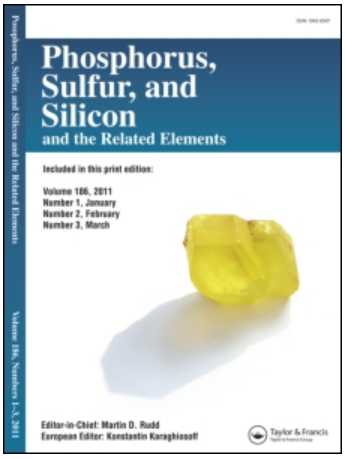


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

New Sulfur Containing Titanacycles

Ursula Westphal[a]; Ralfsteudel[a]
[a] Institut fur Anorganische und Analytische Chemie Sekr. C 2, Technische Universitat Berlin, Berlin 12, Germany

To cite this Article Westphal, Ursula and Ralfsteudel(1992) 'New Sulfur Containing Titanacycles', Phosphorus, Sulfur, and Silicon and the Related Elements, 65: 1, 151 — 155
To link to this Article: DOI: 10.1080/10426509208055341
URL: http://dx.doi.org/10.1080/10426509208055341

Phosphorus, Sulfur, and Silicon, 1992, Vol. 65, pp. 151–155

NEW SULFUR CONTAINING TITANACYCLES [1]

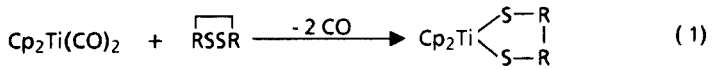
URSULA WESTPHAL AND RALF STEUDEL
Institut für Anorganische und Analytische Chemie, Sekr. C 2,
Technische Universität Berlin, D-1000 Berlin 12, Germany

Abstract Titanocenedicarbonyl, $Cp_2Ti(CO)_2$, activates the sulfur-sulfur bond in organic disulfides and sulfur homocycles like S_6,S_7 and S_8. Cyclic disulfides form chelating ligands with sulfur atoms attached to the Ti atom. The reaction with S_6 yields a new compound with an eight sulfur atoms containing ligand. The novel titanocene compounds have been used as precursors for the synthesis of a series of methylene polysulfides.

INTRODUCTION

Cp_2TiS_5 is an excellent precursor for the preparation of sulfur homocycles and cyclic methylene polysulfides[2,3]. New possibilities in ring size and number of sulfur and methylene groups are opened up by the synthesis of titanocene chelating ligands containing sulfur and methylene groups.

The reaction of $Cp_2Ti(CO)_2$ with cyclic organic disulfides[4] is a new route to generate this kind of ligands:



(1)

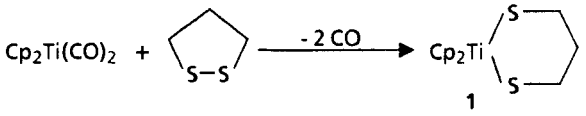
$Cp_2Ti(CO)_2$ has also been reacted with S_6, S_7 and S_8 under various conditions to obtain Cp_2TiS_X complexes with other ring sizes than six as in Cp_2TiS_5.

REACTIONS AND PRODUCTS

In 1974 Shaver et al. synthesized a new titanocene-sulfur compound with three methylene groups, according to equation (2).[5]

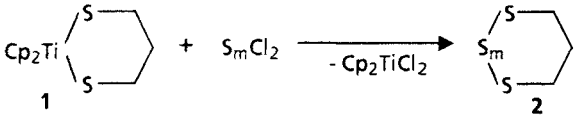
$$C_3H_6(SH)_2 + CH_3Li \xrightarrow[-CH_4, -LiCl]{Cp_2TiCl_2} \underset{\mathbf{1}}{Cp_2TiC_3H_6S_2} \qquad (2)$$

We observed that compound **1** can also be obtained by the reaction of $Cp_2Ti(CO)_2$ with the corresponding organic disulfide.

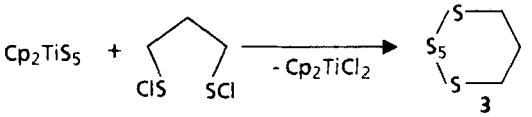


(3)

1 was identified by C,H-analysis, ^1H NMR and UV spectra. Obviously, this reaction is very suitable for the synthesis of new sulfur containing ligands. The reaction of **1** with various sulfur chlorides or organic bissulfenyl chlorides yields a number of new methylene sulfides. For instance, **1** reacts with a mixture of sulfur chlorides of different chain length to yield a mixture of cyclic sulfur-rich methylene sulfides of corresponding ring sizes (equation 4).



(4)



(5)

The methylene sulfide mixture **2** was identified by HPLC and UV spectra. The heptasulfide **3** was synthesized according to equation (5) in order to use its HPLC retention time as a reference for the peak assignment in the HPLC analysis of mixture **2**. **3** was also characterised by ^1H NMR spectroscopy.

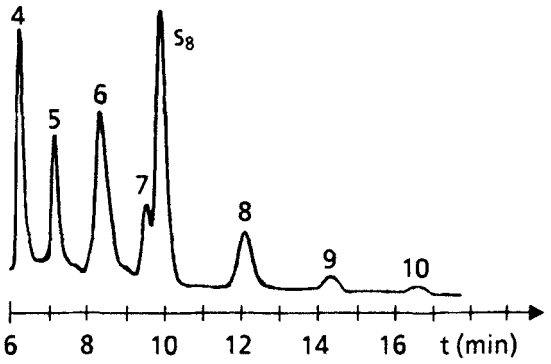


FIGURE 1 HPLC Analysis of the $C_3H_6S_n$-mixture obtained by reaction (4)

The numbers given in Fig. 1 correspond to the values of n. The signals were assigned by comparison with **3** and on the basis of the linear relationship between the logarithm of the capacity factor and the number of sulfur atoms as shown in FIGURE 2.[6]

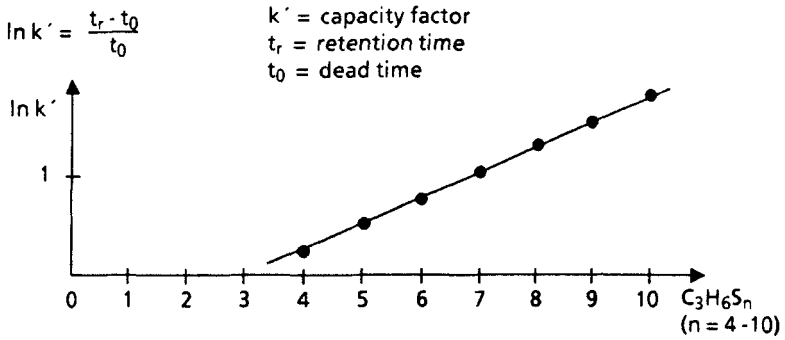


FIGURE 2 Logarithm of the capacity factor of $C_3H_6S_n$ (n = 4 -10) as a function of n

The UV absorption spectra of the chromatographically separated products of reaction (4) were measured during the continuing HPLC analysis using a Waters diode array detector. The increasing number of sulfur atoms in the ring causes a bathochromic shift (see TABLE 1).[7]

TABLE 1 UV Absorption maxima of the methylene sulfides $C_3H_6S_n$ (n = 4-10)

Reaction products	UV Absorption maxima (nm)
$C_3H_6S_3$	218, 278
$C_3H_6S_4$	218, 298
$C_3H_6S_5$	222, 306
$C_3H_6S_6$	224, 314
$C_3H_6S_7$	222, 318
$C_3H_6S_8$	222, 325
$C_3H_6S_9$	224, 328
$C_3H_6S_{10}$	224, 338

The reaction of $Cp_2Ti(CO)_2$ with S_8 in boiling hexane yields Cp_2TiS_5 only (equation 6).[8] No reaction is taking place at room temperature because of the high activation energy of S_8.

The reaction of $Cp_2Ti(CO)_2$ with S_6 proceeds at 0°C and yields a dark red solid, which was identified as a new titanocene compound by HPLC, ^1H NMR and UV spectra.

$$Cp_2Ti(CO)_2 + 5/8\ S_8 \xrightarrow{-2\ CO} Cp_2TiS_5 \qquad (6)$$

$$Cp_2Ti(CO)_2 + S_6 \xrightarrow{-2\ CO} Cp_2TiS_X + S_Z \qquad (7)$$

4 ^1H NMR: 6.32 ppm s (Cp)
UV: 218, 298, 442, 532 nm
t_r = 9.35 min

The reaction of **4** with sulfur chlorides and subsequent identification of the resulting sulfur homocycles as well as the reaction with propylene bissulfenyl chloride indicate that **4** contains eight sulfur atoms. The new compound has not been isolated from the mixture so far, but its reactions were monitored by HPLC. The treatment of **4** with sulfurdichloride yields S_9, the reaction with disulfurdichloride results in S_{10} (equations 8 and 9).

HPLC analysis of the reaction mixture of **4** with propylene bissulfenylchloride shows a HPLC peak with exactly the same retention time and UV spectrum as the compound $C_3H_6S_{10}$ obtained from reaction (5) (see FIGURE 1 and 2).

$$Cp_2TiS_x + SCl_2 \xrightarrow[-\,Cp_2TiCl_2]{} S_9 \qquad (8)$$

$$Cp_2TiS_x + S_2Cl_2 \xrightarrow[-\,Cp_2TiCl_2]{} S_{10} \qquad (9)$$

$$Cp_2TiS_x + C_3H_6(SCl)_2 \xrightarrow[-\,Cp_2TiCl_2]{} \underset{\mathbf{5}}{C_3H_6S_{10}} \qquad (10)$$

The new titanocene complex **4** obviously reacts as a transfer reagent for eight sulfur atoms.

ACKNOWLEDGEMENT

Support by the Deutsche Forschungsgemeinschaft and Verband der Chemischen Industrie is gratefully acknowledged. We thank Dipl.-Chem. H. Balz for helpful discussions.

REFERENCES

1. Part 151 of the series "Sulfur Compounds"; for Part 150 see C.R. Williams, J.G. MacDonald, D.N. Harpp, R. Steudel and S. Förster, Sulfur Lett., in print.
2. M. Schmidt, B. Block, H.D. Block, H.Köpf, and E.Wilhelm, Angew. Chem. 80, 660 (1968); Angew. Chem. Int. Ed. Engl. 7, 632 (1968).
3. R. Steudel, S. Förster and J. Albertsen, Chem. Ber. 124 (1991), in print.
4. G. Fachinetti and C. Floriani, J. Chem. Soc. Dalton Trans. 2433 (1974).
5. A. Shaver and J. M. McCall, Organometallics, 3, 1823 (1984).
6. R. Steudel and E.-M. Strauss, Z. Naturforsch., Teil B, 38, 719 (1983).
7. R. Steudel, D. Jensen, P. Göbel and P. Hugo, Ber. Bunsenges. Phys. Chem. 92, 118 (1988).
8. G. Müller and J. L. Peterson, J. Org. Chem. 111, 91 (1974).