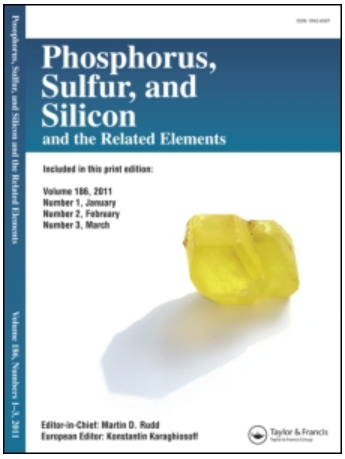

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Synthesis, Structure, and Reactions of $Cp_2TiSe_3S_2$ and Cp_2TiSe_4S (Cp'= ^{Z}-$C_5H_4CH_3$)[1]

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SYNTHESIS, STRUCTURE, AND REACTIONS OF $Cp'_2TiSe_3S_2$ AND Cp'_2TiSe_4S ($Cp' = \eta^5\text{-}C_5H_4CH_3$)[1]

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Abstract Reaction of $Cp'_4Ti_2Se_4$ with either SCl_2 or S_2Cl_2 in a molar ratio of 1:1 provides the new complexes Cp'_2TiSe_4S or $Cp'_2TiSe_3S_2$, the ^1H NMR spectra of which and the structure of the second complex are reported.

INTRODUCTION

The symmetrical dinuclear titanocene complex $Cp'_4Ti_2Se_4$ **1** containing two bridging diselenide units is a valuable reagent for the synthesis of cyclic selenium sulfides [2,3]. For instance, reaction of **1** with two moles of S_2Cl_2 provided the eight-membered heterocycle 1,2,5,6-Se_4S_4 while SCl_2 yielded the six-membered ring 1,4-Se_4S_2 [2,4]:

$$Cp'_2Ti(\mu\text{-}Se_2)_2TiCp'_2 + 2S_xCl_2 \longrightarrow 2\ Cp'_2TiCl_2 + Se_4S_{2x} \qquad x = 1,2$$

In this work we report on the reactions of **1** with SCl_2 and S_2Cl_2 in a molar ratio of 1:1.

REACTIONS AND PRODUCTS

When $Cp'_4Ti_2Se_4$, dissolved in CS_2, was treated with 1 equivalent of S_2Cl_2 at 20°C Cp'_2TiCl_2 was formed but ^1H NMR and HPLC analysis of the reaction mixture indicated that $Cp'_2TiSe_3S_2$ **2** rather than the expected $Cp'_2TiSe_4S_2$ had formed. The results indicate that reactions (2) and (3) had taken place:

$$Cp'_2Ti(\mu\text{-}Se_2)_2TiCp'_2 + S_2Cl_2 \rightarrow Cp'_2TiCl_2 + Cp'_2TiSe_4S_2$$

$$Cp'_2TiSe_4S_2 \longrightarrow Cp'_2TiSe_3S_2 + Se$$

2 was isolated by preparative high-performance liquid chromatography and forms monoclinic crystals of space group $P2_1/n$ with the lattice dimensions a = 701.6, b = 1690.1, c = 1318.8 pm and ß = 98.06°. A full X-ray structural analysis refined to R = 0.099 showed the metallacycle to be of chair-conformation with two Ti-Se bonds of length 253 ± 2 pm. The sulfur atoms occupy positions 3 and 4 (Ti = 1) but site 3 is seemingly also occupied by Se due to the typical disorder known from other crystalline SeS compounds. Therefore, no accurate SS, SSe, and SeSe bond distances could be determined. Mixtures of compounds of type $Cp_2TiSe_xS_y$ (x+y=5) have been reported before [5,6], but never had pure species been isolated and the $Cp'_2TiSe_3S_2$ (titanocene 2,4,6-triselenide 3,5-disulfide) reported in this work has not been observed before. **2** reacts at 20°C in CS_2 solution with S_2Cl_2 to give 1,2,5-Se_3S_4 [2], and with Se_2Cl_2 to the well known 1,2-Se_5S_2, previously accessible only from Cp_2TiSe_5 and S_2Cl_2 [7]; Se_3S_4 and Se_5S_2 have been identified by ^{77}Se NMR spectra [2,8] and their characteristic retention time in reversed-phase HPLC [9].

Table 1. Proton chemical shifts (in ppm) of $Cp'_2TiSe_3S_2$ and Cp'_2TiSe_4S (s= singlet, m=multiplet)

signal type	$Cp'_2TiSe_3S_2$	Cp'_2TiSe_4S
s	1.98 (3H)	1.98 (3H)
s	2.34 (3H)	2.34 (3H)
m	5.91 (1H)	
m	5.99 (1H)	5.97 (2H)
m	6.09 (3H)	6.04 (2H)
m	6.11 (1H)	6.13 (2H)
m	6.25 (1H)	
m	6.28 (1H)	6.30 (2H)

A second pure titanocene polyselenidesulfide was obtained from reaction (4):

$$Cp'_2Ti(\mu\text{-}Se_2)_2TiCp'_2 + SCl_2 \longrightarrow Cp'_2TiCl_2 + Cp'_2TiSe_4S \quad (4)$$

According to the synthesis the sulfur atom of Cp'_2TiSe_4S (3) should occupy position 4 of the metallacycle which therefore should possess a mirror plane. This is in fact demonstrated by the ^1H NMR spectrum of 3 which - in contrast to the spectrum of 2 - exhibits two singlets for the methyl groups and only four multiplets for the C_5H_4 units (see Table 1). The ring protons of 2 give rise to 6 multiplets, one of which of threefold intensity due to overlapping resonances; 2, therefore, cannot have a mirror plane. The analogous molecule Cp'_2TiS_4Se has recently been prepared from $Cp'_4Ti_2S_4$ and $SeOCl_2$ [10].
For further details of the work reported here see ref. 4.

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