Sulfur Compounds, 199[◇]

Novel Titanocene Thiolato Complexes and Their Application in Preparing New Sulfur-Containing Heterocycles

Ralf Steudel*, Monika Kustos, Vera Münchow, and Ursula Westphal

Institut für Anorganische und Analytische Chemie, Technische Universität Berlin,
Sekr. C 2, D-10623 Berlin, Germany
Fax: (internat.) +49(0)30/31426519
E-mail: steudel@wap0204.chem.tu-berlin.de

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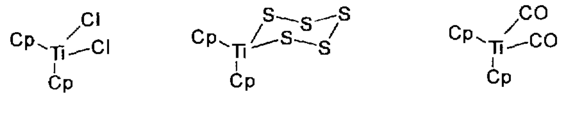
Treatment of $Cp_2Ti(CO)_2$ (**3**) with the di- and polysulfanes 1,2,4-$(CH_2)_2S_3$, C_4S_6 (**9**), $C_7H_{10}S_3$ (**11**), 1,2,4,6-$(CH_2)_3S_4$ (**16**), $C_6H_{10}S_6$ (**19**), and S_6 affords the titanocene chelate complexes $Cp_2TiS_3(CH_2)_2$ (**8**), $(Cp_2Ti)_2C_4S_6$ (**10**), $Cp_2TiS_3C_7H_{10}$ (**13**), $Cp_2TiS_2C_7H_{10}$ (**14**), $Cp_2TiS_4(CH_2)_3$ (**17**), $Cp_2TiS_6C_6H_{10}$ (**20**), and Cp_2TiS_8 (**23**). **14** is also obtained from Cp_2TiCl_2 (**1**) and the geminal dithiol of norbornane. The analogous reaction with the dithiol of dicyclopentadiene yields $Cp_2TiS_2C_{10}H_{12}$ (**15**). In ligand transfer reactions, **8** reacts with SCl_2 to give 1,2,3,5-tetrathiane (**25**), **10** provides **9** on reaction with Cl_2, **13** when treated with S_2Cl_2 affords $C_7H_{10}S_5$ (**12**), **15** reacts with S_2Cl_2 to give $C_{10}H_{12}S_4$, **17** and SCl_2 yield 1,2,3,5,7-pentathiepane (**18**), **20** is converted to $C_6H_{10}S_7$ (**22**) on reaction with SCl_2, and **23** yields S_{10} and 1,2-$C_6H_4S_{10}$ (**24**) when it is allowed to react with S_2Cl_2 or 1,2-$C_6H_4(SCl)_2$, respectively. With phosgene, thiophosgene, and thionyl chloride, compound **15** yields the corresponding dithiocarbonate **26**, the trithiocarbonate **27** and the trisulfane 2-oxide **28**. The structure of **27** was determined by X-ray crystallography.

Introduction

Thiolato complexes of titanocene Cp_2Ti ($Cp = \eta^5\text{-}C_5H_5$) have been known since 1962. They are typically prepared from Cp_2TiCl_2 (**1**) by nucleophilic displacement of the chloride ligands by thiolate anions R^1S^-[1,2], dianions $^-S{-}R^2{-}S^-$[3], or polysulfide anions S_x^{2-}[4], resulting in species such as $Cp_2Ti(SR^3)_2$, $Cp_2\overline{TiSR^4S}$, and Cp_2TiS_5 **2**. Other routes include the reaction of the dithiol $Cp_2Ti(SH)_2$, with dichlorosulfanes S_nCl_2[5] or with phthalimido derivatives of the type $RS_x{-}NR$ ($x = 1, 2$)[6], and the treatment of Cp_2TiCl_2 with $RSSi(CH_3)_3$[7].

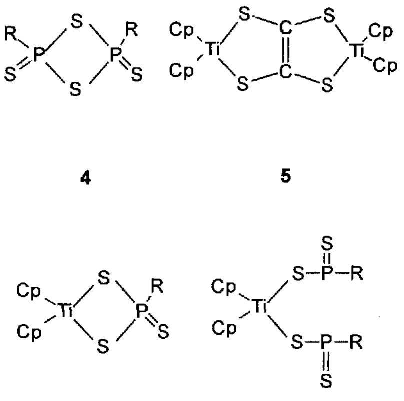
Scheme 1



1 **2** **3**

More recently, the application of titanocene dicarbonyl $Cp_2Ti(CO)_2$ (**3**) has provided a considerable number of novel thiolato complexes of titanocene. Organic disulfanes react with **3** with insertion of the Cp_2Ti unit into the sulfur-sulfur bond to give $Cp_2Ti(SR)_2$ and carbon monoxide[8]. Cyclooctasulfur on refluxing with **3** in hexane yields **2**[9]. Even carbon disulfide[10] and Laweson's reagent **4**[11] are reduced by **3** resulting in complexes **5**, **6**, and **7**:

Scheme 2



4 **5** **6** **7**

Trisulfanes RSSSR react with **3** to give the expected disulfanido complexes $Cp_2Ti(SR)(SSR)$[12], while from S_7NH and **3**, the complex $Cp_2Ti(\mu\text{-}S_2)(\mu\text{-}S_5)NH$, containing a nine-membered ring, was obtained[13].

Titanocene thiolate complexes, such as those mentioned above, have been extensively used for the synthesis of novel sulfur-rich compounds by ligand transfer reactions[14]. The Ti−S bonds in these complexes react with certain S−Cl bonds and other non-metal halides to give **1** and a compound having a new non-metal−sulfur bond. Examples are the preparation of S_7 from **2** and S_2Cl_2[15], of S_8NH from

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[◇] Part 198: R. Steudel, Y. Drozdova, K. Miaskiewicz, R. H. Hertwig, W. Koch, *J. Am. Chem. Soc.* **1997**, *119*, 1990.

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Cp_2TiS_7NH and SCl_2[16], and of the twelve-membered ring R_2CS_{11} from $Cp_2Ti(\mu\text{-}S_2)_2CR_2$ and S_7Cl_2[17]. Numerous novel cyclic and acyclic sulfur compounds have been prepared in this way. To extend this synthetic method even further new titanocene thiolate complexes are needed.

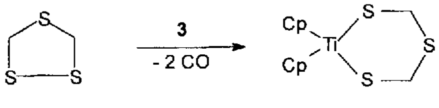
Here, we report the synthesis and characterization of eight new titanocene thiolato complexes and their application in the preparation of sulfur heterocycles containing between 2 and 10 sulfur atoms.

Results and Discussion

Titanocene Thiolato Complexes

We treated cyclic organic di- and trisulfanes with **3** and obtained mono- and dinuclear complexes by insertion of Cp_2Ti into one or two of the S–S bonds[18]. 1,2,4-Trithiolane reacted with **3** at room temperature in *n*-hexane to give complex **8**, which was isolated as a black material in 37% yield and identified by its elemental analysis, EI-mass, IR, ^1H- and ^{13}C-NMR spectra.

Scheme 3

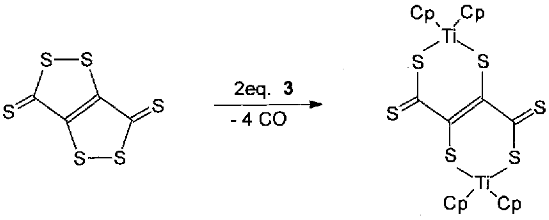


8

The mass spectrum showed signals for the molecular ion as well as for typical fragments such as Cp_2TiS^{+1} and $C_2H_5S_3^+$. The six-membered metallacycle of **8** can be assumed to exist in the chair conformation, as is found in **2** and in $(iPrC_5H_4)_2Ti(\mu\text{-}S_2)_2CH_2$[19]. The latter two complexes are rigid in solution at ambient temperatures. In contrast, the ^1H-NMR spectrum of **8** exhibits only two signals; one for the methylene groups and one for the Cp ligands. This observation indicates that a rapid conformational isomerization of the six-membered ring of **8** takes place, resulting in magnetic equivalence of the axially and equatorially arranged methylene protons and Cp ligands. However, at lower temperatures (−81 °C) two signals are observed for the Cp ligands, and the methylene groups give rise to two doublets, as would be expected for a rigid conformation. The coalescence temperature T_C was determined as −7 °C, from which the free activation enthalpy was calculated as 50.6 kJ mol^{-1}. This value compares well with the 55.3 kJ mol^{-1} reported for 1,2,3-trithiane[20] and the 59.2 kJ mol^{-1} determined for $Cp_2Ti(\mu\text{-}S_2)_2CH_2$[19], while for **2** a figure of 76.3 kJ mol^{-1} has been obtained[21].

To ascertain whether organic bisdisulfanes react with **3** in an analogous manner as disulfanes, we treated the bicyclic tetracarbon hexasulfide **9**[22] at 20 °C in THF solution with **3** and obtained the dinuclear complex **10** in 70% yield.

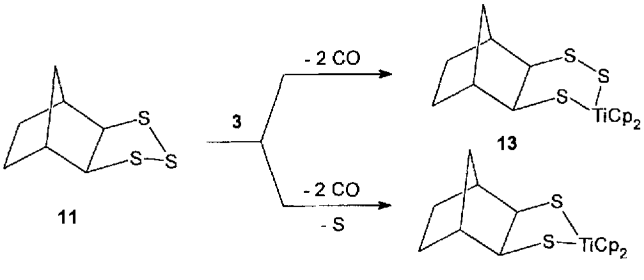
Scheme 4



9 **10**

The air-stable green product **10** did not melt below 300 °C and was found to be soluble in chlorinated hydrocarbons. It reacted with chlorine at 20 °C to give **9** and **1**, thus proving the connectivity. The ^1H-NMR spectrum of **10** in $CDCl_3$ exhibited two signals for the Cp ligands, as in the case of the other six-membered metallacycles mentioned above.

Scheme 5



11 **13** **14**

The trithiolane **11** was used to test the behavior of **3** towards cyclic trisulfanes. Compound **11** was prepared from norbornene and elemental sulfur, a reaction which yields the corresponding pentathiepane $C_7H_{10}S_5$ (**12**) as a minor product[23]. Treatment of **11** in *n*-hexane with **3** under exclusion of oxygen provided the expected product (**13**) in 61% yield, formed as a result of insertion of titanocene into one of the S–S bonds of **11**. In addition, a small amount of $Cp_2TiS_2C_7H_{10}$ (**14**) was isolated by fractional crystallization.

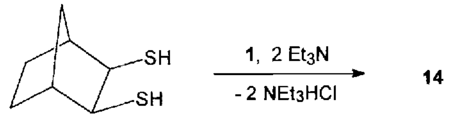
Scheme 6

12 **15**

The formation of **13** and **14** is in line with the observation that **3** reacts with acyclic trisulfanes to give $Cp_2Ti(SSR)(SR)$ as well as $Cp_2Ti(SR)_2$[12]. The main product **13** forms violet, air-stable crystals and is moderately soluble in CS_2 and CH_2Cl_2, less so in THF and $CDCl_3$, and insoluble in acetone, benzene or DMSO. The complex was characterized by infrared, mass, ^1H-NMR and UV/Vis spectroscopy, as well as by elemental analysis. In the MS, the molecular ion was observed at *m/z* = 368; a characteristic fragment ion was $Cp_2TiS_3^+$ (at *m/z* = 274). As expected, the reaction of **13** with S_2Cl_2 afforded **12** and **1**.

The minor product **14** (Scheme 5) forms green crystals, which are only stable at temperatures below 4°C, and decompose slowly in dichloromethane or THF solution even at 0°C. Nevertheless, the molecular ion was observed in the mass spectrum of **14** at $m/z = 336$ together with the characteristic fragment ion $Cp_2TiS_2^+$ at $m/z = 242$. To further characterize **14**, it was synthesized by an independent method from **1** and the geminal dithiol of norbornane $C_7H_{10}(SH)_2$ in the presence of an amine.

Scheme 7



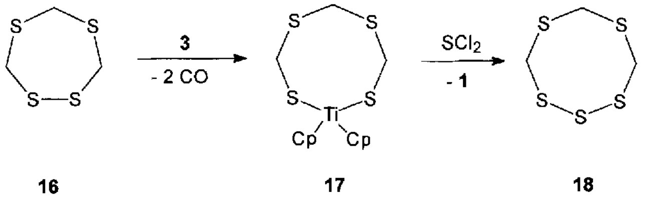
The dithiolato complex **14** was obtained in 65% yield. In an analogous manner, the dithiol of dicyclopentadiene $C_{10}H_{12}(SH)_2$[23b] was treated with **1** and triethylamine, thereby affording the corresponding titanocene chelate complex **15** in 45% yield. This was obtained as a green solid, stable in air at 20°C. Both **14** and **15** were characterized by ^{1}H-NMR, mass, and infrared spectra. Since **14** slowly decomposes in solution, even at low temperatures, it could not be obtained in high purity. Dichlorodisulfane reacts with **15** in CS_2 at 20°C to give **1** and the known tetrasulfane $C_{10}H_{12}S_4$[24].

The insertion of the titanocene unit of **3** into S–S bonds does not always provide thiolato complexes which are sufficiently stable to be fully characterized. However, even if the complex is unstable and obtainable only as a crude product, it may still be a useful precursor for the preparation of new C-S heterocycles by ligand transfer reactions. Three examples of highly reactive titanacycles with ring sizes 8 and 9 are presented here:

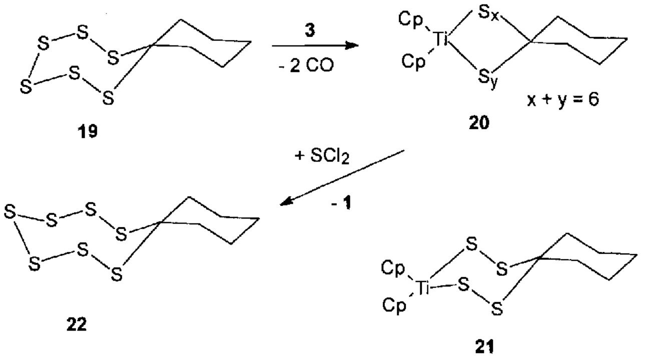
(1) On reaction of **3** with 1,2,4,6-tetrathiepane **16**[25] in THF at 20°C, an aubergine-colored precipitate was obtained in low yield which presumably was **17**, since it reacted with SCl_2 in CS_2 to give the novel 1,2,3,5,7-pentathiocane **18**. The latter was identified from its mass and ^{1}H-NMR spectra. The MS showed the molecular ion at $m/z = 202$ and peaks attributable to the loss of S_2, $S_3C_2H_4$, and other typical fragments. While the proton NMR spectrum of **16** shows singlets ($\delta = 4.24$ and 4.28) in a 2:1 intensity ratio, the spectrum of **18** consists of singlets ($\delta = 4.04$ and 4.22) in a 1:2 ratio. An isomer of **18** has been isolated from the seeds of *Parkia speciosa* and was characterized by mass and ^{1}H-NMR spectroscopy (singlets at $\delta = 4.25$ and 4.30; intensity ratio 2:1)[26]. The authors were unable to decide whether they had isolated 1,2,4,5,7-pentathiocane or **18**. Our results clearly show that the natural product must have been the former.

(2) The spirocyclic hexathiepane cyclohexylidene hexasulfane **19**[17] reacted with **3** at 20°C in THF with insertion of Cp_2Ti. The expected product **20** was obtained as a black solid in 28% yield. By-products were **2**, the known violet $Cp_2Ti(\mu\text{-}S_2)_2C_6H_{10}$ (**21**), and traces of S_8.

Scheme 8



Scheme 9

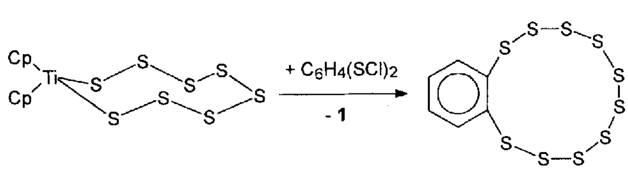


A fresh solution of **20** was grass-green but decomposed with the formation of **2** and **21**. Such mixtures could be analyzed by reversed-phase HPLC: the retention times increased in the order **2** < **21** < **20** (eluent: methanol). Due to this decomposition the product **20** was always contaminated by some **2** and **21** and single crystals could not be grown. While the mass spectrum and the sharp singlet ($\delta = 6.13$) in the ^{1}H-NMR spectrum prove the identity of **20**, the connectivity of the Ti–S–C heterocycle could not be demonstrated. As in similar cases, the carbenoid Cp_2Ti obviously inserts into one specific S–S bond, resulting in only one product (most probably $x = y = 3$ or $x = 2$, $y = 4$). The general formula of **20** follows from its reaction with SCl_2, which yields cyclohexylidene heptasulfane $C_6H_{10}S_7$ (**22**) and **1** (see below). The heptathiocane **22** had previously been observed only by HPLC as part of the homologous series $C_6H_{10}S_n$[17].

(3) The S–S bonds of cyclooctasulfur S_8 do not react with **3** at 20°C, but on refluxing in hexane for several days the formation of **2** was observed[9]. All previous attempts to synthesize mononuclear titanocene polysulfides with more than five sulfur atoms had failed. Since we had succeeded in preparing a nine-membered metallacycle Cp_2TiS_7NH from **3** and S_7NH, we treated S_6 and S_7 in *n*-hexane with **3** at 20°C and obtained a precipitate consisting of several Cp_2TiS_x molecules ($x = 5$, 7, and 8 in both cases). Traces of S_8 were also formed. By recrystallization from CS_2, almost pure Cp_2TiS_8 was obtained as a dark-red solid. The retention times of the three Cp_2TiS_x species in reversed-phase HPLC (C18/methanol) were found to increase with increasing value of x. The retention indices RS[27] of Cp_2TiS_5 (491), Cp_2TiS_7 (651), and Cp_2TiS_8 (744) depend linearly on x (correlation coefficient 0.999), demonstrating that these species are members of a homologous series. Their UV/Vis spectra, recorded on-line during HPLC

analysis using a diode-array detector, are very similar (maxima at 216–220, 298–314, and 489–492 nm). Cp_2TiS_8 (**23**) was characterized by elemental analysis, mass and ^1H-NMR spectra. In the MS, only $Cp_2TiS_5^+$ and S_8^+ as well as their fragments were observed, decomposition products which are also formed in solution. The ^1H-NMR spectrum showed only one singlet at $\delta = 6.33$ (Cp_2TiS_5 in CS_2: $\delta = 6.10$ and 6.24 at 30°C[4]), indicating ring inversion of the metallacycle at ambient temperatures. Obviously, **23** is not the result of a simple insertion reaction. One has to assume that S_6 and S_7 are first converted into reactive intermediates, which then give several Cp_2TiS_x molecules (x = 5, 7, 8).

Scheme 10



23 **24**

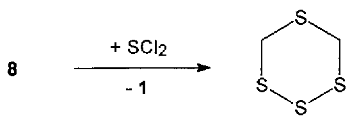
Further evidence for the nature of Cp_2TiS_8 comes from its reactions with dichlorosulfanes and organic disulfenyl chlorides. While Cp_2TiS_8 and S_2Cl_2 give **1** and S_{10}, the aforementioned mixture of Cp_2TiS_x molecules yields a mixture of **1**, S_7, S_9, and S_{10} when treated with S_2Cl_2 in CS_2 at 20°C. Such reactions can most easily be monitored by HPLC analysis, since the retention times of all products are known[28]. Benzo-1,2-disulfenyl chloride $C_6H_4(SCl)_2$ is converted into $C_6H_4S_{10}$ (**24**) when it is allowed to react with **23**. The decasulfane was identified from its retention time and by its mass spectrum, which shows the molecular ion at m/z = 396 and fragment ions of the tpye $C_6H_4S_n^+$ (n = 7, 4, 3).

Ligand-Transfer Reactions

The ligand-transfer reactions described above served the purpose to identify the precursor titanocene complex. Below, we report the synthesis of new sulfur-containing heterocycles to further demonstrate the usefulness of titanocene chelates for ring synthesis.

By reaction of **8** with SCl_2 in CS_2 at 20°C, 1,2,3,5-tetrathiane (**25**) was obtained in 13% yield.

Scheme 11



25

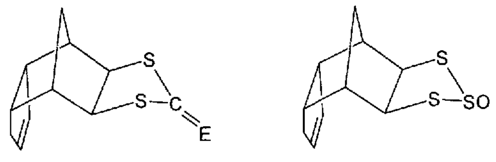
Compound **25** had previously been observed as a component of the complex mixtures obtained from S_8, Na_2S, formaldehyde, and acetic acid[29], as well as by GC-MS analysis of the extract obtained from shiitake mushrooms *Lentinus edodes*[30].

When the cyclohexylidene thiolato complex **20** was treated with SCl_2 in CS_2 at 20°C, the heptasulfane **22** was obtained in 30% yield. Its mass spectrum showed the molecular ion at m/z = 306 and on HPLC analysis a single peak was observed, demonstrating its purity.

Thiolato complexes react not only with S–Cl compounds with ligand transfer, but certain C–Br and C–Cl compounds may also be used. This has previously been shown for C_6H_5COCl[8], $C_6H_5CH_2Br$[31], $(COCl)_2$[32], and triphenylmethyl chloride[33]. We have now found that phosgene and thiophosgene react with **15** in CS_2 at 20°C, to give the corresponding dicyclopentadiene derivatives **26** and **27**, respectively.

The dithiocarbonate **26** is an air-stable, colorless solid, which was obtained in 50% yield. In the case of thiophosgene, the reaction with **15** was monitored by HPLC analysis and the only products detected were **1** and **27**. The structure of **27** was determined by X-ray diffraction on a single crystal obtained from $CHCl_3$ solution. The molecules exhibit C_1 symmetry (Figure 1) and the trithiocarbonate unit is planar (sum of valence angles at C11: 360.1°).

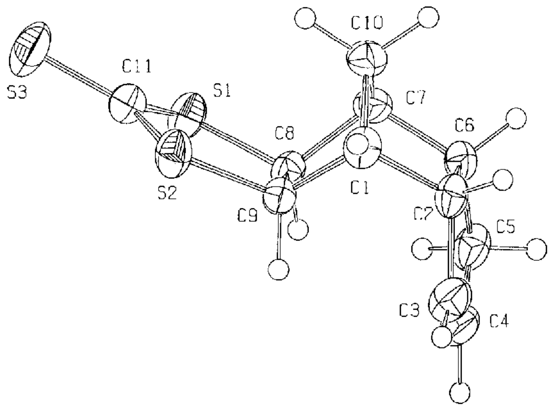
Scheme 12



26: E = O
27: E = S

28

Figure 1. Molecular structure of **27**[a]

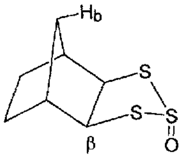
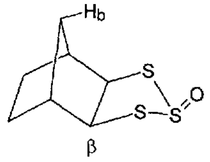
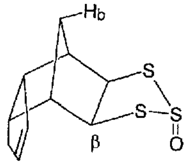
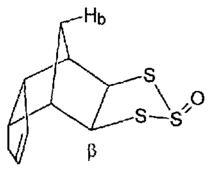


[a] Selected bond lengths [pm], bond angles [°] and torsion angles [°]: C8–S1 181.8(4), C9–S2 182.9(5), C11–S2 170.6(5), C11–S3 165.7(5), C11–S1 172.6(5), C3–C4 136.6(7), C4–C5 146.9(7), C8–C9 155.5(6); S1–C11–S2 116.1(3), S1–C11–S3 121.5(3), S2–C11–S3 122.3(3); S1–C8–C9–S2 –5.7(4), C11–S2–C9–C8 1.4(3).

The structure of the $C_{10}H_{12}$ unit is similar to that found in other dicyclopentadiene derivatives[34]. The CC double bond is localized between C3 and C4.

The S–Cl bonds of thionyl chloride are less reactive towards titanocene thiolato complexes than those of sulfenyl chlorides, but in some cases reaction does occur at

Table 1. Characteristic ^1H- and $^{13}C\{^1H\}$-NMR chemical shifts for 4-oxo-3,4,5-trithiatricyclo[5.2.1.$0^{2,6}$]decane[36] and for **28** (δ values in ppm)

	Hb	Cβ	Cβ'
	1.95	71.32	71.32
	2.50	79.90	79.90
 Isomer A	2.09	64.4	67.6
 Isomer B	n.a. [a]	72.7	77.1

[a] Not assigned (the signals of 11 protons overlap to form two broad multiplets in the region of δ = 2.2 to 2.8).

ambient temperatures[35], compound **15** being one such instance. The new trithiolane-2-oxide of dicyclopentadiene (**28**) was obtained in 90% yield from **15** and $SOCl_2$ in CS_2 at 20°C. While the HPLC analysis of **28**, its mass spectrum (molecular ion at m/z = 244) and the microanalysis were indicative of a pure compound, the $^{13}C\{^1H\}$-NMR spectrum exhibited 20 instead of 10 signals. The spectrum may be explained as shown in Table 1, by assuming the presence of two conformational isomers A and B in an approximate 2:1 molar ratio. Similar observations have been made for the trisulfate-2-oxide of norbornane, obtained from the geminal dithiol and thionyl chloride[36]. In this case, the *endo* and *exo* forms were obtained in a 65:35 ratio and the NMR spectra were assigned as shown in Table 1. We therefore assume that isomer A of **28** is the *endo* and B the *exo* form.

Summarizing, it can be stated that the insertion of the titanocene fragment Cp_2Ti, generated in situ from $Cp_2Ti(CO)_2$, into sulfur–sulfur bonds of heterocycles provides a new route to larger, more sulfur-rich heterocycles under mild conditions. The initially formed titanocene thiolato complexes may be relatively unstable in solution and therefore sometimes difficult to obtain in high purity. However, their rapid reaction with sulfenyl chlorides and certain carbon-chlorine compounds such as $COCl_2$ and $CSCl_2$ provides cyclic di- and polysulfanes, which are inaccessible by other routes.

We are grateful to Prof. Dr. *E. Fanghänel* for a sample of C_4S_6. This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Verband der Chemischen Industrie*.

Experimental Section

Spectrometers: ^1H NMR: Bruker ARX 200, WH 270, and ARX 400. The samples were dissolved in deuterated solvents, the proton residues of which were used as internal references. IR: Perkin-Elmer 580B. MS: Varian MAT 311A spectrometer in the EI mode with ionizing energy of 70 eV. The microanalyses were performed on a Perkin-Elmer 2400 or a Hewlett-Packard 185 CHN analyser.

Chromatography: The HPLC equipment consisted of a Gynkotek High Precision Pump 300 CS (flow: 2 ml/min), Negetti and Zamba NZ 190 Sixport injector (loop: 10 μl), Waters-Millipore Radial-Pak cartridge column (length: 100 mm, inner diameter: 8 mm) with octadecylsilane (particle size: 10 μm), Water Series 440 absorbance detector (λ = 254 nm) and Hitachi D-2000 Chromato-Integrator. Methanol was used as eluent. The retention index values RS are based on the retention times of S_6, S_8, S_9, and S_{10}[27].

Chemicals: The solvents and reagents Et_2O, MeO*t*Bu, THF, *n*-hexane (all Na), Et_3N ($MgSO_4$), CS_2, $CHCl_3$, CH_2Cl_2, *n*-pentane (all P_4O_{10}) were distilled from the drying agents given in brackets. SCl_2 and S_2Cl_2 were purified by standard methods[37]. $Cp_2Ti(CO)_2$[38], $C_7H_{10}S_3$[23a], $C_7H_{10}(SH)_2$[23b], and $C_{10}H_{12}(SH)_2$[24] were prepared as reported. Other solvents and chemicals were used as obtained without purification. $Cp_2Ti(CO)_2$ and the dithiols were handled with strict exclusion of air and moisture (Schlenk technique), and with exclusion of light. The silica gel used was obtained from Merck (60 F_{254}).

2,2-Dicyclopentadienyl-1,3,5-trithia-2-titanacyclohexane (**8**): 370 mg (1.58 mmol) of titanocene dicarbonyl in 100 ml of *n*-hexane was added over a period of 150 min to an emulsion of 180 mg (1.45 mmol) of 1,2,4-trithiolane in 100 ml of *n*-hexane. The color of the reaction mixture changed from yellow via brown to green. The mixture was stirred for 15 h at 20°C and then filtered. The precipitate was extracted for 10 min with 150 ml of carbon disulfide. The insoluble, violet solid was separated by filtration, the filtrate was concentrated, and the remaining black solid (**8**) washed with 20 ml of *n*-hexane and dried; yield 160 mg (37%); m.p. >150°C. – $C_{12}H_{14}S_3Ti$ (302.3): calcd. C 47.7, H 4.7, S 31.8; found C 45.7, H 4.7, S 32.0. – UV/Vis (*n*-pentane): λ_{max} (%) = 197 (84), 207 (100), 217 (72), 254 (sh), 336 (13), 412 (8), 598 (5). – MS (130°C): m/z (%) = 302 (12) [M^+], 178 (100). – ^1H NMR [200 MHz, CS_2 with $\Phi(C_6D_6)$ = 40%, 20°C]: δ = 5.78 (s, 10H), 4.34 (s, 4H); (400 MHz, [D_8]toluene, −81.4°C): δ = 5.76 (s, 5H), 5.15 (s, 5H), 4.78 (d, ^2J = 14.4 Hz, 2H), 3.91 (d, ^2J = 14.4 Hz, 2H); T_C = −7°C, $\delta\upsilon$ = 242 Hz. – $^{13}C\{^1H\}$ NMR [50 MHz, CS_2 with $\Phi(C_6D_6)$ = 40%]: δ = 43.6, 111.3[39] (Φ = volume fraction).

Preparation of $(Cp_2Ti)_2C_4S_6$ (**10**): 207 mg (0.86 mmol) of **9** was added to a solution of 403 mg (1.72 mmol) of **3** in 50 ml of THF. On stirring the solution for 12 h the color changed from violet to green. The solvent was then evaporated until a volume of around 25 ml remained, whereupon **10** precipitated on storing of the solution at −78°C for 2 days; yield 359 mg (70%); m.p. >300°C. – $C_{24}H_{20}S_6Ti_2$ (596.5): calcd. C 48.3, H 3.4, S 32.3; found C 47.4, H 3.0, S 31.3. – UV/Vis (methanol): λ_{max} (%) = 220 (100), 310 (37), 443 (6), 710 (10). – RS = 390. – MS (200°C): m/z (%) = 564 (0.5)

[$M^+ - S$], 240 (100). – ^1H NMR (400 MHz, $CDCl_3$): δ = 6.11 (s, 10H), 5.77 (s, 10H)[40].

Preparation of $Cp_2TiS_3C_7H_{10}$ (**13**): 520 mg (2.73 mmol) of **11** dissolved in 5 ml of *n*-hexane was added to a solution of 640 mg (2.73 mmol) of **3** in 100 ml of *n*-hexane. After stirring for 16 h at 20°C, **13** precipitated and was separated by filtration. The volume of the filtrate was reduced to 50 ml. Storing the concentrated solution for 24 h at −26°C yielded a small amount of **14** as a green precipitate, which was isolated by filtration and dried in vacuo. Characterization see below. **13** was purified by extracting the crude product with two 50 ml portions of CH_2Cl_2, adding 20 ml of *n*-hexane to the combined extracts and storing this solution at −78°C for 16 h. This resulted in the deposition of a pink precipitate; yield 610 mg (61%), m.p. 187°C. – $C_{17}H_{20}S_3Ti$ (368.4): calcd. C 55.4, H 5.5; found C 55.5, H 5.4. – UV/Vis (methanol): λ_{max} (%) = 236 (100), 346 (73), 514 (1), 665 (1). – Retention index[27] RS = 437. – MS (220°C): *m/z* (%) = 368 (0.5) [M^+], 97 (100). – ^1H NMR (400 MHz, CS_2/[D_8]THF): δ = 6.73 (s, 5H), 6.18 (s, 5H), 4.21 (dd, *J* = 2 Hz, 1H), 3.68 (1H), 2.93 (br dd, *J* = 2 Hz, 1H), 2.72 (br dd, *J* = 2 Hz, 1H), 1.92 (br d, ^2J = 11 Hz, 1H), 1.76–1.40 (m, 4H), 1.08 (dd, ^2J = 11 Hz, 1H)[40].

Preparation of $Cp_2TiS_2C_7H_{10}$ (**14**): 1.66 g (10.4 mmol) of $C_7H_{10}(SH)_2$ and 2.9 ml (20.8 mmol) of Et_3N in 10 ml of toluene were added to a suspension of 2.58 g (10.4 mmol) of **1** in 100 ml of toluene. The reaction mixture was stirred at 20°C for 3 h, resulting in a color change from red to dark-green. The mixture was then filtered and the precipitate was washed with 10 ml of toluene, which was added to the filtrate. After evaporation of the solvent, the residue was suspended in 30 ml of CS_2. Complex **14** precipitated from the filtrate of this suspension on storage at −78°C for 24 h; yield 1.77 g (65%), m.p. 155°C. – $C_{17}H_{20}S_2Ti$ (336.4): calcd. C 60.7, H 6.0; found C 58.4, H 5.8. – MS (140°C): *m/z* (%) = 336 (12) [M^+], 178 (100). – ^1H NMR (400 MHz, $CDCl_3$): δ = 6.55 (s, 5H), 6.50 (s, 5H), 4.88 (d, ^3J = 1.5 Hz, 2H), 1.92 (m, 2H), 1.82 (dt, ^2J = 10 Hz, ^3J = 2 Hz, 1H), 1.40 (dm, ^2J = 7.5 Hz, 2H), 1.30 (dm, ^2J = 7.5 Hz, 2H), 0.92 (dt, ^2J = 10 Hz, ^3J = 2 Hz, 1H).

Preparation of $Cp_2TiS_2C_{10}H_{12}$ (**15**): 1.00 g (5 mmol) of $C_{10}H_{12}(SH)_2$ and 1.4 ml (10 mmol) of Et_3N in 10 ml of toluene were added to a suspension of 1.26 g (5 mmol) of **1** in 20 ml of toluene. The reaction mixture was stirred at 20°C for 3 h, resulting in a color change from red to green and precipitation of **15**. The product was filtered off and washed with four 10 ml portions of toluene. After drying in vacuo, the solid was suspended in 100 ml of water. Filtration and desiccation over P_4O_{10} afforded **15** as a green powder; yield 840 mg (45%), m.p. 156°C (dec.). – $C_{20}H_{22}S_2Ti$ (374.4): calcd. C 64.2, H 5.9; found C 63.9, H 5.8. – MS (280°C): *m/z* (%) = 374 (22) [M^+]. – ^1H NMR (270 MHz, $CDCl_3$): δ = 6.53 (s, 5H), 6.45 (s, 5H), 5.91 (m, 1H), 5.73 (m, 1H), 5.00 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 4.94 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 2.95 (m, 1H), 2.30 (m, 3H), 2.05 (m, 2H), 1.94 (dm, ^2J = 10 Hz, 1H), 1.84 (br), 1.15 (dm, ^2J = 10 Hz, 1H)[41].

Preparation of $Cp_2TiS_4(CH_2)_3$ (**17**) *and $(CH_2)_3S_5$* (**18**): 80 mg (0.34 mmol) of **3** in 25 ml of THF was added to a solution of 50 mg (0.29 mmol) of **16** in 50 ml of THF over a period of 1 h. The reaction mixture became violet in color. After stirring for 15 h at 20°C, the mixture was filtered, the solvent was evaporated and 25 mg (25%) of crude **17** remained as a dark-violet solid. In order to characterize **17**, it was treated with SCl_2 according to the general procedure given in the next Section, resulting in **18**. From 25 mg of crude **17** and SCl_2, was obtained 5 mg of crude **18** (9% based on the tetrathiepane used to prepare **17**) as an almost colorless powder; m.p. 70°C. – $C_3H_6S_5$ (202.4): calcd. C 17.8, H 3.0, S 79.2; found C 19.1, H 3.0, S 77.8. – MS (100°C): *m/z* (%) = 202 (16) [M^+], 45 (100). – ^1H NMR (200 MHz, CD_2Cl_2): δ = 4.22 (s, 4H), 4.04 (s, 2H)[39].

General Procedure for the Reaction of Titanocene Complexes with Cl_2, SCl_2 or S_2Cl_2: To a solution of the titanocene complex in CS_2 (except **10**: CCl_4) was added a solution of SCl_2 or S_2Cl_2 in CS_2 (or Cl_2 in CCl_4) until the color of the reaction mixture had changed to orange-red. 1 g of silica gel was then added to adsorb **1**. The suspension was stirred for several minutes and filtered, the residue was washed with CS_2, the filtrate was concentrated, and the remaining residue was redissolved in MeO*t*Bu. After filtration and storage of the solution at −50°C for 24 h, the products were isolated.

Preparation of $Cp_2TiS_6C_6H_{10}$ (**20**): 120 mg (0.51 mmol) of **3** in 40 ml THF was added to a solution of 100 mg (0.36 mmol) of **19** in 60 ml of THF over a period of 1 h. The reaction mixture became brown in color. The mixture was stirred for 15 h at 20°C, concentrated, and the residue was subjected to repeated column chromatography on silica gel using MeO*t*Bu with Φ(*n*-hexane) of 33% as eluent. On evaporation of the solvent from the green fractions (R_f = 0.80), **20** was obtained as a black powder; yield 45 mg (28%), m.p. 85°C. – $C_{16}H_{20}S_6Ti$ (452.6); contaminated with traces of **2** and **21**. – UV/Vis (methanol): $Ä_{max}$ (%) = 225 (100), 318 (40), 469 (8), 650 (4). – RS = 693. – MS (160°C): *m/z* (%) = 429 (0.5), 388 (1) [$M^+ - S_2$], 81 (100). – ^1H NMR (200 MHz, CD_2Cl_2): δ = 6.13 (s, 10H), 1.0–2.2 (m, 10H)[39]. For further characterization see next Section.

Preparation of 7,8,9,10,11,12,13-Heptathiaspiro[5.7]tridecane $C_6H_{10}S_7$ (**22**): Reaction of 20 mg of **20** with SCl_2 according to the general procedure given above. $C_6H_{10}S_7$ (306.6); yield 4 mg (30%), m.p. 65°C. – RS = 893. – MS (100°C): *m/z* (%) = 306 (9) [M^+], 114 (100)[39].

Preparation and Derivatization of Cp_2TiS_8 (**23**): To 400 mg (2.1 mmol) of S_6 in 160 ml of *n*-hexane, 370 mg of **3** (1.6 mmol) dissolved in 50 ml of *n*-hexane was added over a period of 10 min. After half the quantity of **3** had been added, the temperature was lowered to 4°C. After stirring for 2 h at 4°C, the red precipitate was filtered off, washed with 20 ml of cold CH_2Cl_2, and extracted with 50 ml of CS_2. The CS_2 solution was filtered and the filtrate was concentrated to dryness yielding 80 mg (12%) of **23** (to be stored at −50°C). Further purification by recrystallization from CS_2. – $C_{10}H_{10}S_8Ti$ (434.6): calcd. C 27.6, H 2.3, S 59.0; found C 26.9, H 2.0, S 58.6. – UV/Vis (methanol): λ_{max} (%) = 216 (100), 298 (37), 492 (7) nm. – ^1H NMR (CS_2): δ = 6.33 (s, 10H)[40].

To a solution of **23** in CS_2 were added dropwise solutions of either (a) S_2Cl_2 or (b) 1,2-benzodisulfenyl chloride in CH_2Cl_2 at −10°C. The reaction was monitored by HPLC. In case (a) the signal of **23** diminished and a peak at the retention time of S_{10} grew, while in case (b) **24** was formed which was precipitated from the solution at −78°C and identified by MS (120°C): *m/z* (%) = 396 (0.2) [M^+], 172 (100). When the mixture of Cp_2TiS_x molecules (x = 5, 7, 8) was treated with $C_6H_4(SCl)_2$ the chromatogram showed $C_6H_4S_7$ (RS = 740), $C_6H_4S_9$ (917), and $C_6H_4S_{10}$ (1016); the RS values of these species show a linear dependence on x (correlation coefficient 0.999).

Preparation of 1,2,3,5-Tetrathiane (**25**): The general procedure given above was followed using 160 mg of **8** and 54 mg of SCl_2; yield 10 mg (13%); m.p. 82°C. – $C_2H_4S_4$ (156.3): calcd. C 15.4, H 2.6; found C 15.2, H 2.8. – MS (160°C): *m/z* (%) = 156 (100) [M^+]. – ^1H NMR (200 MHz, CD_2Cl_2): δ = 4.50 (s, br). – $^{13}C\{^1H\}$ NMR (50 MHz, CD_2Cl_2): δ = 39.5.

Preparation of exo-5-Oxa-4,6-dithiatetracyclo[$7.3.1^{2,8}.0^{3,7}$]tridec-10-ene (**26**) *and of exo-5-Thia-4,6-dithiatetracyclo[$7.3.1^{2,8}.0^{3,7}$]tridec-10-ene* (**27**): To a solution of 1.47 g (3.86 mmol) of **15** in 200 ml of CH_2Cl_2 was added 2 ml of a solution of $COCl_2$ in toluene (c = 1.93 M). The color of the reaction mixture changed immediately from green to red. After 30 min, the mixture was filtered through a silica gel column. The silica gel was washed with CH_2Cl_2 and the colorless washings were pooled. The solvent was evaporated and the white powder obtained was recrystallized from CH_2Cl_2 with addition of *n*-hexane. On storing the solution at −18°C for 24 h, 400 mg (50%) of **26** were obtained; m.p. 70°C. – $C_{11}H_{12}S_2O$ (224.3): calcd. C 58.9, H 5.4; found C 59.0, H 5.3. – MS (25°C): *m/z* (%) = 224 (31) [M^+], 98 (100). – ^1H NMR (200 MHz, $CDCl_3$): δ = 5.74 (m, 1H), 5.58 (m, 1H), 4.18 (dd, ^3J = 9 Hz, ^4J = 2 Hz, 1H), 4.00 (dd, ^3J = 9 Hz, ^4J = 2 Hz, 1H), 3.21 (m, 1H), 2.69 (m, 1H), 2.42 (dm, ^3J = 5 Hz, 1H), 2.39–2.18 (m, 4H), 1.64 (dm, ^2J = 11 Hz, 1H). – $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 199.6, 132.7, 131.3, 54.1, 53.3, 50.9, 50.4, 47.4, 43.0, 35.8, 32.4. – IR (KBr): $\tilde{\nu}$ = 1635 cm^{-1} (CO).

In an analogous manner **27** was obtained from $CSCl_2$; m.p. 120°C. – $C_{11}H_{12}S_3$ (240.4): calcd. C 55.0, H 5.0; found C 54.0, H 5.0. – UV (methanol): λ_{max} (%) = 205 (50), 250 (6), 320 (100). – RS = 371. – MS (80°C): *m/z* (%) = 240 (60) [M^+], 98 (100). – ^1H NMR (400 MHz, $CDCl_3$): δ = 5.79 (m, 1H), 5.59 (m, 1H), 4.55 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 4.38 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H), 3.25 (m, 1H), 2.72 (m, 1H), 2.57 (br d, ^3J = 5 Hz, 1H), 2.45 (br d, ^3J = 11 Hz, 1H), 2.41 (br d, ^3J = 5 Hz, 1H), 2.34 (dm, ^3J = 18 Hz, 1H), 2.20 (dm, ^3J = 18 Hz, 1H), 1.76 (br d, ^3J = 11 Hz, 1H). – $^{13}C\{^1H\}$ NMR (68 MHz, $CDCl_3$): δ = 230.0, 132.2, 130.8, 64.3, 61.1, 52.6, 50.0, 47.1, 42.1, 36.1, 31.9. – IR (KBr): $\tilde{\nu}$ = 1043 cm^{-1} (C=S).

Preparation of 5-Oxo-exo-4,5,6-trithiatetracyclo[$7.3.1^{2,8}.0^{3,7}$]tridec-10-ene (**28**): To a solution of 650 mg (1.5 mmol) of **15** in 100 ml of CS_2 was added 15 ml of a solution of $SOCl_2$ in CS_2 (c = 0.1 M). The color of the reaction mixture changed immediately from green to red. After 30 min, 2 g of silica gel was added. After stirring for 30 min, the suspension was filtered, and the solvent was evaporated. 330 mg (90%) of **28** was obtained as a yellow powder; m.p. 55–85°C (mixture of isomers A and B). – $C_{10}H_{12}S_3O$ (244.4): calcd. C 49.1, H 5.0; found C 49.7, H 5.0. – MS (80°C): *m/z* (%) = 244 (15) [M^+], 131 (100). – ^1H NMR (200 MHz, $CDCl_3$): δ = 5.79 (m, 1H_A, 1H_B), 5.65 (m, 1H_A, 1H_B), 4.90 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H_A), 4.82 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H_A), 4.80 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H_B), 4.72 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1H_B), 3.4–3.2 (m, 2H_A, 2H_B), 2.81–2.69 (m, 5H), 2.55–2.2 (m, 6H), 2.09 (br d, ^2J = 11 Hz, 1H_A), 1.60 (br d, ^2J = 11 Hz, 1H_A), 1.52 (br d, ^2J = 11 Hz, 1H_B). – $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 132.6 (A), 132.2 (B), 131.6 (B), 130.6 (A), 77.1 (B), 72.7 (B), 67.6 (A), 64.4 (A), 52.0 (B), 51.5 (A), 50.4 (B), 47.5 (B), 46.0 (A), 44.0 (A), 41.5 (B), 40.3 (A), 35.5 (B), 35.2 (B), 31.8 (A), 31.1 (B). – IR (KBr): $\tilde{\nu}$ = 1101 cm^{-1} (SO).

Determination of the Crystal Structure of **27**[42]: Single crystals were grown from $CHCl_3$. Crystal data (from 22 reflections, 7° < θ < 15°): orthorhombic, space group $Pbn2_1$ (No. 33, transformed to $Pna2_1$ before calculation); a = 1036.5(8), b = 951.8(1), c = 1086.4(7) pm, V = 1071(2) × 10^6 pm^3, Z = 4, d_{calc} = 1.485 g cm^{-1}, μ(Mo-K_α) = 0.62 mm^{-1}; crystal size 0.15 × 0.4 × 0.5 mm; Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation (71.069 pm) graphite monochromator; T = 298 K; ω-2θ scan, $2\theta_{max}$ = 50°; 2116 reflections measured, 982 independent reflections, 947 reflections with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXS-86). Atomic coordinate and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares on F^2 (126 parameters, unit weights, SHELX-76). The positions of all hydrogen atoms were calculated according to ideal geometry. Conventional R = 0.028; residual electron density +0.194/−0.183 e$Å^{-3}$.

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[42] Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-406081, the names of the authors, and the journal citation.

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