicarbonyls were made from the corresponding dichlorides [17] by treatment with $HgCl_2$ activated magnesium and carbon monoxide in tetrahydrofuran, as described by Sikora et al. [18]. When $(MeC_5H_4)_2Ti(CO)_2$ or $(Me_3SiC_5H_4)_2Ti(CO)_2$ was used the volume of CS_2 was reduced to 5 ml by evaporation after complete reactions, the mixture kept at −20 °C for 12 h, the precipitate separated, washed with 10 ml n-hexane, and extracted into CH_2Cl_2. Yield in the case of **3**: 0.54 g (31%) from 1.66 g of $(Me_3SiC_5H_4)_2Ti(CO)_2$.

$(CH_3C_5H_4)_4Ti_2C_2S_4$ (2). ^{1}H-NMR $\delta(CDCl_3)$: 2.01s, (me), 5.75br, (Cp); ^{13}C-NMR $\delta(CDCl_3)$: 16.4 (Me), 109.5, 115.3, 123.2, (Cp), 168 (C=C); EI-MS (70 eV): m/z 564 (70% M^+), 485 (54% M^+ − MeCp), 405 (82% M^+ − 2meCp − H), 318 (BP $(MeCp)_2Ti_2Cp$), 206 (62% $(MeCp)_2Ti$) and further signals. Found: C, 56.26; H, 5.31. $C_{26}H_{28}Ti_2S_4$ (564.57) calcd.: C, 55.32; H, 5.00%.

$(Me_3SiC_5H_4)_4Ti_2C_2S_4$ (3). ^{1}H-NMR $\delta(CDCl_3)$: 0.219s, (Me), 5.96 br, (Cp); ^{13}C-NMR $\delta(CDCl_3)$: 0.295 (Me), 113.9br, 117.5 br, 129.7, (Cp), 173.2 (C=C). EI-MS (70 eV): m/z 796 (52% M^+), 659 (35% M^+ − Me_3SiCp), 322 (42% $(Me_3SiCp)_2Ti$), 73 (100% Me_3Si) and further signals. Found: C, 50.30; H, 6.24. $C_{34}H_{52}Ti_2Si_4S_4$ (797.19) calcd.: C, 51.23; H, 6.58%.

Compounds **4**–**7** were prepared analogously. The higher solubility of **5** nd **7** than of **4** and **6** results in higher yields. In a typical procedure, to a solution of 100 mg of **2** (0.18 mmol) in 80 ml CH_2Cl_2 at 0 °C was added dropwise a solution of ca. 0.18 mmol of S_2Cl_2 in 6 ml of CH_2Cl_2 with exclusion of light. (The exact amount of S_2Cl_2 needed was determined prior to reaction in a separate experiment involving HPLC monitoring of the mixture during the S_2Cl_2 addition). The volume was reduced in a vacuum to ca. 20 ml, and the solution then subjected to chromatography at $\leqslant$ 15 °C in the dark (column length 100 cm, diameter 25 mm, Bio-Beads SX4 as stationary phase, CH_2Cl_2 as eluent, flow 15 ml/h). After ca. 24 h a blue fraction containing **7** was obtained, from which 14 mg (18%) of **7** was isolated by evaporation. Solids **4**–**7** are air-stable at 20 °C but light sensitive. In solution slow decomposition takes place.

$(C_5H_5)_2TiC_2S_5$ (4). Found: C, 39.26; H, 5.60 (H_2O). $C_{12}H_{10}TiS_5$ (362.43) calcd.: C, 39.76; H, 2.78%.

$(C_5H_5)_2TiC_2S_6$ (5). ^{1}H-NMR: $\delta(CDCl_3)$: 6.50s, (Cp); EI-MS (70 eV): m/z 394 (7% M^+), 362 (21% $Cp_2TiC_2S_5$), 355 (9% Cp_4Ti_2), 330 (7% $Cp_2TiC_2S_4$), 298 (19% $Cp_2TiC_2S_3$), 222 (22% Cp_2TiCS), 178 (100% Cp_2Ti), and further signals. Found: C, 36.94; H, 2.87. $C_{12}H_{10}TiS_6$ (394.50) calcd.: C, 36.54; H, 2.56%.

$(MeC_5H_4)_2TiC_2S_5$ (6). ^{1}H-NMR $\delta(CDCl_3)$: 6.35 dd, (Cp), 2.31s (Me); EI-MS (70 eV): m/z 390 (M^+), 276 (M^+ − Me), 256 (S_8), 64 (100% S_2) and further signals, low ion current. Found: C, 44.8; H, 4.0. $C_{14}H_{14}TiS_5$ (390.48) calcd.: C, 43.06; H, 3.61%.

Preparation of C_2S_8

To a solution of 200 mg **1** in 50 ml of CH_2Cl_2, a solution of 96 mg of S_2Cl_2 in 1.15 ml of CH_2Cl_2 was added in the dark. After addition of 200 ml n-pentane the mixture was cooled to −78 °C for 12 h, the precipitate formed was filtered off, and dissolved in little CH_2Cl_2, and the solution subjected to column chromatography (see preparation of **7** above). The combined fractions containing C_2S_8 (HPLC analysis) were evaporated to half of their original volume in a vacuum at 0 °C with exclusion of light, and the solution kept at −78 °C for 24 h to give 13 mg of orange crystals of C_2S_8. The Raman spectrum of this material showed S–S stretching vibrations at 434, 475, and 504 cm^{-1}, and a C=C stretching vibration at 1446 cm^{-1}.

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