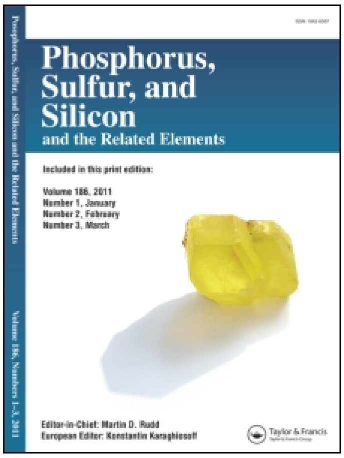

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Ralf Steudel[a]; Detlef Jensen[a]; Maria Papavassiliou[a]
[a] Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, Berlin, Fed. Rep. Germany

To cite this Article Steudel, Ralf , Jensen, Detlef and Papavassiliou, Maria(1989) 'Dinuclear Titanocene Chalcogenides as Sulfur and Selenium Transfer Reagents in Ring Synthesis1', Phosphorus, Sulfur, and Silicon and the Related Elements, 41: 3, 349 — 353
To link to this Article: DOI: 10.1080/10426508908039724
URL: http://dx.doi.org/10.1080/10426508908039724

Phosphorus, Sulfur and Silica, Vol. 41, pp. 349–353
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DINUCLEAR TITANOCENE CHALCOGENIDES AS SULFUR AND SELENIUM TRANSFER REAGENTS IN RING SYNTHESIS [1]

RALF STEUDEL, DETLEF JENSEN, AND MARIA PAPAVASSILIOU
Institut für Anorganische und Analytische Chemie der
Technischen Universität Berlin, Sekr. C 2,
D - 1000 Berlin 12, Fed. Rep. Germany

Abstract The dinuclear titanocene complexes $Cp_4Ti_2S_6$, $Cp_4Ti_2S_4$ and $Cp_4Ti_2Se_4$ have been reacted with SCl_2, S_2Cl_2, and Se_2Cl_2, respectively. The reaction products are rings of type S_n (n = 6...20) and six-, seven- and eight-membered rings of type Se_xS_y, respectively, which have been characterized by HPLC, Raman and Se-NMR spectroscopy, as well as X-ray diffraction on single crystals.

INTRODUCTION

Titanocene pentasulfide, Cp_2TiS_5 ($Cp = C_5H_5$), has been used as a sulfur transfer reagent which under mild conditions delivers 5 sulfur atoms in exchange for two halogen atoms. In this way, the homocyclic rings S_6, S_7, S_9, S_{10}, S_{11}, S_{12}, S_{13}, S_{15}, and S_{20} have been prepared by reaction with suitable sulfur halides [2], [3,4], and with Se_2Cl_2 the heterocyclic Se_2S_5 has been obtained [5]. In a similar fashion, titanocene pentaselenide, Cp_2TiSe_5, provided Se_5S by reaction with SCl_2, Se_5S_2 by reaction with S_2Cl_2 and Se_7 with Se_2Cl_2 [6]. These mixed sulfur-selenium rings are interesting links between the electrically insulating elemental sulfur and the semiconducting elemental selenium. In this work we report how the symmetrical dinuclear titanocene chalcogenides $Cp_4Ti_2S_6$, $Cp_4Ti_2S_4$, and $Cp_4Ti_2Se_4$ prepared by Rauchfuss et al. [7,8] can be used as sulfur and selenium transfer reagents. These compounds contain $-S_3-$, $-S_2-$, and $-Se_2-$ units, respectively, bridging the two Cp_2Ti moieties.

REACTIONS AND PRODUCTS

All reactions have been carried out in carbon disulfide solution at 20°C. When $Cp_4Ti_2S_4$ was treated with SCl_2 in molar ratios of 1:1 and 1:2 the following reactions occurred:

$$Cp_4Ti_2S_4 + SCl_2 \longrightarrow Cp_2TiS_5 + Cp_2TiCl_2 \qquad (1)$$
$$Cp_4Ti_2S_4 + 2\ SCl_2 \longrightarrow S_6 + 2\ Cp_2TiCl_2 \qquad (2)$$

It is obvious that in reaction (2) the S_6 is formed from the intermediate Cp_2TiS_5 which is known to react with SCl_2 to give S_6 (and S_{12}) [2].

$Cp_4Ti_2Se_4$ reacted with SCl_2 in a *similar fashion to give the six*-membered selenium sulfide 1,4-Se_4S_2:

$$Cp_4Ti_2Se_4 + 2\ SCl_2 \longrightarrow 1,4\text{-}Se_4S_2 + 2\ Cp_2TiCl_2 \qquad (3)$$

1,4-Se_4S_2 forms dark red crystals the Raman spectrum of which shows typical signals of SeS and SeSe stretching modes but no SS stretching lines. In reaction (3) the symmetrical complex Cp_2TiSe_4S most likely is an intermediate.

The reactions with S_2Cl_2 and Se_2Cl_2 are more complicated. Not surprizingly, $Cp_4Ti_2S_4$ reacts with two moles of S_2Cl_2 to give mainly S_8 but traces of S_7 and Cp_2TiS_5 are formed in addition:

$$Cp_4Ti_2S_4 + 2\ S_2Cl_2 \longrightarrow S_8 + 2\ Cp_2TiCl_2 \qquad (4)$$

Most likely the first step is the formation of Cp_2TiS_6 which either reacts with S_2Cl_2 to give S_8 or decomposes to the more stable Cp_2TiS_5 which reacts with S_2Cl_2 to yield S_7:

$$Cp_4Ti_2S_4 + S_2Cl_2 \longrightarrow Cp_2TiS_6 + Cp_2TiCl_2 \quad (5)$$
$$Cp_2TiS_6 \longrightarrow Cp_2TiS_5 + \text{"S"} \quad (6)$$
$$Cp_2TiS_5 + S_2Cl_2 \longrightarrow Cp_2TiCl_2 + S_7 \quad (7)$$

Se_2Cl_2 and $Cp_4Ti_2S_4$ also react to give a seven- and an eight-membered chalcogen ring; these are of composition Se_3S_4 and Se_4S_4. Their structures are as follows:

Their formation can be explained by the following sequence of reactions which are analogous to equ. (4) - (7):

$$Cp_4Ti_2S_4 + Se_2Cl_2 \longrightarrow Cp_2TiS_4Se_2 + Cp_2TiCl_2 \quad (8)$$
$$Cp_2TiS_4Se_2 + Se_2Cl_2 \longrightarrow Cp_2TiCl_2 + 1,2,5,6\text{-}Se_4S_4 \quad (9)$$
$$Cp_2TiS_4Se_2 \longrightarrow Cp_2TiS_4Se + \text{"Se"} \quad (10)$$
$$Cp_2TiS_4Se + Se_2Cl_2 \longrightarrow Cp_2TiCl_2 + 1,2,5\text{-}Se_3S_4 \quad (11)$$

In the ^{77}Se-NMR spectrum 1,2,5,6-Se_4S_4 shows one singlet at 657 ppm and 1,2,5-Se_3S_4 exhibits two singlets at 1155 and 1080 ppm in an 1:2 intensity ratio (in CS_2 versus Me_2Se; all values ± 2 ppm). Most interestingly the very same products are obtained from the "inverse" reaction between $Cp_4Ti_2Se_4$ and S_2Cl_2:

$$Cp_4Ti_2Se_4 + S_2Cl_2 \longrightarrow Cp_2TiSe_4S_2 + Cp_2TiCl_2 \quad (12)$$

$$Cp_2TiSe_4S_2 + S_2Cl_2 \longrightarrow Cp_2TiCl_2 + 1,2,5,6\text{-}Se_4S_4 \quad (13)$$
$$Cp_2TiSe_4S_2 \longrightarrow Cp_2TiSe_3S_2 + \text{"Se"} \quad (14)$$
$$Cp_2TiSe_3S_2 + S_2Cl_2 \longrightarrow Cp_2TiCl_2 + 1,2,5\text{-}Se_3S_4 \quad (15)$$

1,2,5,6-Se_4S_4 crystallizes in space group $C\bar{1}$. The structure is disordered due to a more or less statistical occupation of the atomic sites in the crown-shaped ring by S and Se atoms, respectively. This has been observed for other Se_nS_{8-n} rings too [9]. The Raman spectrum of 1,2,5,6-Se_4S_4 is in agreement with the proposed structure [8].

Treatment of $Cp_4Ti_2S_6$ with S_2Cl_2 basically yielded the sulfur homocycles S_7, S_8, and S_{10} with minor amounts of S_{15} and S_{20}. These products can be formed as follows:

$$Cp_4Ti_2S_6 + S_2Cl_2 \longrightarrow Cp_2TiS_8 + Cp_2TiCl_2 \quad (16)$$
$$Cp_2TiS_8 + S_2Cl_2 \longrightarrow Cp_2TiCl_2 + S_{10} \quad (17)$$
$$Cp_2TiS_8 \longrightarrow Cp_2TiS_5 + \text{"}S_3\text{"} \; (\longrightarrow S_8) \quad (18)$$
$$Cp_2TiS_5 + S_2Cl_2 \longrightarrow Cp_2TiCl_2 + S_7 \quad (19)$$

Possibly the intermediate formation of S_5Cl_2 is responsible for the products S_{15} and S_{20} [4]:

$$Cp_4Ti_2S_6 + 2\ S_2Cl_2 \longrightarrow Cp_2TiCl_2 + Cp_2TiS_5 + S_5Cl_2 \quad (20)$$
$$Cp_2TiS_5 + S_5Cl_2 \longrightarrow S_{10},\ S_{15},\ S_{20},\ Cp_2TiCl_2 \quad (21)$$

DISCUSSION

Our results clearly indicate that the primary attack of sulfur and selenium chlorides on dinuclear titanocene chalcogenides occurs at one Ti center only with formation of Cp_2TiCl_2 and the corresponding mononuclear chalcogenide Cp_2TiE_n (E = S, Se; n = 5-8) which then either reacts further with chalcogen halides or stabilizes by ring contraction since only Cp_2TiE_5 complexes are stable with simple Cp ligands [10]. Generally, the dinuclear titanocene complexes used in this work are more reactive than the corresponding mononuclear complexes of type Cp_2TiE_5.

ACKNOWLEDGEMENT

We are grateful to the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie for generous support.

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