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Sulphur compounds

CXLV *. Synthesis and properties of $Cp_2TiS_2SiR_2$, $Cp_2TiS_2GeR_2$, and $Cp'_2TiS_2SnR_2$ ($Cp = \eta^5$-C_5H_5, $Cp' = \eta^5$-$C_5H_4CH_3$, and $R = C_6H_5$)

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Abstract

The halides $(C_6H_5)_2SiCl_2$, $(C_6H_5)_2GeBr_2$, and $(C_6H_5)_2SnCl_2$, react with Li_2S and $(\eta^5$-$C_5H_4R)_2TiCl_2$ (R = H, CH_3) to give respectively the four-membered titanacycles $Cp_2TiS_2Si(C_6H_5)_2$, $Cp_2TiS_2Ge(C_6H_5)_2$, and $Cp'_2TiS_2Sn(C_6H_5)_2$ which have been characterized by ^1H NMR, mass and UV spectroscopy. The new compounds form green crystals, which react with sulphur chlorides with precipitation of $(C_5H_4R)_2TiCl_2$. This reaction provides a route to formerly unknown sulphur-rich heterocycles of Group 14 elements.

Introduction

Titanocene chalcogenide complexes such as Cp_2TiS_5 (1), Cp_2TiSe_5 (2) and others have been used very successfully in the synthesis of a large number of sulphur homocycles [2,3], selenium homo- and hetero-cycles [4,5], and sulphur-rich heterocycles with carbon, phosphorus, arsenic and other ring constituents [6–9]. Two examples are given in eqs. 1 and 2:

$$Cp_2TiS_5 + S_2Cl_2 \rightarrow S_7 + Cp_2TiCl_2 \qquad (1)$$

$$Cp_2TiSe_5 + S_2Cl_2 \rightarrow Se_5S_2 + Cp_2TiCl_2 \qquad (2)$$

In order to explore new routes to the scarcely known sulphur-rich heterocycles with Si, Ge, and Sn as ring atoms [10–12], we have synthesized titanacycles containing four-membered TiS_2E rings (E = Si, Ge, Sn). The first such compound, $(C_5H_4CH_3)_2TiS_2Si(CH_3)_2$ (**3**), had been reported by Rauchfuss *et al.* [13], and forms green air-stable crystals containing a planar TiS_2Si cycle. Compound **3** reacts with disulphur dichloride, S_2Cl_2, to give $(C_5H_4CH_3)_2TiCl_2$ and extremely

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* For Part CXLIV see ref. 1.

moisture-sensitive compounds of type $(CH_3)_2SiS_n$ [14]. To obtain less sensitive and, it was hoped, crystalline derivatives, we have now treated diphenyl-silicon, -germanium, and -tin dihalides with Li_2S and titanocene dichloride according to eqs. 3, 4 and 5:

$$Cp_2TiCl_2 + 2Li_2S + (C_6H_5)_2SiCl_2 \rightarrow Cp_2TiS_2Si(C_6H_5)_2 + 4LiCl \quad (3)$$

$$Cp_2TiCl_2 + 2Li_2S + (C_6H_5)_2GeBr_2 \rightarrow Cp_2TiS_2Ge(C_6H_5)_2 + 2LiCl + 2LiBr \quad (4)$$

$$Cp'_2TiCl_2 + 2Li_2S + (C_6H_5)_2SnCl_2 \rightarrow Cp'_2TiS_2Sn(C_6H_5)_2 + 4LiCl \quad (5)$$

For the reaction shown in eq. 3 a solution of $(C_6H_5)_2SiCl_2$ in THF was treated at ambient temperature with Li_2S followed by Cp_2TiCl_2. After 24 h stirring the dark solution was evaporated to dryness and the residue extracted with CH_2Cl_2. After filtration and addition of n-hexane to the extract at −78°C dark green microcrystals of $Cp_2TiS_2Si(C_6H_5)_2$ (**4**) appeared; these are air stable for long periods. Satisfactory analytical data (C, H) were obtained for **4** (see Experimental).

The germanium and tin derivatives, $Cp_2TiS_2Ge(C_6H_5)_2$ (**5**) and $Cp'_2TiS_2Sn(C_6H_5)_2$ (**6**) were prepared analogously from $(C_6H_5)_2GeBr_2$ and $(C_6H_5)_2SnCl_2$.

All the compounds form air-stable, green microcrystals, fairly soluble in CS_2, $CHCl_3$ and CH_2Cl_2 to give green solutions which are stable if air is excluded. Attempts to grow single crystals have so far failed. The identities of **4**, **5**, and **6** are based on elemental analysis and mass and ^1H NMR spectra. The mass spectra show the molecular ions and various characteristic fragment ions. The ^1H NMR spectra of all compounds are in accord with the assumption of a planar four-membered TiS_2E metallacycle as a central unit. The purity of all the compounds was checked by reversed-phase HPLC analysis using octadecylsilane as a stationary phase and acetonitrile as an eluent. By use of a diode-array detector the UV spectra of **4**–**6** were recorded at the time of their chromatographic separation

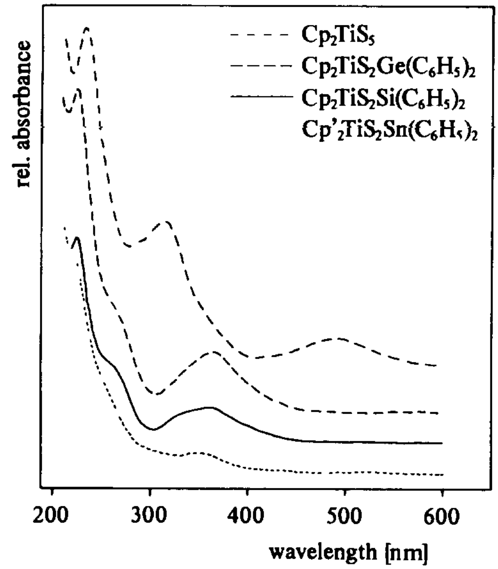

Fig 1. UV spectra of **4**–**6**.

Table 1

Retention times (t_R) and retention indices (RS) [18] for five titanocene chelate complexes in reversed-phase HPLC (data of S_6, S_8, S_9, and S_{10} are given for comparison; eluent, CH_3CN; octadecylsilane as a stationary phase, dead time 0.71 min)

Compound	t_R (min)	RS
$Cp_2TiS_2Si(C_6H_5)_2$	2.11	439
$Cp_2TiS_2Ge(C_6H_5)_2$	2.13	443
$Cp'_2TiS_2Sn(C_6H_5)_2$	3.46	629
Cp_2TiS_5	2.26	468
Cp'_2TiS_5	2.65	531
S_6	3 26	608
S_8	5 38	778
S_9	8.20	911
S_{10}	11.07	1002

(range, 190–800 nm; solvent, acetonitrile). The spectra are shown in Fig. 1; no absorption was observed in the range 600–800 nm.

The UV absorption spectra of **4**, **5** and **6** are rather similar, with bands near 220, 350, and between 550 and 600 nm, the last being responsible for the green colour of the solutions. The spectrum of Cp_2TiS_5 is quite different (see Fig. 1), showing that the ring size of the metallacycle is of crucial importance.

The retention behaviour of the new compounds in high-pressure liquid chromatography (HPLC) is shown in Table 1. Since **4** and **5** rapidly react with methanol to give titanocene methoxy complexes, acetonitrile had to be used as eluent. While the retention times (t_R) of **4** and **5** are very similar, **6** shows a considerably higher t_R value, which is due to the two additional methyl groups, as can also be seen from the retention times of Cp_2TiS_5 and Cp'_2TiS_5 given in Table 1. Since t_R values depend on the geometry of the apparatus used as well as on the flow rate, retention indices (RS) are also given in Table 1; these are independent of such parameters [18], since they give the relative retention compared with those of reference materials. RS data are based on the sulphur homocycles S_6, S_8, S_9, and S_{10} as reference substances [18].

Attempts to obtain similar titanium compounds from Mes_2SiCl_2 and Mes_2GeCl_2 (Mes = 2,4,6-trimethylphenyl) failed. In the case of Mes_2GeCl_2 reaction 6 took place, and the four-membered heterocycle $(Mes_2GeS)_2$ (**7**) was isolated. This compound, identified by elemental analysis, molecular mass determination, and mass spectrometry, forms colourless crystals which are air stable for long periods, its synthesis from hexamesitylcyclotrigermane and S_8 was reported previously, but no molecular mass measurement was made [19].

$$2Mes_2GeCl_2 + 2Li_2S \rightarrow (Mes_2GeS)_2 + 4LiCl \qquad (6)$$

When a solution of $Cp_2TiS_2Si(C_6H_5)_2$ (**4**), in CS_2, was treated with S_2Cl_2 at −78°C the colour changed from green to red and Cp_2TiCl_2 separated from the solution. The mass spectrum of the residue after removal of the solvent exhibited the molecular ion for $(C_6H_5)_2SiS_4$ (**8**), indicating that reaction 7 had taken place:

$$Cp_2TiS_2Si(C_6H_5)_2 + S_2Cl_2 \rightarrow (C_6H_5)_2SiS_4 + Cp_2TiCl_2 \qquad (7)$$

To our knowledge, **8** represents the first example of an Si–S heterocycle with neighbouring S–S bonds. Well known examples of related rings are the cyclic compounds $(Et_2SiS)_3$, $(Et_2Si)_4S$, $(Et_2Si)_4S_2$, and $(Et_2Si)_3S_2$ [12b]. It is to be expected that reactions of the novel $Cp_2TiS_2Si(C_6H_5)_2$, $Cp_2TiS_2Ge(C_6H_5)_2$, and $Cp_2TiS_2Sn(C_6H_5)_2$ with sulphur chlorides and organic sulphenyl chlorides will provide new non-metallic heterocyclic compounds containing Si–S, Ge–S and Sn–S bonds, respectively. Work on these reactions is in progress.

Experimental

The following spectrometers were used: Varian MAT 311 A mass spectrometer (EI, 70 eV); Bruker WP 80 NMR spectrometer. Chemical shifts are given in ppm relative to internal $Si(CH_3)_4$. The molecular weight of $(Mes_2GeS)_2$ was determined by a KNAUER vapour pressure osmometer 11.00.

HPLC equipment: Varian 5000 pump (microprocessor controlled) with Valco loop injector (10 μl), Waters Radial Pak 10C18 reversed-phase column (length 10 cm, inner diameter 8 mm) contained in a compression module, UV absorbance detector operating at 210 nm, Waters 990 diode-array detector with NEC APC III computer (512 diodes, range 190–800 nm). Commercially available acetonitrile (for chromatography) was used as an eluent. All manipulations were carried out with exclusion of air and moisture at ambient temperature. Solvents were carefully dried and distilled. $(C_6H_5)_2GeBr_2$ was prepared as described by Harris and Johnson [15,16] from $GeCl_4$, C_6H_5Br and Br_2. Mes_2SiCl_2 and Mes_2GeCl_2 were prepared as described by Wiberg and Neruda [17].

Preparation of $Cp_2TiS_2Si(C_6H_5)_2$ (4). To a solution of 10 mmol $(C_6H_5)_2SiCl_2$ in 10 ml of anhydrous THF at room temperature was added a suspension of 20 mmol of Li_2S in 10 ml of THF. After 10 min stirring the mixture was greenish-yellow. A solution of Cp_2TiCl_2 (10 mmol) in 10 ml of THF was added and the mixture stirred for 24 h. The olive-brown solution was evaporated to dryness and the residue extracted with 50 ml CH_2Cl_2. The extract was filtered, then diluted with 50 ml of hexane, and the CH_2Cl_2 evaporated off. Cooling to −78°C (20 h) afforded 1.66 g of dark green microcrystals (39% yield).

$(C_5H_5)_2TiS_2Si(C_6H_5)_2$ (4): ^1H NMR ($CDCl_3$): δ 7.86–7.74 m; 7.38–7.30 m (C_6H_5); 6.49 s (Cp). EI-MS ($T = 120°C$): m/z 424 (74%, $Cp_2TiS_2Si(C_6H_5)_2^+$); 359 (100%, $CpTiS_2(C_6H_5)_2^+$); 282 (39%, $CpTiS_2Si(C_6H_5)^+$) and further signals. UV (CH_3CN): 195 nm (100%); 222 nm (30%); 246 nm (11%); 278 nm (6%); 342 nm (9%), 575 nm (4%). Anal. Found: C, 60.9; H, 4.8. $C_{22}H_{20}TiS_2Si$ (424.50) calc.: C, 62.2; H, 4.8%.

Preparation of $Cp_2TiS_2Ge(C_6H_5)_2$ (5). This was prepared analogously from 10 mmol of $(C_6H_5)_2GeBr_2$, 20 mmol of Li_2S and 10 mmol of Cp_2TiCl_2 was carried out as described above (1.64 g yield; 35%).

$(C_5H_5)_2TiS_2Ge(C_6H_5)_2$ (5): ^1H NMR ($CDCl_3$): δ 7.80–7.60 m; 7.57–7.20 m (C_6H_5); 6.39 s (Cp). EI-MS ($T = 120°C$): m/z 470 (20%, $Cp_2TiS_2Ge(C_6H_5)_2^+$); 405 (44%, $CpTiS_2Ge(C_6H_5)_2^+$); 328 (13%, $CpTiS_2Ge(C_6H_5)^+$); 222 (100%, $CpTiS(C_6H_5)^+$) and further signals. UV (CH_3CN): 195 nm (100%); 222 nm (32%); 350 nm (6%); 600 nm (2%). Anal. Found: C, 54.3; H, 4.2. $C_{22}H_{20}TiS_2Ge$ (469.02) calc.: C, 53.6; H, 4.3%.

Preparation of $Cp'_2TiS_2Sn(C_6H_5)_2$ (6). This was prepared analogously from 10 mmol of $(C_6H_5)_2SnCl_2$, 20 mmol of Li_2S and 10 mmol of Cp'_2TiCl_2. The product mixture contained several of the known heterocycles $((C_6H_5)_2SnS)_x$. It was purified by extraction with hexane (2.12 g yield; 39%).

$(CH_3C_5H_4)_2TiS_2Sn(C_6H_5)_2$ (**6**): ^1H NMR ($CDCl_3$): δ 7.77–7.64 m; 7.40–7.30 m (C_6H_5); 6.12 m (Cp); 2.15 s (CpMe). EI-MS (T = 180°C): m/z 544 (25%, $Cp'_2TiS_2Sn(C_6H_5)_2^+$); 465 (74%, $Cp'TiS_2Sn(C_6H_5)_2^+$); 387 (40%, $Cp'TiS_2Sn(C_6H_5)^+$); 77 (100%, $C_6H_5^+$) and further signals. UV (CH_3OH): 225 nm (100%); 354 nm (sh 12%); 550 nm (2%). Anal. Found: C, 52.5; H, 4.5. $C_{24}H_{24}TiS_2Sn$ (543.19) calc.: C, 53.1; H, 4.5%.

Reaction of Mes_2GeCl_2 with Li_2S and Cp_2TiCl_2 (7). This was carried out analogously from 10 mmol of Mes_2GeCl_2, 20 mmol of Li_2S, and 10 mmol of Cp_2TiCl_2. The main product was, unexpectedly, the known $(Mes_2GeS)_2$ (7), in 10% yield.

$(Mes_2GeS)_2$ (7): ^1H NMR ($CDCl_3$): δ 6.77 s ($Me_3C_6H_2$); 2.48 s; 2.26 s ($(CH_3)_3C_6H_2$). EI-MS (T = 200°C): m/z 686 (2%, M^+); 567 (100%, M^+-Mes); 344 (60%, Mes_2GeS^+) and further signals. Anal. Found: C, 63.3; H, 7.0. $C_{36}H_{44}Ge_2S_2$ (686.06) calc.: C, 63.0; H, 6.5%. Molecular mass determined osmometrically in CH_2Cl_2: 680 ± 20.

Reaction of $Cp_2TiS_2Si(C_6H_5)_2$ with S_2Cl_2 (8). A solution of 0.5 mmol S_2Cl_2 in 10 ml CS_2 was added during 30 min to a solution of 0.5 mmol of $Cp_2TiS_2Si(C_6H_5)_2$ in 20 ml of CS_2 at −78°C. The colour turned from green to red. The solution was evaporated to dryness and the residue extracted with n-pentane (−78°C; 20 ml). The insoluble Cp_2TiCl_2 was filtered off and the extract evaporated to dryness. The colourless waxy $S_4Si(C_6H_5)_2$ obtained was stable in an inert atmosphere below −20°C. No side products were observed.

$(C_6H_5)_2SiS_4$ (**8**): ^1H NMR ($CDCl_3$): δ 7.88–7.65 m; 7.59–7.36 m (C_6H_5). EI-MS (T = 25°C): m/z 310 (1%, $(C_6H_5)_2SiS_4^+$); 278 (2%, $(C_6H_5)_2SiS_3^+$); 246 (2%, $(C_6H_5)_2SiS_2^+$); 214 (4%, $(C_6H_5)_2SiS^+$); 64 (100%, S_2^+) and further signals.

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