Preparation of 17 Sulfur-Rich Chain-Like Thiaalkanes $R{-}S_x{-}R'{-}S_y{-}R$ and $R{-}S_x{-}R'{-}S_y{-}R'{-}S_z{-}R$ ($x, y, z > 2$) from Titanocene Thiolate Complexes[‡]

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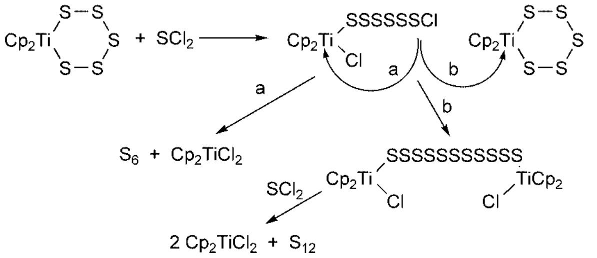
Two novel $Cp_2Ti(Cl)S_3R'S_3Tr$ complexes have been prepared by reaction of the six-membered metallacycles Cp_2TiS_4R' ($Cp = \eta^5\text{-}C_5H_5$, $R' = CMe_2$, $1,1\text{-}C_6H_{10}$) with the sulfenyl chloride TrSCl ($Tr = CPh_3$) at 20 °C. These complexes were treated with: (a) sulfenyl chlorides (RSCl or RSSCl) to obtain 11 new thiaalkanes of the type $R–S_x–R'–S_y–R$ (R = Tr, $4\text{-}ClC_6H_4$, $2\text{-}C_{10}H_7$; $x = 3$, $y > 2$), or (b) with SO_2Cl_2, SCl_2 or S_2Cl_2 to prepare six sulfur-rich species of the type $Tr–S_x–R'–S_y–R'–S_z–Tr$ (x, $z = 3$, $y > 3$), as well as Cp_2TiCl_2. The thiaalkanes decompose upon heating to give mixtures of various linear and cyclic polysulfanes R_2S_n and $R'S_m$.

Introduction

Thiaalkanes are derivatives of alkanes (including cycloalkanes) in which some of the CH_2 groups have been replaced by sulfur atoms. Numerous compounds of this type are known, both chain-like and cyclic and mainly with a single sulfane unit $-S_x-$ ($x = 1, 2,...$) between two organic residues R.[1] In a narrower sense, thiaalkanes are compounds with two or more sulfane units separated by organic groups, for example $R{-}S_x{-}R'{-}S_y{-}R''$. In the following we restrict our discussion to chain-like species of this type. While thiaalkanes with single sulfur atoms or disulfane groups have been prepared in large numbers by the classical methods of organosulfur chemistry,[2] and are widely used as chemically resistant polymers,[3] almost no such species with either tri-, tetra-, penta- or hexasulfane units are known.[4] This is most surprising and unsatisfactory in the light of the biological activity of many thiaalkanes, in particular cyclic species, which makes them interesting to the pharmaceutical industry as well as for applications in agroscience.[1,5] In this work we report on the synthesis of chain-like sulfur-rich thiaalkanes with two and three polysulfane units from suitable titanocene thiolate complexes by ligand-transfer reactions.

In recent years a number of mono- and dinuclear titanocene thiolate complexes have been used to synthesize sulfur-rich homocycles, heterocycles and linear organic polysulfanes R_2S_n ($n > 2$) by reaction with organic or inorganic S−Cl compounds.[1,6] These reactions take place at 25 °C or below and often proceed quantitatively. A good example is the synthesis of the homocycles S_6 and S_{12} from titanocene pentasulfide Cp_2TiS_5 (**1**; $Cp = \eta^5\text{-}C_5H_5$) and sulfur dichloride[7] shown in Scheme 1.



Scheme 1

The nucleophilic attack of the chlorine atoms of SCl_2 on the titanium atom opens the metallacycle producing an intermediate that either reacts intramolecularly by route (a) to give S_6 and Cp_2TiCl_2, or intermolecularly with another molecule of **1** to give a second linear intermediate which then reacts with SCl_2 to form S_{12} [route (b)]. While the reactive intermediates shown in Scheme 1 are hypothetical, the related dinuclear complex $(Cp_2TiCl)_2S_3$ has been isolated and characterized by X-ray crystallography.[8] Mononuclear complexes of the type $Cp_2TiX(S_xR)$ with sulfanido ligands containing more than one sulfur atom have also been isolated (e.g., X = Cl or SR with aryl or alkyl groups R; x = 2, 3[9]).

In this work we show how titanocene complexes with thiaalkane ligands can be used to prepare the title compounds containing up to 12 sulfur atoms. Most useful in

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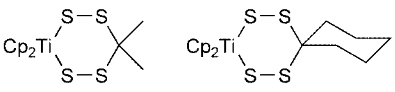
this context were the two metallacycles $Cp_2TiS_4CMe_2$ (**2a**) and $Cp_2TiS_4C_6H_{10}$ (**2b**) first prepared by Giolando and Rauchfuss[10] from Cp_2TiS_5 and acetone or cyclohexanone, respectively (Scheme 2).



2a **2b**

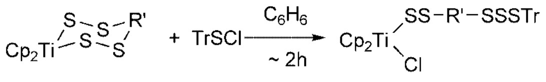
Scheme 2

These air-stable compounds are soluble in organic solvents. Both complexes have been used before to synthesize heterocyclic sulfur compounds by reaction with dichlorosulfanes S_nCl_2.[11,12]

Results and Discussion

Ring-Opening Reaction with Ph_3CSCl

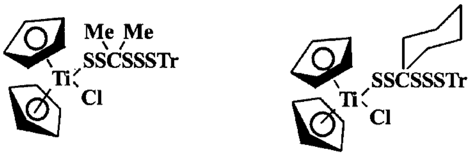
One aim of this work was to isolate the chain-like intermediates of the type shown in Scheme 1. To stabilize these reactive species we have chosen a particularly bulky substituent R on the sulfenyl chloride. Reaction of complexes **2a** or **2b** with triphenylmethylsulfenyl chloride Ph_3CSCl (tritylsulfenyl chloride, TrSCl) in a molar ratio of 1:1 at 20 °C in benzene produced the violet complexes **3a** and **3b** as shown in Scheme 3.



R': CMe_2 (**3a**), C_6H_{10} (**3b**)

Scheme 3

These reactions could easily be followed by HPLC analysis of the reaction mixtures since the retention times of **3a** and **3b** are higher than those of all other components in the mixture. Therefore, the corresponding peaks were well separated. Single crystals of **3a** and **3b** could not be obtained due to their instability in solution but the spectroscopic results (^1H and ^{13}C NMR, IR, Raman, UV/Vis) as well as their reactivity towards SCl compounds support the connectivities shown in Scheme 4 (see Exp. Sect.). In the ^1H NMR spectrum of **3a** there appears one singlet each for the cyclopentadienyl (δ = 6.36 ppm) and methyl protons (δ = 1.69 ppm) besides the multiplet of the phenyl hydrogens near δ = 7.32 ppm. The violet color of the novel complexes in solution is caused by an absorption peaking at 560 ± 4 nm (in MeOH).



(3a) **(3b)**

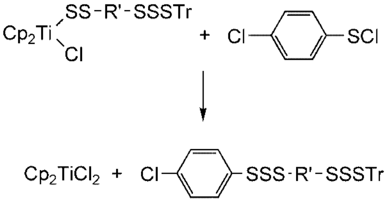
Scheme 4

In the solid state complexes **3a** and **3b** are stable at 4 °C for several weeks but they decompose in solution at 20 °C, especially in the presence of air, with formation of Cp_2TiCl_2 and an ochre precipitate. Chlorinated solvents also initiate a slow decomposition. Therefore, the samples always contained a few percent of Cp_2TiCl_2 (probably with formation of mixed crystals) which also originates from the side reaction of TrSCl with **3a** or **3b**, respectively. However, for preparative purposes the purity was sufficient (see below). The content of Cp_2TiCl_2 can be determined by ^1H NMR spectroscopy (singlet at δ = 6.57 ppm). Complexes **3a** and **3b** are well soluble in benzene and carbon disulfide, but less so in *n*-hexane and methanol.

Attempts to isolate the corresponding complexes using other sulfenyl chlorides such as TrSSCl, $4-ClC_6H_4SCl$ and $2-C_{10}H_7SCl$ failed due to rapid decomposition of the ring-opened complexes and their consecutive reactions with the sulfenyl chlorides.

Synthesis of Thiaalkanes

Treatment of complexes **3a** or **3b** with one equivalent of ClC_6H_4SCl in CS_2 at 20 °C expectedly yields the asymmetrical hexathiaalkanes **4a** and **4b** shown in Scheme 5. These reactions are rapid, as indicated by the immediate color change from violet to orange-red on addition of the sulfenyl chloride to the complexes **3a** and **3b**, respectively. The reactions are also very clean: only one peak was observed in the HPLC analysis of the isolated products **4a** and **4b** (besides the solvent peak).

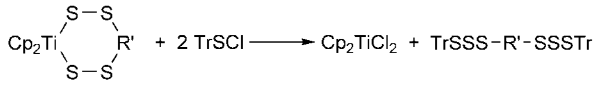


R': CMe_2 (**4a**); C_6H_{10} (**4b**)

Scheme 5

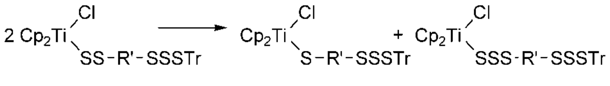
Both bis-trisulfanes **4a** and **4b** could be isolated in high purity as grayish-white powders in yields of 42% and 41%, respectively.

When we tried to synthesize the symmetrical bis-trisulfanes $Tr-S_3-R'-S_3-Tr$ by reaction of complexes **2a** and **2b** with *two* equivalents of TrSCl, according to Scheme 6, rather complex reaction mixtures were obtained regardless of whether the reaction was carried out in CS_2, CH_2Cl_2 or benzene at 20 °C.



Scheme 6

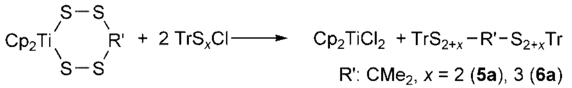
The reaction times of more than 15 hours for complete, or nearly complete, disappearance of the starting materials evidently favor side reactions, for example a sulfur transfer between the intermediate sulfanido complexes as shown in Scheme 7.



Scheme 7

As a consequence, three major thiaalkane products were detected by HPLC analysis, namely the expected $(TrS_3)_2R'$, the asymmetrical $TrS_3R'S_4Tr$ and the sulfur-rich $(TrS_3R')_2S_4$. The latter product most probably arises from the autoxidation of the intermediate $Cp_2TiCl(S_2R'S_3Tr)$ (see below). In addition, several minor products of similar retention time were detected but not identified. The identification of members of a homologous series is sometimes possible by inter- and extrapolation of the retention indices as they are linear functions of the sulfur content.[1,13] In other cases the independent preparation of the suspected species is necessary, and will be described below. Because of the complex composition of the reaction mixture no workup has been attempted since, even under an inert atmosphere, too many side-products were formed. Treatment of complexes **2a** and **2b** with TrCl also did not give the desired product $(TrS_2)_2R'$ since the reaction rate at 20 °C was very low, allowing parallel decomposition reactions.

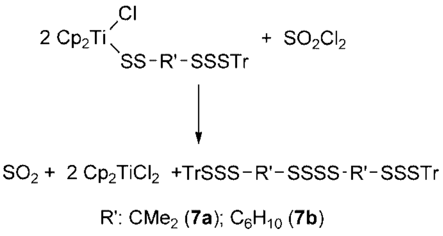
More successful were the reactions of complexes **2a** and **2b** with the sulfur-rich derivatives TrS_xCl with $x = 2$ and 3 resulting in the bis-tetra- and -pentasulfanes **5a,b** and **6a,b** (Scheme 8).



Scheme 8

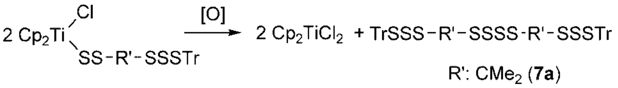
The starting materials TrS_xCl were prepared according to published procedures[14] and the reaction took place in benzene at 20 °C. The reactivity of TrS_xCl ($x = 0-3$) towards titanocene polysulfido complexes evidently increases with increasing x. $Tr-S_4-CMe_2-S_4-Tr$ (**5a**) was isolated in 7% yield as a champagne-colored powder of m.p. 55 °C while the cyclohexylidene derivative $Tr-S_4-C_6H_{10}-S_4-Tr$ (**5b**) melts at 60 °C (yield 34%). The corresponding bis-pentasulfanes $Tr-S_5-R'-S_5-Tr$ (**6a,b**) were obtained analogously in 67% and 26% yields, respectively.

The two particularly sulfur-rich thiaalkanes $Tr-S_3-R'-S_4-R'-S_3-Tr$ (**7a,b**), mentioned above, were obtained as pure materials by oxidation of complexes **3a** and **3b**, respectively, with sulfuryl chloride in CS_2 solution at 20 °C (see Scheme 9; yields: 41% **7a**, 45% **7b**).



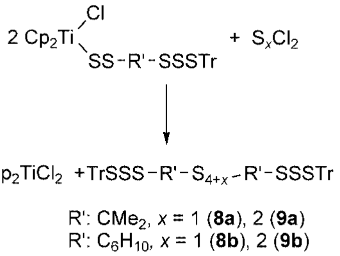
Scheme 9

Alternatively, **7a** could be obtained from **3a** by autoxidation with air in organic solvents at 20 °C (Scheme 10; yield 15%). Insoluble titanium-containing side products were observed as an ochre precipitate.



Scheme 10

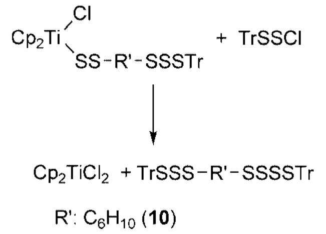
Even more sulfur-rich derivatives were obtained by cleavage of complexes **3a** and **3b** with SCl_2 or S_2Cl_2 (Scheme 11), resulting in the corresponding penta- and hexasulfanes **8a,b** and **9a,b** (undecathia- and dodecathiaalkanes; yields: 19−36%).



Scheme 11

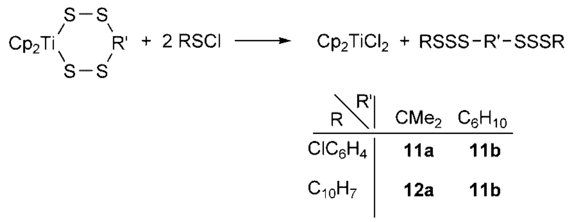
These grayish-white or yellowish powder-like substances are soluble in methyl *tert*-butyl (MTB) ether.

Finally, we observed that various sulfenyl chlorides (RSCl) and disulfane chlorides (RSSCl) react with the complexes **3a** and **3b** to give the corresponding thiaalkanes. For example, TrSSCl and **3b** produced the heptathiaalkane $Tr{-}S_3{-}C_6H_{10}{-}S_4{-}Tr$ **10** (Scheme 12).



Scheme 12

The easily accessible aromatic sulfenyl chlorides ClC_6H_4SCl and $C_{10}H_7SCl$ produced the symmetrical bistrisulfanes **11a,b** and **12a,b** in 6−28% yield on reaction with complexes **2a** and **2b** (Scheme 13).



R \ R'	CMe_2	C_6H_{10}
ClC_6H_4	**11a**	**11b**
$C_{10}H_7$	**12a**	**11b**

Scheme 13

General Properties of the Novel Thiaalkanes

The thiaalkanes prepared in this work can be stored for several weeks at 4 °C without decomposition. They are readily soluble in carbon disulfide, benzene and MTB ether, but less so in *n*-hexane, *n*-pentane and methanol. As with other polysulfanes,[1] heating initiates decomposition reactions. This can best be seen from the mass spectra of compounds **11a,b** and **12a,b**, which are of the type $R{-}S_3{-}R'{-}S_3{-}R$. The temperatures required to evaporate these large molecules in a high vacuum (150−200 °C) result in complete decomposition, and no molecular ions were observed. However, all major peaks in the EI mass spectra could be assigned to cations of the following degradation and interconversion products: R_2S_n ($n = 0{-}4$), $R'S_m$ ($m = 1{-}5$), RS_3R', RS_2, RS, and related smaller fragments. Some of these polysulfanes are known as pure compounds.[1] Evidently, the S−S bonds break homolytically on heating and the fragments recombine to form chain-like species R_2S_n and cyclic polysulfanes $R'S_m$. The observation of R_2, however, indicates that C−S bonds are also broken on electron impact.

During the HPLC analyses of the reaction mixtures it was once more observed that the retention time of the members of a homologous series, differing only in the number of sulfur atoms, systematically depends on the number of sulfur atoms. This can best be shown if the retention index (RS) is used which is independent of the chromatographic system and is therefore a characteristic property of these compounds (similar to the NMR chemical shift).[15] To determine RS values the sulfur homocycles S_x ($x = 6, 8, 9, 10$) are used as reference substances and their retention times t_R are measured under the same conditions. Then, their capacity factors $k' = (t_R - t_0)/t_0$ are calculated (t_0: dead time), the logarithms of which depend linearly on the number of sulfur atoms (n_S) as follows: $\ln k' = a + b \times n_S$. The latter relationship can be used to calculate a formal n_S value for any other substance by substituting its k' value into this equation. The formal n_S value obtained in this way defines the retention index of the novel substance as follows: $RS = 100 \times n_S$. From the RS values of three members of the series $Tr{-}S_x{-}CMe_2{-}S_x{-}Tr$ ($x = 3, 4, 5$) the following linear regression has been derived: $RS = 568 + 128 \times x$ ($r = 0.998$). For the analogous cyclohexylidene species $Tr\text{-}S_x\text{-}C_6H_{10}\text{-}S_x\text{-}Tr$ we obtained: $RS = 662 + 134 \times x$ ($r = 0.997$). These relationships can be used to estimate the retention times of other members of these series by inter- and extrapolation. Pure methanol was used as the eluent in both cases.

Considerably longer homologous series have been observed for the species $(TrS_3CMe_2)_2S_x$ ($x = 4{-}11$) and $(TrS_3C_6H_{10})_2S_x$ ($x = 4{-}12$). In these cases the linear regressions are: $RS = 965 + 60 \times x$ ($r = 0.9997$) and $RS = 1147 + 61 \times x$ ($r = 0.99986$). The slopes of these functions are practically identical. The higher members of these series were prepared by reaction of complexes **3a** and **3b** with solutions of chlorosulfanes S_nCl_2 ($n > 2$) obtained by chlorination of elemental sulfur.[16]

The NMR and vibrational spectra of the novel thiaalkanes mainly show the presence of the corresponding organic groups R and R′ with little, if any, dependence on the number of sulfur atoms. Even the Raman spectra contain little information about the SS bonds, the stretching vibrations of which usually show up as strong lines in the 400−520 cm^{-1} region. However, compared to the strongest lines of the organic substituents (e.g. Tr: 1002 cm^{-1}, $C_{10}H_7$: 1380 cm^{-1}), the SS stretching vibrations often gave rise to only relatively weak signals in the indicated region. Therefore, the Raman spectra have not been listed in the Exp. Sect.[17]

Summary

We have synthesized two new titanocene polysulfido complexes $Cp_2TiCl(S_2R'S_3Tr)$ and 17 novel chain-like thiaalkanes by reaction of Ti−S bonds with S−Cl compounds (sulfenyl chlorides, sulfuryl chloride and sulfurchlorides). The thiaalkanes are of types $R{-}S_x{-}R'{-}S_y{-}R$ (x, $y > 2$) and $R\text{-}S_x{-}R'{-}S_y{-}R'{-}S_z{-}R$ ($x, z = 3$, $y > 3$) and have been isolated in moderate to low yields as colorless, grayish-white or grayish-yellow powder-like substances ($R = CPh_3$, 4-ClC_6H_4; $R' = CMe_2$, 1,1-C_6H_{10}). To the best of our knowledge, these are the most sulfur-rich acyclic thiaalkanes of these types ever prepared. It has previously been shown that polysulfido ligands coordinated to a titanium atom can be utilized for ligand-transfer reactions with S−Cl compounds and other metals can also function as coordination centers (e.g. Zn[18]). Since a large number

of thiolate complexes of main group and transition metals are known[19] the ligand-transfer method bears a tremendous potential for further research in synthetic sulfur chemistry.

Experimental Section

General:[17] The reactions were carried out with exclusion of moisture using carefully dried solvents. The chromatographic system has been described previously (HPLC with UV absorbance detector).[12] Octadecylsilane (C18) was used as the stationary phase throughout and pure methanol as the eluent. The following spectrometers were used: mass spectrometer AMD Intectra (based on Varian MAT 311A equipment) with 70 eV electron energy; NMR spectrometer WH 270 and ARX 200 by Bruker. FT-IR spectrometer Magna System 750 by Nicolet; Raman spectrometer Ramanor U 1000 by Jobin Yvon, equipped with krypton ion laser (647 nm), and FT-Raman spectrometer RFS 100 by Bruker with Nd-YAG laser (1064 nm). UV/Vis diode array spectrometer 990 by Waters (190−800 nm; on-line connected to the chromatographic system). With one exception (**12b**) NMR spectra were recorded at 200 MHz. ^{13}C NMR spectra are ^{1}H broad-band decoupled. Elemental analyses were performed using a Hewlett−Packard CHN analyzer 185 as well as a Perkin−Elmer Series II CHNS analyzer 2400.

Synthesis of Chloro(3,3-dimethyl-7,7,7-triphenyl-1,2,4,5,6-pentathiaheptyl)titanocene (3a): TrSCl (1.75 g, 5.63 mmol) and **2a** (1.57 g, 4.51 mmol) were stirred in benzene at 30−40 °C for 150 min. After removal of the solvent in vacuo the residue was dissolved in CS_2 (30 mL), *n*-pentane (70 mL) was added and the solution was cooled to −26 °C whereupon a mixture of **3a** and Cp_2TiCl_2 (ca. 10%) crystallized out, which was isolated, washed with *n*-pentane (30 mL) and dried in air (red-blue powder). Yield: 2.4 g (2.16 g of pure **3a**, 73%). The Cp_2TiCl_2 can be removed by stirring the solution with silica gel but the yield is then dramatically lower. M.p. (dec.): 133 °C. $C_{32}H_{31}ClS_5Ti$ (659.3): calcd. C 57.29, H 4.72, S 21.89 (Cp_2TiCl_2 content taken into account); found C 55.33, H 4.72, S 22.21. The low carbon value is explained by titanium carbide formation on combustion in the CHN analyzer. UV/Vis (methanol): λ_{max} (%) = 223 nm (100), 241 (87), 295 (23), 382 (7), 556 (9). ^{1}H NMR (CD_2Cl_2): δ = 7.32 (m, 15 H), 6.36 (s, 10 H), 1.69 (s, 6 H) ppm. Retention index (RS): 570.

Synthesis of Chloro(3-cyclohexylidene-7,7,7-triphenyl-1,2,4,5,6-pentathiaheptyl)titanocene (3b): TrSCl (1.00 g, 3.22 mmol) and **2b** (1.00 g, 2.57 mmol) were stirred in benzene at 30−40 °C for 180 min. After removal of the solvent in vacuo the residue was dissolved in CS_2 (20 mL), *n*-pentane (60 mL) was added and the solution was cooled to −26 °C for 15 h, whereupon a mixture of **3a** and Cp_2TiCl_2 (ca. 10%) crystallized out, which was isolated, washed with *n*-pentane (40 mL) and dried in air (red-blue powder). Yield: 0.77 g (0.69 g of pure **3b**, 39%). The Cp_2TiCl_2 can be removed by stirring the solution with silica gel but the yield is then dramatically lower. M.p. (dec.): 95−100 °C. $C_{35}H_{35}ClS_5Ti$ (699.3): calcd. C 58.92, H 4.94, S 20.64 (Cp_2TiCl_2 content taken into account); found C 58.42, H 4.64, S 18.72. UV/Vis (methanol): λ_{max} (%) = 209 nm (100), 240 (49), 288 (15), 383 (4), 564 (7). ^{1}H NMR (CD_2Cl_2): δ = 7.32 (m, 15 H), 6.37 (s, 10 H), 1.2−2.2 (multiplets, 10 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 23.0, 24.9, 35.4, 71.5, 73.3, 115.9, 127.2, 128.0, 130.4, 143.5 ppm. RS: 686.

Synthesis of 1-(4-Chlorophenyl)-3-{1-methyl-1-[(triphenylmethyl)-trisulfanyl]ethyl}trisulfane (4a): A mixture of $4\text{-}ClC_6H_4SCl$ (1 mL) and CS_2 (49 mL) was used to titrate a solution of **3a** (0.45 g, 0.68 mmol) in 50 mL of CS_2 dropwise until the violet color had changed to orange-red. After filtration the solution was shaken with ca. 0.5 g of silica gel for a few minutes to remove residual Cp_2TiCl_2 (color change to yellow).The gel was filtered off and washed with CS_2 (50 mL). Removal of the solvent produced an oil which was dissolved in a mixture of MTB ether (5 mL) and *n*-pentane (10 mL). The solvent was partly evaporated until a turbidity appeared, whereupon the solution was cooled to −78 °C. After decantation from the precipitated oil the solution was evaporated in vacuo and the residue dissolved in MTB ether (5 mL) and *n*-pentane (5 mL). Stepwise cooling of this solution to −50 °C produced a champagne-colored powder which was isolated and washed with *n*-pentane (35 mL). Yield: 0.17 g (42%). M.p. 90−95 °C. $C_{28}H_{25}ClS_6$ (589.4): calcd. C 57.06, H 4.28, S 32.65; found C 57.09, H 4.37, S 31.93. UV/Vis (methanol): λ_{max} (%) = 207 nm (100), 238 (44), 277 (12), 316 (6). ^{1}H NMR (CD_2Cl_2): δ = 7.55 (dm, 2 H), 7.33 (m, 17 H), 1.69 (s, 6 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 28.3, 64.9, 73.4, 127.3, 128.0, 129.3, 130.3, 131.9, 134.5, 135.6, 143.3 ppm. RS: 908.

Synthesis of 1-(4-Chlorophenyl)-3-{1-[(triphenylmethyltri)sulfanyl]cyclohexyl}trisulfane (4b): In analogy to the preparation of **4a**, complex **3b** (0.27 g, 0.39 mmol) was titrated. After removal of the silica gel the solvent was evaporated in vacuo producing an oil which was dissolved in a small amount of MTB ether followed by partial evaporation of the solvent until a sticky foam had formed. Upon addition of MTB ether (5 mL) this turned into a beige powder. After addition of *n*-pentane (25 mL) and cooling to −50 °C for 2 h a crystalline product was obtained which was filtered off and washed with *n*-pentane. Yield: 0.10 g (41%). M.p. 162 °C. $C_{31}H_{29}ClS_6$ (629.4): calcd. C 59.16, H 4.64, S 30.57; found C 59.32, H 4.86, S 29.25. UV/Vis (methanol): λ_{max} (%) = 207 nm (100), 238 (39), 278 (13), 315 (6). ^{1}H NMR (CD_2Cl_2): δ = 7.52 (dm, 2 H), 7.33 (m, 17 H), 1.2−2.2 (multiplets, 10 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 23.0, 25.0, 35.4, 70.8, 75.3, 127.3, 128.1, 129.3, 130.4, 131.9, 134.4, 135.9, 143.3 ppm. RS: 1080.

Synthesis of 1-{1-Methyl-1-[(triphenylmethyl)tetrasulfanyl]ethyl}-3-(triphenylmethyl)tetrasulfane (5a): Solid TrSSCl (1.50 g, 4.37 mmol) was added in portions and with stirring to a solution of **2a** (0.76 g, 2.18 mmol) in benzene (100 mL). Stirring for 30 min resulted in a color change to red. After evaporation of the solvent the residue was dissolved in CH_2Cl_2 (50 mL) and shaken with some silica gel (5 min). After filtration and evaporation of the solvent the residue was recrystallized from a CS_2/*n*-pentane mixture (5:25). Yield: 0.12 g (7%). M.p.: 55 °C. $C_{41}H_{36}S_8$ (785.3): calcd. C 62.71, H 4.62, S 32.67; found C 62.95, H 4.85, S 33.03. UV/Vis (methanol): λ_{max} (%) = 231 nm (100), 301 (22). ^{1}H NMR ($CDCl_3$): δ = 7.30 (m), 1.58 (s) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.0, 64.3, 73.7, 127.3, 128.0, 130.3, 143.0 ppm. RS: 1071.

Synthesis of 1-(Triphenylmethyl)-3-{1-[(triphenylmethyl)tetrasulfanyl]cyclohexyl}tetrasulfane (5b): Preparation in analogy to the synthesis of **5a** from complex **2b** (0.25 g, 0.64 mmol), TrSSCl (0.44 g, 1.29 mmol) in benzene (30 mL) and using less CH_2Cl_2 (20 mL). Yield: 0.18 g (34%). M.p.: 60 °C. $C_{44}H_{40}S_8$ (825.3): calcd. C 64.03, H 4.89, S 31.08; found C 64.03, H 4.95, S 30.25. UV/Vis (methanol): λ_{max} (%) = 217 nm (100), 261 (22), 305 (13). ^{1}H NMR ($CDCl_3$): δ = 7.34 (m), 1.2−2.3 (multiplets) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.7, 24.8, 26.9, 35.6, 70.4, 73.6, 127.2, 128.0, 130.2, 143.0 ppm. RS: 1186.

Synthesis of 1-{1-Methyl-1-[(triphenylmethyl)pentasulfanyl]ethyl}-3-(triphenylmethyl)pentasulfane (6a): Solid **2a** (0.18 g, 0.52 mmol) was added in small portions with stirring to TrSSSCl (0.40 g, 1.07 mmol) in benzene (25 mL). After 10 min the solvent was evaporated, the residue was dissolved in CH_2Cl_2 (20 mL) and shaken with ca. 0.1 g of silica gel for a few minutes to remove Cp_2TiCl_2. After filtration and partial evaporation of the solvent excess *n*-pentane was added followed by complete evaporation of the solvent. The grayish-white residue was recrystallized from *n*-pentane. Yield: 0.30 g (67%). M.p.: 50 °C. $C_{41}H_{36}S_{10}$ (849.4): calcd. C 57.98, H 4.27; found C 58.51, H 3.75. UV/Vis (methanol): λ_{max} (%) = 240 nm (100), 294 (41). ^{1}H NMR (CD_2Cl_2): δ = 7.33 (m, 30 H), 1.71 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.9, 64.8, 73.9, 127.3, 128.0, 130.3, 142.9 ppm. RS: 1212.

Synthesis of 1-(Triphenylmethyl)-3-{1-[(triphenylmethyl)pentasulfanyl]cyclohexyl}pentasulfane (6b): TrSSSCl (0.48 g, 1.28 mmol) was added in small portions with stirring to complex **2b** (0.25 g, 0.64 mmol) in benzene (30 mL). After 10 min the solvent was removed in vacuo, the residue dissolved in CH_2Cl_2 (20 mL) and shaken with some silica gel until the color had changed to yellow. After filtration and evaporation of the solvent the crude product was recrystallized twice from a CS_2/*n*-pentane mixture (5:25 mL) by cooling to −78 °C. Yield: 0.15 g (26%). M.p.: 60 °C. $C_{44}H_{40}S_{10}$ (889.5): calcd. C 59.42, H 4.53, S 36.05; found C 60.14, H 4.60, S 34.26. UV/Vis (methanol): λ_{max} (%) = 209 nm (100), 263 (19), 298 (11). ^{1}H NMR ($CDCl_3$): δ = 7.28 (m), 1.2−2.1 (multiplets) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.8, 24.8, 35.4, 70.9, 73.8, 127.3, 128.0, 130.3, 143.0 ppm. RS: 1338.

Synthesis of Bis{1-methyl-1-[(triphenylmethyl)trisulfanyl]ethyl}-tetrasulfane (7a). Method A: A solution of 0.61 mL of SO_2Cl_2 in 9.4 mL of benzene was added rapidly but dropwise to complex **3a** (0.90 g, 1.37 mmol) in CS_2 (80 mL) until the color had changed from purple to orange-red. After filtration the solution was shaken with some silica gel to remove residual Cp_2TiCl_2. Filtration and evaporation of the solvent yielded a yellow oil which was dissolved in MTB ether (30 mL). Cooling to −78 °C gave an oily residue which was dissolved again in MTB ether and the solvent evaporated again. Yield: 0.25 g (41%).

Method B: Complex **3a** (0.41 g, 0.59 mmol) was dissolved in a mixture of benzene (150 mL), CS_2 (75 mL) and CH_2Cl_2 (25 mL) and stirred for 3 days resulting in a red-brown solution and an ochre precipitate. The filtered solution was stirred with little silica gel for 5 min. and this was then filtered off and washed with CS_2 (25 mL). Evaporation of the solvent gave an oily residue which was dissolved in a mixture of CH_2Cl_2 (3 mL), *n*-pentane (6 mL) and ethanol (15 mL). On cooling to −78 °C the product precipitated as a beige powder. Yield: 0.04 g (15%).%). M.p.: 54 °C. $C_{44}H_{42}S_{10}$ (891.5): calcd. C 59.28, H 4.75, S 35.97; found C 58.91, H 4.97, S 36.41. UV/Vis (methanol): λ_{max} (%) = 213 nm (100), 297 (9). ^{1}H NMR (CD_2Cl_2): δ = 7.31 (m, 30 H), 1.71 (s, 12 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 28.6, 64.8, 73.1, 127.3, 128.0, 130.3, 143.3 ppm. RS: 1217.

Synthesis of Bis{1-methyl-1-[(triphenylmethyl)trisulfanyl]cyclohexyl}tetrasulfane (7b): Preparation in analogy to **7a** (method A) from **3b** (0.77 g, 1.10 mmol) in 80 mL of benzene. After the color change from purple to orange-red the solvent was evaporated, the residue dissolved in 50 mL CS_2 and stirred with some silica gel. The solution was filtered and the residue washed with 20 mL of CH_2Cl_2. Evaporation of the solvent resulted in an oil which was dissolved in a mixture of 10 mL of CH_2Cl_2 and 50 mL of MTB ether. At −78 °C an oil precipitated which was isolated by decantation and dissolved in 50 mL of MTB ether. After complete evaporation of the solvent a champagne-colored powder was obtained. Yield: 0.24 g (45%). M.p.: 60 °C. $C_{50}H_{50}S_{10}$ (971.6): calcd. C 61.81, H 5.19; found C 59.93, H 5.47. UV/Vis (methanol): λ_{max} (%) = 208 nm (100), 297 (7). ^{1}H NMR (CD_2Cl_2): δ = 7.31 (m, 30 H), 1.2−2.2 (multiplets, 20 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 23.0, 25.0, 35.7, 70.8, 73.3, 127.3, 128.1, 130.4, 143.3 ppm. RS: 1397.

Synthesis of Bis{1-methyl-1-[(triphenylmethyl)trisulfanyl]ethyl}-pentasulfane (8a): A solution of SCl_2 (1 mL) in CS_2 (50 mL) was added dropwise and with stirring to a solution of **3a** (0.90 g, 1.37 mmol) in CS_2 (80 mL) until the color had changed from blue to red-orange. After filtration some silica gel was added with stirring. The solid was filtered off and washed with CS_2 (20 mL). The solvent of the combined solutions was evaporated and the oily residue dissolved in MTB ether (25 mL). Cooling yielded a precipitate which was isolated and dissolved again in MTB ether. Removal of the solvent produced a beige powder. Yield: 0.20 g (32%). M.p.: 52 °C. $C_{44}H_{42}S_{11}$ (923.5): calcd. C 57.22, H 4.58, S 38.19; found C 57.42, H 4.88, S 37.31. UV/Vis (methanol): λ_{max} (%) = 212 nm (100), 297 (9). ^{1}H NMR (CD_2Cl_2): δ = 7.34 (m, 30 H), 1.74 s, 12 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 28.6, 65.0, 73.6, 127.3, 128.1, 130.0, 143.3 ppm. RS: 1252.

Synthesis of Bis{1-[(triphenylmethyl)trisulfanyl]cyclohexyl}pentasulfane (8b): Preparation in analogy to **8a** from complex **3b** (0.83 g, 1.19 mmol). Yield: 0.14 g (23%). M.p.: 58 °C. $C_{50}H_{50}S_{11}$ (1003.67): calcd. C 59.84, H 5.02, S 35.14; found C 59.30, H 4.75, S 33.94. UV/Vis (methanol): λ_{max} (%) = 208 nm (100), 297 (8). ^{1}H NMR (CD_2Cl_2): δ = 7.32 (m, 30 H), 1.2−2.3 (multiplets, 20 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 23.0, 25.0, 35.6, 70.9, 75.3, 127.3, 128.1, 130.3, 143.3 ppm. RS: 1451.

Synthesis of Bis{1-methyl-1-[(triphenylmethyl)trisulfanyl]ethyl}-hexasulfane (9a): A solution of S_2Cl_2 (1 mL) in CS_2 (50 mL) was added dropwise and with stirring to a solution of **3a** (0.81 g, 1.23 mmol) in CS_2 (80 mL) until the color had changed from violet to orange-red. After stirring for 5 min the precipitated Cp_2TiCl_2 was filtered off and the filtrate was shaken with a small amount of silica gel for 5 min. The solids were filtered off and washed with CS_2 (50 mL); the combined filtrates were evaporated and the resulting oil was dissolved in a mixture of MTB ether and CS_2 (40:5 mL). Evaporation of the solvent gave a foam-like product which was pulverized, dissolved in CS_2/ethanol/MTB ether (10:10:5 mL) and cooled to −78 °C. Most of the solvents (CS_2 and ether) were removed on a rotary evaporator and the ethanolic solution was decanted off from the oily product. The latter was mixed with CH_2Cl_2/*n*-hexane/ethanol (7:20:20) and cooled to −78 °C whereupon a sticky precipitate was obtained. This was isolated, dissolved in a CH_2Cl_2/*n*-hexane/ethanol (7:20:10) mixture and this was cooled to −78 °C, resulting in a solid precipitate. Yield: 0.11 g (19%). M.p.: 55 °C. $C_{44}H_{42}S_{12}$ (955.6): calcd. C 55.30, H 4.43, S 40.27; found C 54.78, H 4.71, S 41.29. UV/Vis (methanol): λ_{max} (%) = 216 nm (100), 297 (12). ^{1}H NMR (CD_2Cl_2): δ = 7.32 (m, 30 H), 1.73 (s, 12 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 28.6, 65.0, 73.4, 127.3, 128.0, 130.3, 143.3 ppm. RS: 1334.

Synthesis of Bis{1-[(triphenylmethyl)trisulfanyl]cyclohexyl}-hexasulfane (9b): Preparation in analogy to **9a** from complex **3b** (0.72 g, 1.03 mmol) in 100 mL of CS_2 by titration with sulfur dichloride. Cp_2TiCl_2 was filtered off and the solution stirred with some silica gel which was then filtered off and the residue washed with 20 mL of CS_2. The solvent was evaporated and the remaining oil dissolved in a mixture of 5 mL of CS_2 and 20 mL of MTB ether. The solvents were evaporated until a turbidity appeared. Cooling to −78 °C resulted in a precipitate which was dissolved in 20 mL of MTB ether. Complete evaporation of the ether yielded a white powder. Yield: 0.19 g (36%). M.p.: 55 °C. $C_{50}H_{50}S_{12}$ (1035.7): calcd. C 57.98, H 4.87, S 37.15; found C 57.30, H 5.23, S 37.65. UV/Vis (methanol): λ_{max} (%) = 208 nm (100), 297 (10). ^{1}H NMR (CD_2Cl_2): δ = 7.33 (m, 30 H), 1.3−2.3 (multiplets, 20 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 23.0, 25.0, 35.5, 71.0, 73.3, 127.3, 128.1, 130.3, 143.3 ppm. RS: 1540.

Synthesis of 1-(Triphenylmethyl)-3-{1-[(triphenylmethyl)trisulfanyl]-cyclohexyl}tetrasulfane (10): TrSSCl (0.22 g, 0.64 mmol) was added in portions to a solution of **3b** (0.45 g, 0.64 mmol) in benzene (60 mL) until the color had changed from violet to orange-red. After evaporation of the solvent the residue was dissolved in CS_2 (50 mL) and stirred with some silica gel for 5 min. After filtration and washing the solid with CS_2 (10 mL) the combined solutions were partly evaporated. Some MTB ether and ethanol were added until a turbidity appeared, whereupon the mixture was cooled to −50 °C. The precipitated oil was isolated by decantation and dissolved in a small amount of CS_2 and excess MTB ether. The solvents were evaporated on a rotary evaporator until a foam appeared which was dried in vacuo (beige powder). Yield: 0.04 g (8%). M.p.: 60 °C. $C_{44}H_{40}S_7$ (793.3): calcd. C 66.62, H 5.08, S 28.30; found C 66.43, H 5.33, S 27.62. UV/Vis (methanol): λ_{max} (%) = 207 nm (100), 267 (10), 298 (5). ^{1}H NMR ($CDCl_3$): δ = 7.30 (m, 30 H), 1.2−2.1 (multiplets, 10 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.78, 24.87, 35.28, 70.33, 73.15, 73.63, 127.16, 127.24, 127.97, 128.02, 130.33, 130.37, 143.12, 143.30 ppm. RS: 1125.

Synthesis of 3-(4-Chlorophenyl)-1-{1-methyl-1-[(4-chlorophenyl)trisulfanyl]ethyl}trisulfane (11a): Under nitrogen, a solution of ClC_6H_4SCl (0.50 g, 2.79 mmol) in CS_2 (10 mL) was added dropwise to complex **3a** (0.49 g, 1.41 mmol) in CS_2 (40 mL). Cp_2TiCl_2 was removed by filtration and stirring with a small amount of silica gel. The resulting clear solution was reduced to 5 mL, mixed with a little *n*-pentane and cooled to −78 °C. The precipitated beige powder was isolated and washed with *n*-pentane. Yield: 0.18 g (28%). M.p.: 49−54 °C. $C_{15}H_{14}Cl_2S_6$ (457.6): calcd. C 39.37, H 3.08, S 42.05; found C 39.15, H 2.89, S 41.87. UV/Vis (methanol): λ_{max} (%) = 214 nm (86), 241 (100), 275 (36), 306 (23). MS (150 °C): *m*/*z* (%) = 350 (1), 318 (17), 286 (73), 249 (21), 222 (9), 175 (45), 143 (100). ^{1}H NMR ($CDCl_3$): δ = 7.53 (dm, 4 H), 7.34 (dm, 4 H), 1.78 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.5, 65.1, 129.3, 131.8, 134.7, 135.3 ppm. RS: 805.

Synthesis of 1-(4-Chlorophenyl)-3-{1-[(4-chlorophenyl)trisulfanyl]-cyclohexyl}trisulfane (11b): Under an atmosphere of nitrogen, a solution of ClC_6H_4SCl (0.37 g, 2.06 mmol) in CS_2 (20 mL) was added dropwise to **3b** (0.40 g, 1.03 mmol) in CS_2 (60 mL) resulting in a color change from violet to orange-red. After filtration, addition of a little silica gel and shaking for 5 min the yellow solution was filtered again and the solvent evaporated in vacuo. The residue was dissolved in MTB ether in an ultrasound bath. Reduction of the volume to 5 mL and cooling to −50 °C yielded a solid precipitate which was isolated and dried in vacuo. Yield: 0.03 g (6%). M.p.: 95 °C. $C_{18}H_{18}Cl_2S_6$ (497.6): calcd. C 43.44, H 3.65, S 38.66; found C 43.02, H 3.78, S 38.17. UV/Vis (methanol): λ_{max} (%) = 206 nm (100), 241 (82), 277 (27), 304 (19). MS (180 °C): *m*/*z* (%) = 350 (2), 318 (20), 289 (43), 286 (34), 254 (4), 222 (6), 210 (19), 178 (13), 175 (64), 145 (82), 143 (78), 114 (63), 108 (47), 81 (100). ^{1}H NMR ($CDCl_3$): δ = 7.53 (dm, 4 H), 7.33 (dm, 4 H), 1.3−2.2 (multiplets, 10 H) ppm. RS: 956.

Synthesis of 1-{1-Methyl-1-[(2-naphthyl)trisulfanyl]ethyl}-3-(2-naphthyl)trisulfane (12a): Solid $C_{10}H_7SCl$ (0.22 g, 1.15 mmol) was added to **3a** (0.20 g, 0.57 mmol) in CS_2 (50 mL) with stirring. After filtration some silica gel was added to remove dissolved Cp_2TiCl_2 and this was then filtered off and washed with CS_2 (10 mL). The combined solutions were evaporated and the oily residue was dissolved in MTB ether in an ultrasound bath. Cooling of the solution to −50 °C gave a white powder which was isolated and dried in air. Yield: 0.04 g (13%). M.p.: 55−57 °C. $C_{23}H_{20}S_6$ (488.8): calcd. C 56.52, H 4.12, S 39.36; found C 55.98, H 4.61, S 38.20. UV/Vis (methanol): λ_{max} (%) = 216 nm (85), 237 (100), 278 (28), 311 (15). MS (200 °C): *m*/*z* (%) = 382 (4), 350 (67), 318 (38), 286 (35), 265 (6), 254 (23), 234 (26), 202 (45), 191 (88), 170 (66), 159 (68), 138 (37), 128 (19), 115 (100), 106 (46). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J_{meta} = 1.9 Hz, 2 H), 7.84 (m, 6 H), 7.67 (dd, J_{ortho} = 8.6 Hz, J_{meta} = 1.9 Hz, 2 H), 7.52 (m, 4 H), 1.78 (s, 6 H) ppm. RS: 952.

Synthesis of 1-(2-Naphthyl)-3-{1-[(2-naphthyl)trisulfanyl]-cyclohexyl}trisulfane (12b): Preparation in analogy to **12a** from **3b** (0.35 g, 0.90 mmol) and $C_{10}H_7SCl$ (0.35 g, 1.80 mmol). After dissolution in MTB ether a little ethanol and *n*-pentane were added and the volume was reduced in vacuo until a turbidity appeared. Stepwise cooling to −50 °C for precipitation and recrystallization from an MTB ether/*n*-hexane mixture with addition of a little ethanol to initiate the precipitation. Grayish-white powder. Yield: 0.09 g (19%). M.p.: 55−60 °C. $C_{26}H_{24}S_6$ (528.9): calcd. C 59.05, H 4.57, S 36.38; found C 58.26, H 4.18, S 35.66. UV/Vis (methanol): λ_{max} (%) = 216 nm (83), 238 (199), 277 (28), 309 (16). MS (160 °C): *m*/*z* (%) = 382 (3), 368 (10), 350 (58), 336 (48), 318 (21), 286 (26), 272 (21), 254 (9), 242 (15), 210 (34), 191 (100), 178 (19). ^{1}H NMR (CD_2Cl_2): δ = 8.06 (d, J_{meta} = 1.9 Hz, 2 H), 7.84 (m, 6 H), 7.69 (dd, J_{ortho} = 8.6 Hz, J_{meta} = 1.9 Hz, 2 H), 7.53 (m, 4 H), multiplets: 2.08−2.13 (4 H), 1.54−1.65 (4 H), 1.31−1.40 (2 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 22.93, 24.78, 35.47, 71.04, 126.80, 126.90, 127.68, 127.72, 127.78, 129.08, 129.54, 132.92, 133.36, 134.21 ppm. RS: 1070.

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