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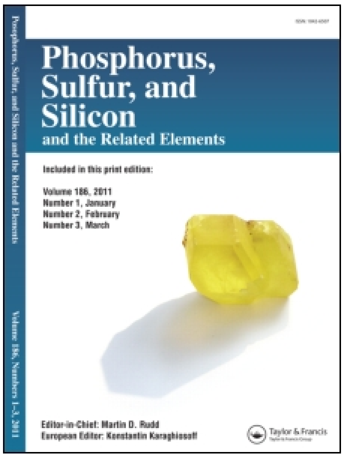

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The Utilization of Titanocene Polysulfide Complexes for the Synthesis of Organic Polysulfanes[1]

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THE UTILIZATION OF TITANOCENE POLYSULFIDE COMPLEXES FOR THE SYNTHESIS OF ORGANIC POLYSULFANES[1]

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Titanocene pentasulfide reacts with Ph_3CCl and CCl_3SCl to give $(Ph_3C)_2S_5$ and $(CCl_3)_2S_7$, respectively, the molecular structures of which show helical CS_nC backbones. $(Ph_3C)_2S_6$ and $(CN)_2S_9$ possess non-helical structures. $C_2H_4(SCl)_2$, $C_6H_4(SCl)_2$, $C_6H_4(SSCl)_2$ and $CH_3C_6H_3(SCl)_2$ react with Cp_2TiS_5 to give the corresponding sulfur-rich heterocycles with up to nine sulfur atoms. Dicyclopentadiene trisulfane is used to prepare the dicyclopentadiene tetra-, penta-, hexa- and octasulfanes by (a) derivatization to SCl or SH compounds followed by sulfur transfer reactions using Cp_2TiS_5, $(Cp'_2ClTi)_2S_3$ or S_2Cl_2 as reagents. Several cyclic, bicyclic and tricyclic organosulfur heterocycles are obtained from $Cp_4Ti_2C_2S_4$ or from $Cp_2TiS_2C_3H_6$ by reactions with SCl_2, S_2Cl_2, $C_2H_4(SCl)_2$, $COCl_2$ or $C_6H_4(SCl)_2$.

INTRODUCTION

Titanocene pentasulfide, $(\eta^5\text{-}C_5H_5)_2TiS_5$, first prepared in 1968, has become a famous sulfur transfer reagent. It reacts with certain halogen compounds with exchange of the S_5 unit for two halogen atoms. The first reaction of this type was the preparation of cyclo-S_7 from S_2Cl_2: [2]

$$Cp_2TiS_5 \quad + \quad S_2Cl_2 \quad \longrightarrow \quad S_7 \quad + \quad Cp_2TiCl_2 \qquad (1)$$

S_7 is much more reactive than S_8 and yields fairly pure dichloroheptasulfane, S_7Cl_2, on treatment with Cl_2 in CCl_4. [3] S_7Cl_2 in turn reacts with Cp_2TiS_5 to give cyclo-S_{12}.[3] In this paper the utilization of S_7, S_7Cl_2, Cp_2TiS_5 and other titanocene polysulfide complexes for the synthesis of cyclic and acyclic organic polysulfanes will be outlined. [4] For a review covering the preparation of inorganic sulfur and selenium compounds from titanocene precursors see ref. 4. [5]

CHAIN-LIKE ORGANIC POLYSULFANES

In recent years the structures of the following sulfur-rich compounds have been determined by X-ray crystallography: $(Ph_3C)_2S_5$ [6], $(Ph_3C)_2S_6$ [6], $(CCl_3)_2S_7$ [7] and $(CN)_2S_9$ [8]. These polysulfanes have been prepared as follows:

$$2\ Ph_3CCl + Cp_2TiS_5 \longrightarrow (Ph_3C)_2S_5 + Cp_2TiCl_2 \qquad (2)$$

This reaction proceeds in CS_2 solution at 20° and the pentasulfane was isolated in 83% yield. [9] It forms colorless crystals of m.p. 156°C; the molecular structure is shown in Figure 1.

The bis(triphenylmethyl)hexasulfane is formed on reaction of Ph_3CSSCl with the dinuclear titanocene complex $Cp'_2Ti(\mu\text{-}S_2)_2TiCp'_2$ ($Cp' = CH_3C_5H_4$): [6]

$$4\ Ph_3CS_2Cl + Cp_4Ti_2S_4 \longrightarrow 2\ (Ph_3C)_2S_6 + 2\ Cp'_2TiCl_2 \qquad (3)$$

The hexasulfane forms triclinic crystals consisting of molecules with a non-helical backbone (Fig. 1). The conformation of a chain of sulfur atoms is given by the signs of the torsional angles (the "motif"). The helical chain of $(Ph_3C)_2S_5$ has the motif ++++ (or ---- for the enantiomer), while the hexasulfane has the motif ++--+. This conformation results in a more compact molecule. [6]

$(CCl_3)_2S_7$ has been prepared from CCl_3SCl and Cp_2TiS_5:

$$2\ CCl_3SCl + Cp_2TiS_5 \longrightarrow (CCl_3)_2S_7 + Cp_2TiCl_2 \qquad (4)$$

$(CCl_3)_2S_7$ forms light-yellow crystals of m.p. 38°C. [7]

The conformation of this heptasulfane is helical again (motif ++++++). No other heptasulfane has so far been structurally characterized.

The crystallization of chain-like polysulfanes is difficult since these compounds form a large number of rotamers in solution while in the crystal only one rotamer is present. An extreme example is the nonasulfane $(CN)_2S_9$ which has been prepared from S_7Cl_2 [8] :

$$S_7Cl_2 + Hg(SCN)_2 \longrightarrow (CN)_2S_9 + HgCl_2 \qquad (5)$$

Since at each SS bond the torsional angle may be either +90° or -90° (±20°), the number of torsional isomers is theoretically larger than 200 (including enantiomers).

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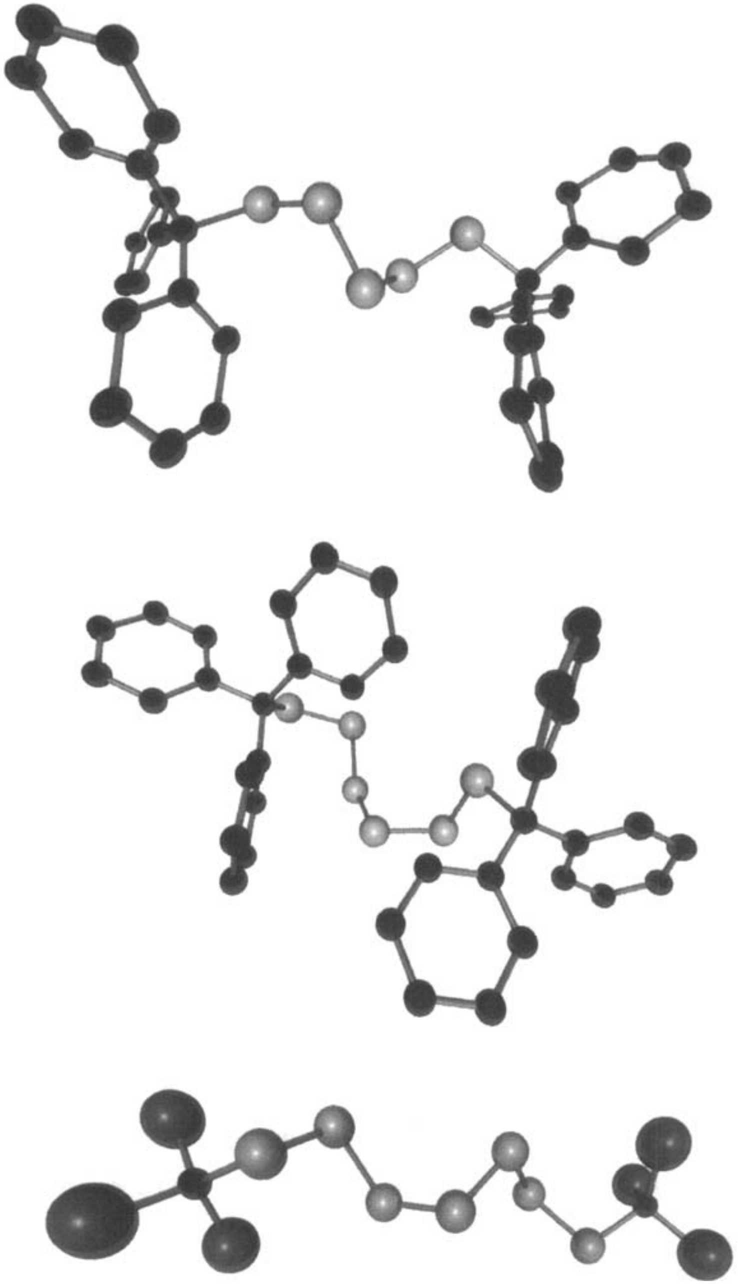

FIGURE 1 Structures of $(Ph_3C)_2S_5$, $(Ph_3C)_2S_6$ and $(CCl_3)_2S_7$ (from top to bottom) as determined by X-ray crystallography.

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Nevertheless, $(CN)_2S_9$ has been obtained as monoclinic crystals of m.p. 36-38°C containing loop-shaped molecules of motif ++--++-+ (see Fig. 2), which strongly resemble the structure of S_{12}.[8]

It is obvious that these sulfur-rich polysulfanes are related to the reaction intermediates formed on vulcanization of elastomers by elemental sulfur. In this reaction polysulfanes are formed initially which are converted to mainly mono- and disulfanes on curing the rubber mixture.

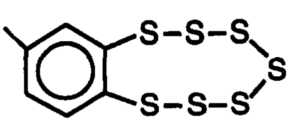
CYCLIC ORGANIC POLYSULFANES

Bifunctional organic SCl compounds react with Cp_2TiS_5 to give cyclic species in analogy to reaction (1). The 1,2-bissulfenylchloride of ethane, $C_2H_4(SCl)_2$, results in a nine-membered ring $C_2H_4S_7$ [9] the conformation of which is shown in Figure 2.[6]

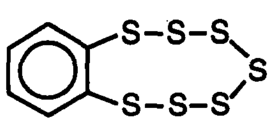
$$1{,}2\text{-}C_2H_4(SCl)_2 \; + \; Cp_2TiS_5 \; \longrightarrow \; C_2H_4S_7 \; + \; Cp_2TiCl_2 \qquad (6)$$

This molecule may be derived from the crown-shaped S_8 by replacement of one atom by a *trans*-C_2H_4 unit.[6]

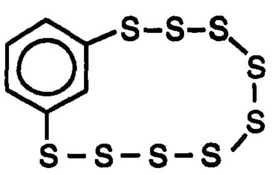
Bissulfenylchlorides $R(SCl)_2$ and $R(SSCl)_2$ derived from benzene or toluene react accordingly and the following species have been obtained as pure substances [6,9,10]:



m.p 84.5°C



m.p. 91°C



m.p. 106°C

To prepare particularly sulfur-rich rings it was thought that a titanocene complex containing more than five sulfur atoms would be helpful. Such a species was formed when $Cp_2Ti(CO)_2$ was reacted with either S_6 or S_7:

$$Cp_2Ti(CO)_2 \; + \; S_6 \; \longrightarrow \; Cp_2TiS_n \;\; (n = 8, 7, 5) \; + \; 2\,CO \qquad (7)$$

This reaction takes place at 20°C in hexane; the precipitated product is a mixture of titanocene complexes from which Cp_2TiS_8 could be isolated as dark-red crystals in low yield.[10,11] Cp_2TiS_8 reacts with S_2Cl_2 to give S_{10} and with $C_3H_6(SCl)_2$ to give $C_3H_6S_{10}$.

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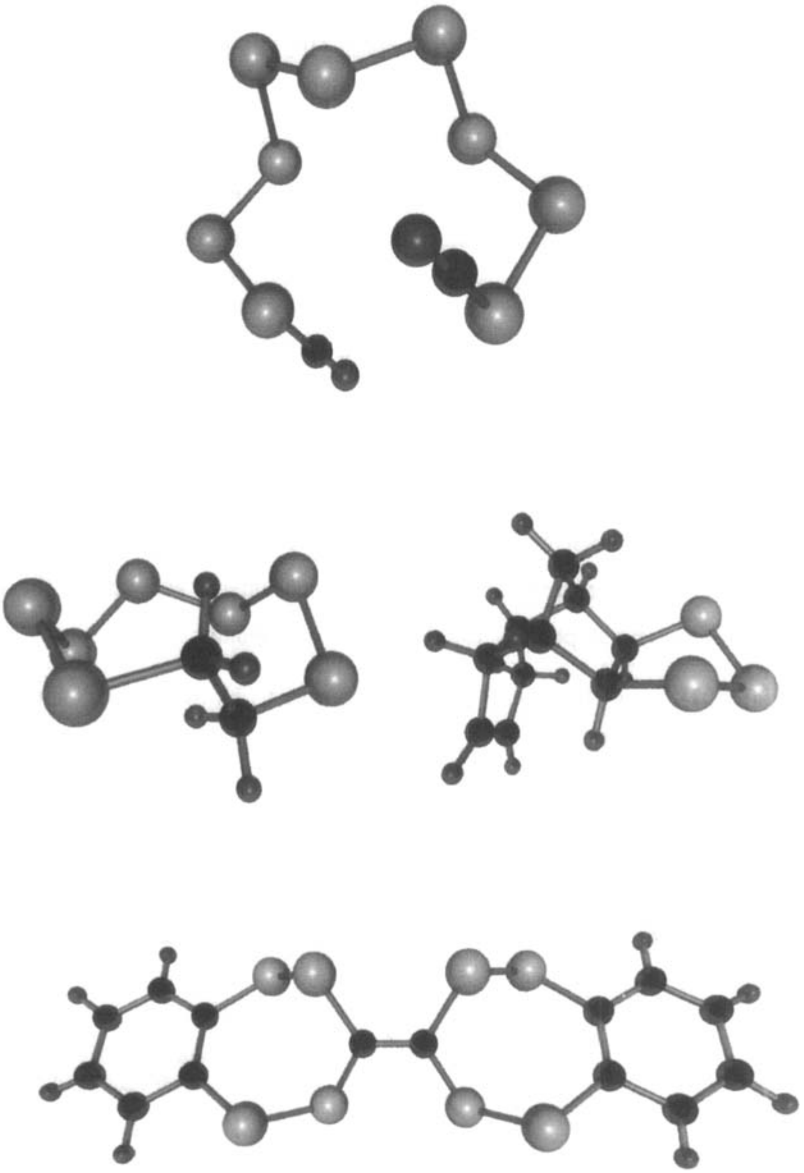
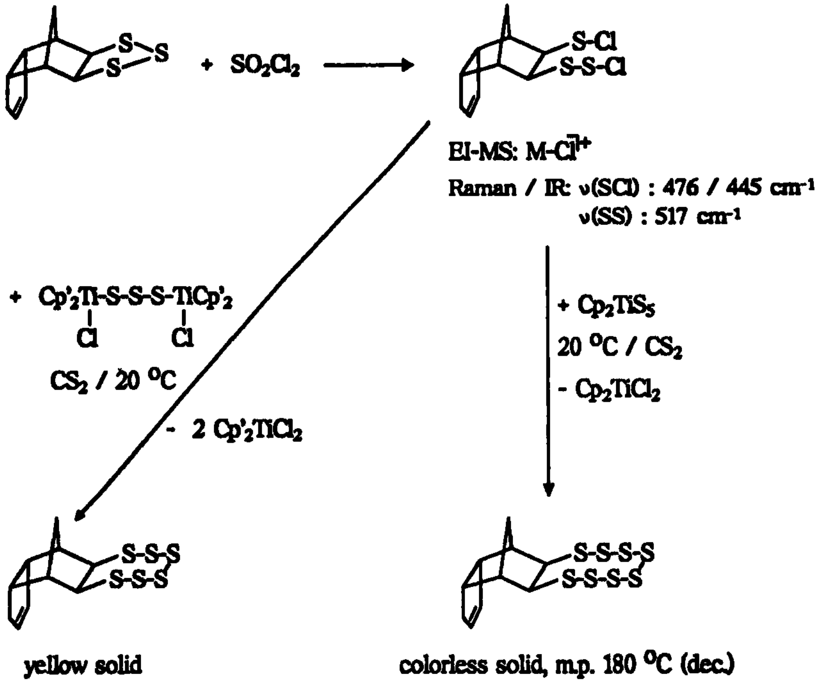


FIGURE 2 Structures of $(CN)_2S_9$ (top), $C_2H_4S_7$ (center left), $C_{10}H_{12}S_3$ (center right) and $C_{14}H_8S_8$ (bottom) as determined by X-ray crystallography.

For the analysis of reaction mixtures containing either titanocene complexes and/or organic polysulfanes the reversed-phase HPLC technique has proven very useful. Homologous compounds R_2S_n (n = 2, 3, ...) show retention times which linearly depend on the number n of sulfur atoms when expressed as logarithm of the capacity factor $k = (t_r - t_0)/t_0$ (t_0 is dead time). After two or three members of such a homologous series have been prepared and their retention times measured, the retention of the other members may be estimated by inter- or extrapolation. [4, 9]

Dicyclopentadiene, $C_{10}H_{12}$, is an inexpensive products of refineries and its reactions with elemental sulfur are of interest in connection with the production of sulfur cement and sulfur concrete. [12] $C_{10}H_{12}$ reacts with S_8 in the presence of NH_3 or Na_2S in toluene/pyridine/DMF mixture (130°C) to give the cyclic trisulfane [13] the structure [14] of which is shown in Figure 2. We have found that $C_{10}H_{12}S_3$ is a useful starting product for the preparation of homologous polysulfanes with up to eight sulfur atoms. There are several possible routes to these compounds:

(a) $C_{10}H_{12}S_3$ is chlorinated by SO_2Cl_2 to give $C_{10}H_{12}(SCl)(SSCl)$ which reacts with Cp_2TiS_5 at 20°C in CS_2 to give $C_{10}H_{12}S_8$ (m.p. 180°C; yield 70%) and with $(Cp'_2TiCl)_2S_3$ [15] to give $C_{10}H_{12}S_6$ (yield 55%)



(8)

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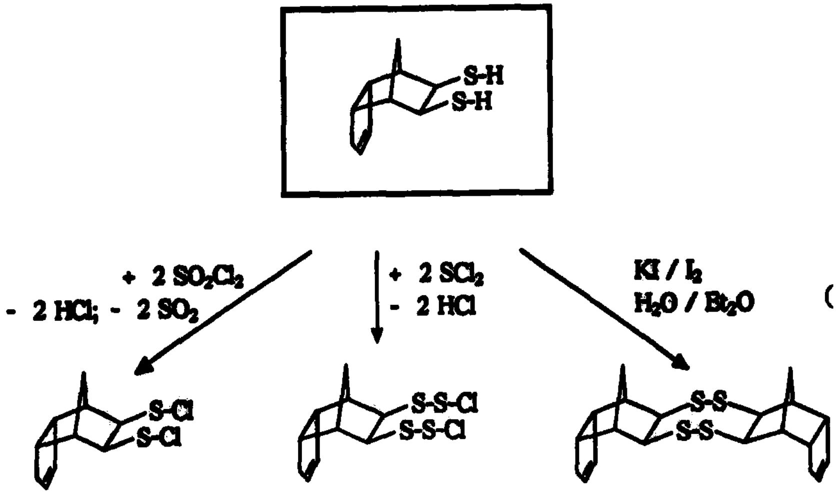
This reaction is the first application of the acyclic dinuclear complex $Cp'_2ClTi(\mu\text{-}S_3)TiClCp'_2$ for the synthesis of polysulfanes; this complex is formed on reaction of $Cp'_2Ti(\mu\text{-}S_2)_2TiCp'_2$ with phosgene [15]:

$$Cp'_4Ti_2S_4 \quad + \quad COCl_2 \longrightarrow Cp'_2ClTi(\mu\text{-}S_3)TiClCp'_2 + COS \qquad (9)$$

Attempts to prepare S_5 from $(Cp'_2ClTi)_2S_3$ and S_2Cl_2 have failed. [14]

(b) Reduction of $C_{10}H_{12}S_3$ by $LiAlH_4$ in THF followed by hydrolysis provides the dithiol $C_{10}H_{12}(SH)_2$ [13] which on treatment with SO_2Cl_2 gives the bissulfenylchloride $C_{10}H_{12}(SCl)_2$, with SCl_2 the analogous $C_{10}H_{12}(SSCl)_2$, while oxidation by I_2/KI in Et_2O/H_2O yields the dimeric disulfane $C_{10}H_{12}(\mu\text{-}S_2)_2C_{10}H_{12}$:



(10)

yellow solid
EI-MS: M^+ (266)
Raman: ν(SCl): 481 cm^{-1}
ν(SCl): 459 cm^{-1}

yellow oil
Raman: ν(SCl): 445 cm^{-1}
ν(SS): 528 cm^{-1}

yield 10%
EI-MS: M^+ (392)
2 conformers

$C_{10}H_{12}(SCl)_2$ on reaction with $(Cp'_2TiCl)_2S_3$ gives the pentasulfane $C_{10}H_{12}S_5$ as a yellow solid. [14] The formely unknown tetrasulfane $C_{10}H_{12}S_4$ was obtained from the dithiol $C_{10}H_{12}(SH)_2$ by reaction with S_2Cl_2 and from the titanocene chelat complex $Cp_2Ti(S_2C_{10}H_{12})$ on reaction with S_2Cl_2. The latter complex is obtained on reaction of Cp_2TiCl_2 with $C_{10}H_{12}(SH)_2$ in the presence of Et_3N and forms green crystals of m.p. 156°C.[14]

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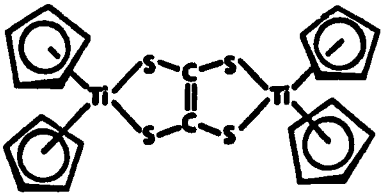
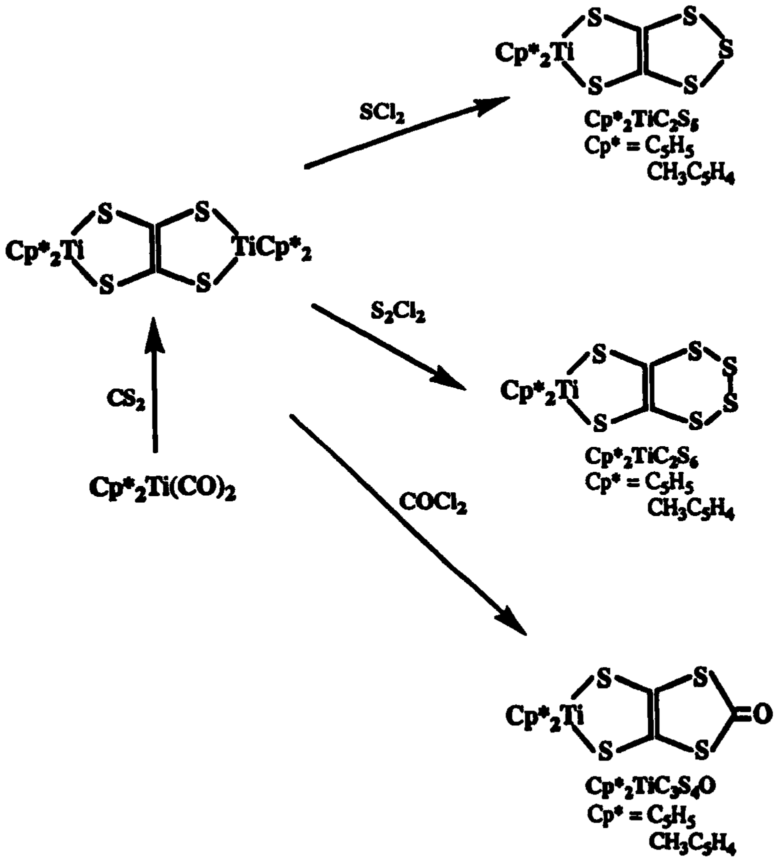
Interesting novel organosulfur heterocycles may also be prepared from the dinuclear $Cp'_4Ti_2C_2S_4$ which is obtained from $Cp'_2Ti(CO)_2$ and CS_2 [16] (Cp' = C_5H_5 or $CH_3C_5H_4$):



(11)

This complex may be cleaved at one titanium center only if one equivalent of reagent is applied [10, 17]:



(12)

These new mononuclear titanocene derivatives may then be reacted with a second reagent to prepare asymmetric bicyclic species, [10, 18] e.g.:

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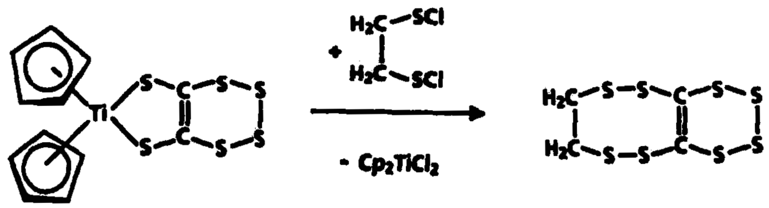
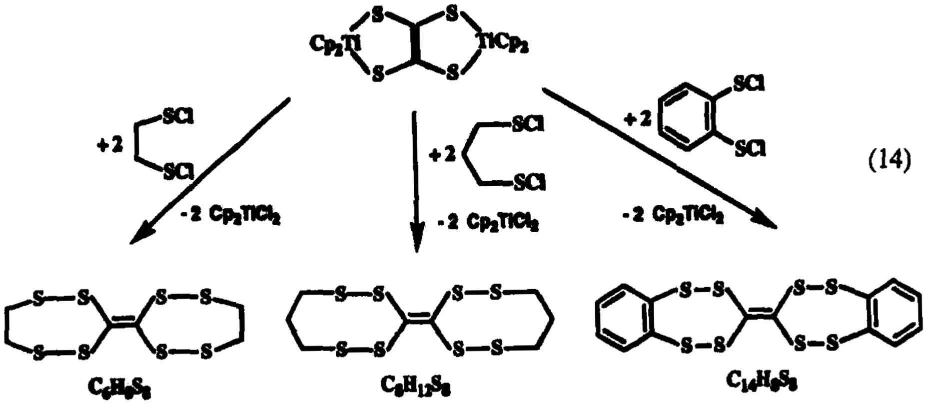


(13)

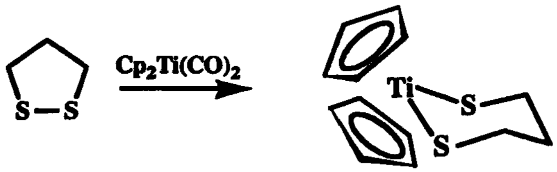
However, when the dinuclear $Cp'_4Ti_2S_4$ is reacted with reagents like 1,2-$C_2H_4(SCl)_2$ directly, the products are of different type: [10, 18]



(14)

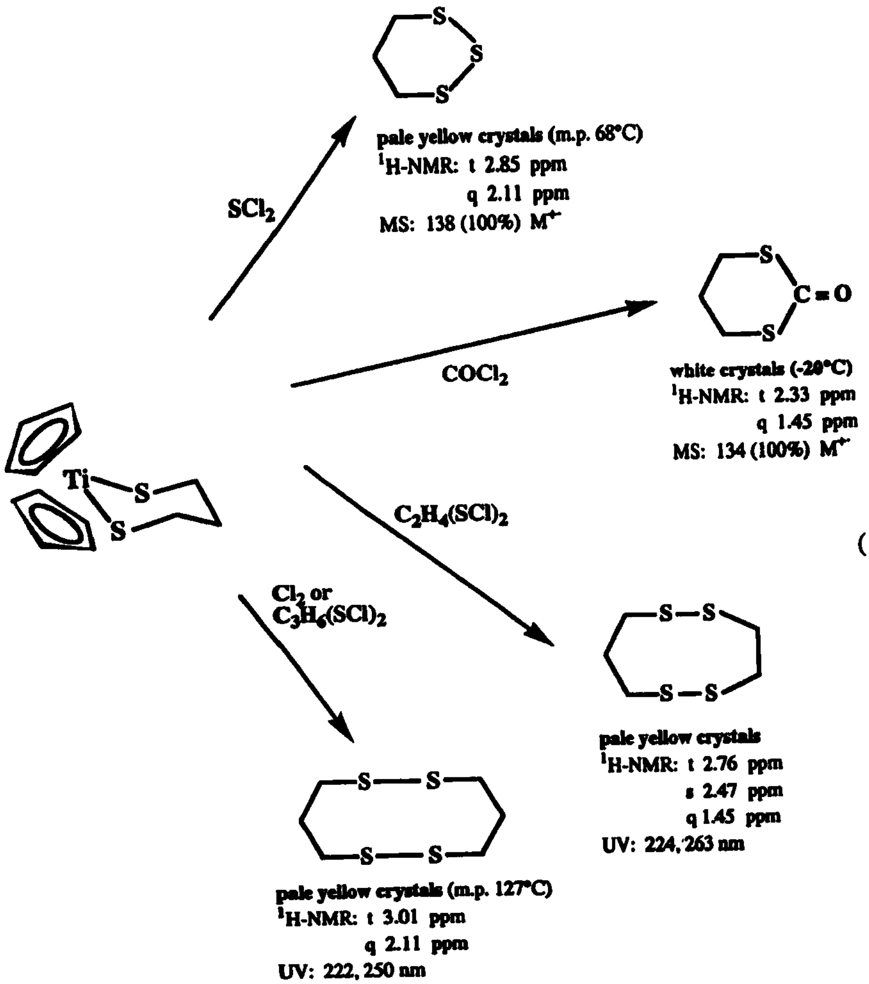
$C_{14}H_8S_8$ has been obtained as single crystals which were subjected to an X-ray structural analysis. The molecules are built from a planar central C_2S_4 unit and two coplanar $C_6H_4S_2$ units (see Fig. 2). The structures of $C_6H_8S_8$ and $C_8H_{12}S_8$ are assumed analogous to the one of $C_{14}H_8S_8$. [19]

Titanocenedicarbonyl was found to react with sulfur-sulfur bonds of di- and trisulfanes with insertion of the Cp_2Ti unit: [11]



(15)

The resulting complex, previously obtained from Cp_2TiCl_2 and the dithiol [20], provides access to many new heterocycles: [10, 20]



(16)

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Various organosulfur heterocycles have been found to occur in plants and mushrooms and often are of biological activity.[4]

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