Titanocene Complexes Based on Benzenehexathiolate Derivatives and 2,3,6,7-Tetrachloronaphthalenetetrathiolate

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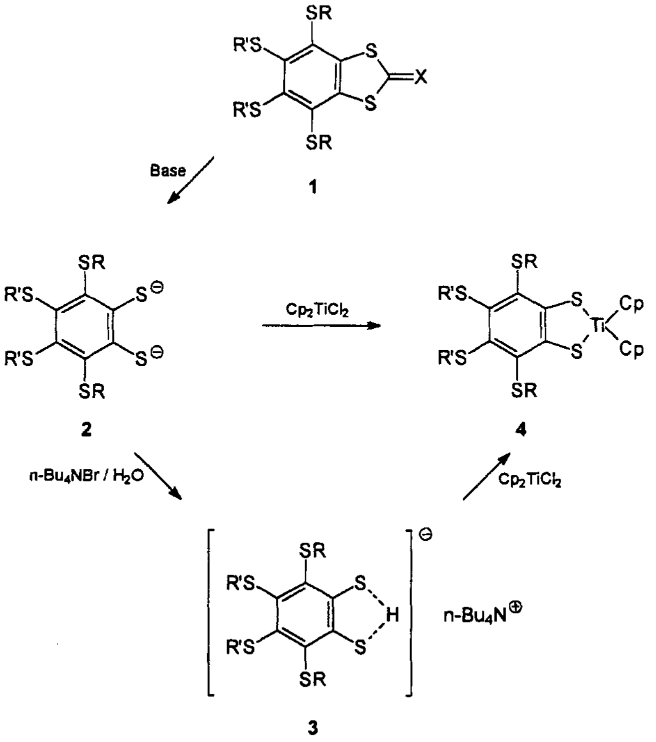
The synthesis and properties of the new (dithiolato)titanocene complexes **4a–d**, **6**, **9** are described. The ligands of these complexes are derived from sodium benzenehexathiolate or 3,4,7,8-tetrachloronaphthobis[1,2]dithiole. Complexes with one, two and three (dithiolato)titanocene units were prepared by use of these dithiolato ligands.

Titanocene complexes with sulfur ligands are able to make the fixed ligands available for further reactions. Because of the stability of the titanocene unit towards nucleophiles these compounds have become important transfer agents[1]. Remarkably in this context is the transfer of oligodisulfides. Thus, Cp_2TiS_5 can be used as an S_5^{2-} source[2]. The otherwise hard-to-obtain sulfur allotropes with an odd number of sulfur atoms are obtainable by using this compound[2].

(Dithiolato)titanocene complexes are also the compounds of choice for the stabilization of the air-sensitive 1,2-dithiolates. It is known, that ligands like benzene- or toluene-1,2-dithiolate (tdt)[3], maleonitrile dithiolate (mnt)[4] or dimercaptoisotrithione (dmit)[5] were used. These compounds allow nucleophilic reactions of the fixed dithiolates to be carried out. For instance, treatment of Cp_2Ti(dmit) with sulfur dichloride gives the corresponding 1,2,3-trithiole[5].

From sodium benzenehexathiolate different 1,3-dithiole-2-thiones **1** are available by selective ring closing reactions with carbon disulfide. The 1,2-dithiolates **2**, **3** were obtained by opening of **1** with bases[6] (Scheme 1). The reaction of the dithiolates **2** with titanocene dichloride leads to the dithiolato complexes **4**. The characteristic green color of these compounds is caused by absorptions at λ = 470 and 640 nm which are typical of 1,3-dithia-2-titanacyclopentenes[3]. All synthesized titanocene complexes show typical C–H vibration bands of the Cp group at $\tilde{\nu}$ = 820 cm^{-1} in their IR spectra. A further characteristic is the mass-spectrometric fragmentation of the compounds **4**. All recorded spectra are very poor in the number of fragments. An intensive peak is obtained at m/z = 178 which corresponds to the mass of Cp_2Ti. Besides, the mass spectra show peaks of $M^+ - 65$ (M^+ – Cp). The NMR signals are in agreement with the structure of **4a–d** [δ = 2.50 (H_3CS), 6.10–6.13 (Cp)].

Scheme 1



	a	b	c
X	S	S	O

	R	R'	R'
a	Me	Me	
b	Me	>C=S	
c	Me	>C=O	
d	>C=S		

From benzenehexathiolate[7] and titanocene dichloride the complex **6** is obtained. It shows the same spectroscopic characteristics (e.g. λ_{max} = 654 nm) as the complexes **4**. The IR spectrum is poor of bands which is in accordance with the high symmetry of **6**. At room temperature a broad ^{1}H-NMR signal is observed at δ = 6 (Cp). It collapses into two signals at +15 °C and a further coalescence of the high-field signal is observable at −15 °C. At −40 °C the flipping of the titanocene units is frozen, only one conformer exists. The intensity ratio (2:1) of the signals is in agreement with the structure of **6**, given in Scheme 2 (see Figure 1). For conformers of (1,2,4,5-benzenetetrathiolato)titanocene complexes see ref.[8].

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Scheme 2

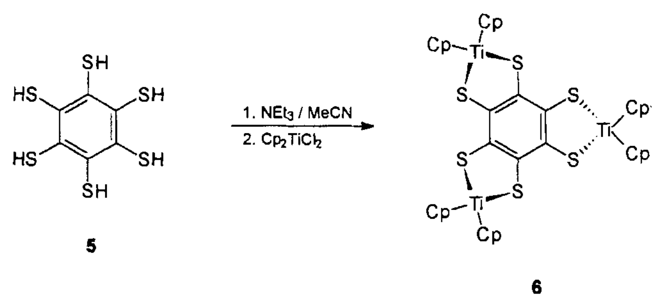
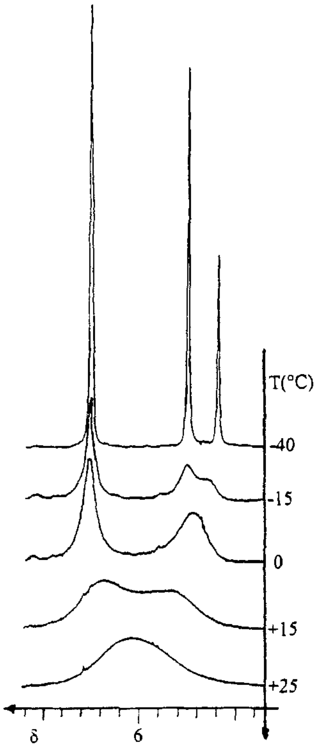


Figure 1. Temperature dependence of Cp signals in the ^{1}H-NMR spectrum of **6**



By using 1,2,5,6-tetrathiacyclopent[*fg*]acenaphthylene **7** we obtained the corresponding tetrathiolate by reduction with sodium tetrahydridoborate. The ligand was isolated as bis(tetra-*n*-butylammonium) salt **8** (cf. ref.[6]). The reaction of **8** with Cp_2TiCl_2 led to complex **9** containing two titanocene units (Scheme 3). In contrast to the products **4** the bistitanocene complex **9** shows absorptions in the NIR range (λ_{max} = 428 nm, 801; brown color). A reason for the NIR absorption could be the 1,3-dithia-2-titanacyclohexene structure in **9** in contrast to the 1,3-dithia-2-titanacyclopentene structure in **4**, connected with a stronger delocalization of the electrons between the titanocene unit and the naphthalenetetrathiolato ligand in **9** compared with the situation in **4** or **6**.

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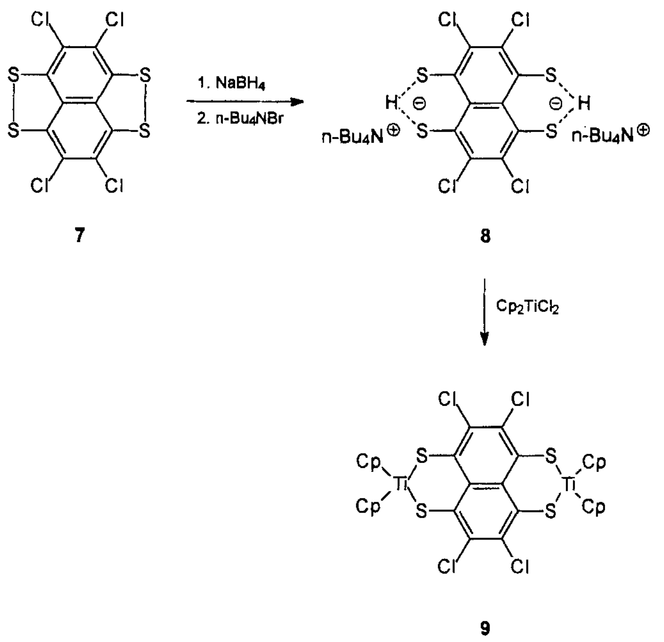
Experimental

NMR: Varian Gemini 300 (25°C, ^{1}H NMR: 300 MHz, ^{13}C NMR: 75 MHz). – IR (KBr): Philips PU 6924 FTIR. – MS (EI): AMD 402. – UV/Vis: Perkin-Elmer Lambda 2.

Scheme 3



2,2-Bis(π-cyclopentadienyl)-4,5,6,7-tetrakis(methylthio)-1,3-dithia-2-titanaindan (**4a**): A solution of titanocene dichloride (110 mg, 0.44 mmol) in 10 ml of acetone was dropped slowly to a stirred solution of tetra-*n*-butylammonium salt **3a**[6] (250 mg, 0.44 mmol) in 15 ml of acetone under inert gas. During 1 min the color turned dark green. The reaction mixture was stirred for 2 h and filtered. The solvent was evaporated from the filtrate. The resulting solid was washed with water and recrystallized from trichloromethane/methanol. – Yield: 140 mg (63%). – IR: $\tilde{\nu}$ = 1280 cm^{-1} (SMe), 820 (Cp). – UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 385 nm (sh, 4.28), 448 (3.79), 641 (3.70). – MS; *m/z* (%): 502 (100) [M$^+$], 437 (36), 183 (93), 178 (33). – ^{1}H NMR ($CDCl_3$): δ = 6.10 (s, 10H), 2.52 (s, 6H), 2.54 (s, 6H). – $C_{20}H_{22}S_6Ti$ (502.63): calcd. C 47.79, H 4.41, S 38.27; found C 48.03, H 4.62, S 37.45. – Mol. mass: 502 (MS).

2,2-Bis(π-cyclopentadienyl)-4,8-bis(methylthio)-1,3,5,7-tetrathia-2-titana-s-indacene-6-thione (**4b**): Tetra-*n*-butylammonium salt **3b**[6] (200 mg, 0.34 mmol) was dissolved in 25 ml of acetone. A solution of titanocene dichloride (86 mg, 0.34 mmol) in 25 ml of acetone was added slowly under inert gas. After stirring of the mixture for 1 h, the precipitated solid was filtered off, washed with methanol and ether and recrystallized from trichloromethane/methanol. – Yield: 140 mg (80%). – IR: $\tilde{\nu}$ = 1063 cm^{-1} (C=S), 818 (Cp). – UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 395 nm (4.34), 475 (3.83), 639 (3.71). – MS; *m/z* (%): 516 (72) [M$^+$], 451 (41), 178 (100). – ^{1}H NMR ($CDCl_3$): δ = 2.50 (s, 6H), 6.13 (s, 10H). – $C_{19}H_{16}S_7Ti$ (516.64): calcd. C 44.17, H 3.12, S 43.44; found C 44.38, H 3.65, S 42.20. – Mol. mass: 516 (MS).

2,2-Bis(π-cyclopentadienyl)-4,7-bis(methylthio)-1,3,5,8-tetrathia-2-titana-s-indacene-6-one (**4c**): A solution of titanocene dichloride (142 mg, 0.57 mmol) in 30 ml of acetone was dropped to a solution of dithiolate **2c**[6] in 15 ml (0.57 mmol) of triethylene glycole under inert gas. After the mixture had been stirred for 2 h, the precipitate was filtered off. The solid was dissolved in trichloromethane and the obtained solution filtered. The filtrate was concentrated to a volume of 1–2 ml and **4c** precipitated by addition of methanol. The product was filtered off, washed with methanol and ether and dried in air. – Yield: 225 mg (79%). – M.p.: ca. 216°C (dec.). –

IR: $\tilde{\nu}$ = 1647 cm^{-1} (C=O), 824 (Cp). – UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 287 nm (4.46), 344 (sh, 3.87), 464 (3.62), 635 (3.61). – MS; *m/z* (%): 500 (72) [M$^+$], 435 (40), 178 (100). – ^{1}H NMR ($CDCl_3$): δ = 2.52 (s, 6H), 6.12 (s, 10H). – $C_{19}H_{16}OS_6Ti$ (500.58): calcd. C 45.59, H 3.22, S 38.43; found C 44.76, H 3.64, S 38.00. – Mol. mass: 500 (MS).

2,2-Bis(π-cyclopentadienyl)-1,3,4,6,7,9-hexathia-2-titanatrindene-5,8-dithione (**4d**): Under inert gas 7,8-dimercapto-1,3,4,6-tetrathia-*as*-indacene-2,5-dithione[6] (200 mg, 0.56 mmol) was suspended in 25 ml of methanol. A solution of sodium methoxide in methanol (0.1 M, 11.2 ml) was added slowly to the suspension and **2d** was formed. A solution of titanocene dichloride (139 mg, 0.56 mmol) in 30 ml of acetone was dropped with stirring to the resulting solution. After the mixture had been stirred for 2 h, the precipitated solid was filtered off and washed with methanol. For further purification the product was dissolved in trichloromethane, the solution filtered, the filtrate concentrated to a volume of 1–2 ml and **4d** precipitated by addition of methanol. The resulting solid was filtered off and washed with methanol and ether. – Yield: 245 mg (82%). – IR: $\tilde{\nu}$ = 1065 cm^{-1} (C=S), 820 (Cp). – UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 276 nm (4.52), 396 (4.41), 475 (3.46), 634 (3.46). – MS; *m/z* (%): 530 (5) [M$^+$], 464 (4), 178 (8), 66 (100). – $C_{18}H_{10}S_8Ti$ (530.64): calcd. C 40.74, H 1.90, S 48.34; found C 39.63, H 2.07, S 47.44. – Mol. mass: 530 (MS).

2,2,5,5,8,8-Hexakis(π-cyclopentadienyl)-1,3,4,6,7,9-hexathia-2,5,8-tritianatrindene (**6**): Benzenehexathiol (**5**)[7] (150 mg, 0.55 mmol) was suspended in 30 ml of dry acetonitrile under inert gas. Triethylamine (0.57 ml, 3.38 mmol) was added to convert the hexathiol into the corresponding thiolate. To the resulting suspension titanocene dichloride (415 mg, 1.66 mmol) was then added with stirring and the mixture turned green. After stirring of the mixture for 2 h, the solvent was removed in vacuo. The residue was dissolved in dichloromethane and the solution filtered. The filtrate was concentrated to a volume of 1 ml and **6** precipitated by addition of methanol. The blue-green solid was filtered off, washed with methanol and ether and recrystallized from dichloromethane/methanol. – Yield: 254 mg (58%). – M.p.: ca. 200°C (dec.). – IR: $\tilde{\nu}$ = 822 cm^{-1} (Cp). – UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 401 nm (sh, 3.90), 486 (3.78), 654 (4.12). – ^{1}H NMR (CD_2Cl_2): δ = 6.02 (br. s); (CD_2Cl_2, −40°C): δ = 6.28 [6.27 (sh)] (15H, s), 5.77 (10H, s), 5.61 (5H, s). – ^{13}C NMR (CD_2Cl_2): δ = 111.79 (br. s) (Cp). – $C_{36}H_{30}S_6Ti_3$ (798.63): calcd. C 54.14, H 3.79, S 24.09; found C 53.75, H 4.02, S 24.03.

4,5,9,10-Tetrachloro-2,7-bis(π-cyclopentadienyl)-1,3,6,8-tetrathia-2,7-dititanapyrene (**9**): Compound **7**[9] (500 mg, 1.28 mmol) was suspended under inert gas in 20 ml of DMF. Then a solution of sodium tetrahydridoborate (200 mg, 5 mmol) in 10 ml of DMF was added to the suspension. The mixture was stirred for 2 h and a solution of tetra-*n*-butylammonium bromide (1.9 g, 5.12 mmol) was added. After stirring of the mixture for 30 min, the precipitate of **8** was filtered off, washed with water, methanol and ether and dried in vacuo. The tetra-*n*-butylammonium salt **8** (300 mg, 0.3 mmol) was dissolved in 30 ml of acetonitrile. A solution of titanocene dichloride (300 mg, 1.0 mmol) in 40 ml of acetonitrile was dropped to this solution. The mixture was stirred for 1 h and the dark brown precipitate was filtered off. The product was washed with water, methanol and ether and dried in vacuo. – Yield: 203 mg (93%). – M.p. >360°C. – IR: $\tilde{\nu}$ = 819 cm^{-1} (Cp). – UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 272 nm (4.80), 277 (4.70), 374 (4.30), 428 (4.30), 801 (3.20). – ^{1}H NMR (CD_3CN): δ = 6.53 (s). – ^{13}C NMR (CD_3CN): δ = 121.52 (Cp). – MS; *m/z* (%): 746 (22) [M$^+$], 390 (39), 358 (100). – $C_{30}H_{20}Cl_4S_4Ti_2$ (746.30): calcd. C 48.26, H 2.68, Cl 19.03, S 17.16; found C 48.89, H 2.60, Cl 19.05, S 18.18. – Mol. mass: 746 (MS).

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