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Reactions of titanocene polyselenide complexes with methyldichloroarsane: synthesis and properties of $(CH_3C_5H_4)_2Ti(\mu_2\text{-}Se_2)_2AsCH_3$ and of $(CH_3As)_2Se_3$

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Abstract

$(C_5H_4CH_3)_4Ti_2Se_4$ reacts at 0 °C in CS_2 with CH_3AsCl_2 in a molar ratio of 1 : 1 to give the novel $(C_5H_4CH_3)_2TiSe_4AsCH_3$, which forms air-stable black-violet crystals that have been characterized by ^1H NMR, mass, and infrared spectra. When a molar ratio of 1 : 2 is used the novel $(CH_3As)_2Se_3$ rather than $(CH_3As)_2Se_4$ is obtained, as orange crystals, together with elemental selenium. $(CH_3As)_2Se_3$ can also be prepared from $(C_5H_4CH_3)_2TiSe_5$ and CH_3AsCl_2 at 20 °C in CS_2; it probably contains five-membered 1,3-As_2Se_3 rings.

Introduction

The titanocene derivatives Cp_2TiS_5 (**1**) and Cp_2TiSe_5 (**2**) react as chalcogen transfer reagents with non-metal halides under mild conditions. This was first shown by the synthesis of S_7 [1] and Se_5S_2 [2] according to reactions 1 and 2:

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

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

Subsequently more than 20 cyclic sulfur or selenium compounds have been obtained by similar reactions [3]. Following the synthesis of the dinuclear titanocene chalcogen derivatives $Cp_2Ti(\mu\text{-}S_2)_2TiCp_2$ (**3**) [8] and $Cp_2Ti(\mu\text{-}Se_2)_2TiCp_2$ (**4**) [9] it was shown that these are equally valuable chalcogen transfer reagents, as can be seen from reactions 3 and 4 [9,10]:

$$Cp_4Ti_2S_4 + 2\ Se_2Cl_2 \rightarrow 1,2,5,6\text{-}Se_4S_4 + 2\ Cp_2TiCl_2 \quad (3)$$

$$Cp_4Ti_2Se_4 + 2\ SCl_2 \rightarrow 1,2\text{-}Se_4S_2 + 2\ Cp_2TiCl_2 \quad (4)$$

These reactions proceed in two steps, as was shown by HPLC analysis of the reaction mixtures at various molar ratios of the reactants: in the first step one titanocene unit is eliminated as Cp_2TiCl_2 and a mononuclear complex is formed [9,10]. Under favorable conditions this intermediate may be isolated and char-

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acterized, as was recently shown by the preparation of $Cp_2TiS_4AsCH_3$ (**5**) by reaction 5 [11]:

$$Cp_2Ti(\mu\text{-}S_2)_2TiCp_2 + CH_3AsCl_2 \rightarrow Cp_2Ti(\mu\text{-}S_2)_2AsCH_3 + Cp_2TiCl_2 \qquad (5)$$

The structure of **5** has been established by X-ray diffraction study: the TiS_4As ring adopts a chair conformation with the methyl group on arsenic in an axial position. Compound **5** is stable in air at 20 ° C and reacts with sulfur halides S_nCl_2 ($n = 1, 2$) to give sulfur-rich arsenic-containing heterocycles [11].

The work described here was concerned with the preparation of the analogous selenium compound according to eq. 6:

$$Cp_2Ti(\mu\text{-}Se_2)_2TiCp_2 + CH_3AsCl_2 \rightarrow Cp_2Ti(\mu\text{-}Se_2)_2AsCH_3 + Cp_2TiCl_2 \qquad (6)$$

The reaction of Cp_2TiSe_5 with methyldichloroarsane was also studied. Since the solubility of **2** and **4** in CS_2 at 0–20 ° C is rather low for $Cp = C_5H_5$, we used $Cp' = CH_3C_5H_4$ as a ligand throughout this work; the corresponding titanocene polysulfide chelate complexes are known to have considerably higher solubility.

Results and discussion

When $Cp'_4Ti_2Se_4$ [9] was treated with CH_3AsCl_2 at 0 ° C in CS_2 solution with exclusion of light reaction 6 took place immediately and Cp'_2TiCl_2 separated from the solution. After filtration and addition of n-hexane to the filtrate at −78 ° C black-violet crystals of $Cp'_2TiSe_4AsCH_3$ (**6**) appeared; these are stable in air at 20 ° C and melt at 168 ° C with decomposition. Satisfactory analytical data (C, H) were obtained for **6** (see Experimental Section). When reaction 6 was carried out at 20 ° C in daylight, the products were Cp'_2TiCl_2, elemental selenium, $(CH_3As)_2Se_3$ (**7**), and Cp'_2TiSe_5 (**8**), rather than **6**.

Compound **6** is fairly soluble in CS_2, $CHCl_3$, and CH_2Cl_2, but only the solutions in CS_2 are stable, and then only at temperatures below −30 ° C in the dark. Attempts to grow single crystals have failed so far.

Reactions such as 1–6 can be monitored readily by reversed-phase HPLC analysis using a UV absorbance detector since all reactants show a strong absorption near 254 nm. The various titanocene chelate complexes under identical conditions exhibit distinctly different retention times (t_R), as the data in Table 1 show; the retention times of S_6 and S_8 are given for comparison. The data show that substitution of all S by Se atoms in analogous compounds results in an increase in t_R.

Table 1

Retention times for various titanocene chelate complexes in reversed-phase HPLC (data of S_6 and S_8 are given for comparison; eluent CH_3OH; octadecylsilane as a stationary phase, dead time 1.34 min)

Compound	t_R (min)	Compound	t_R (min)
Cp'_2TiS_5	2.91	Cp'_2TiSe_5	3.99
$Cp'_4Ti_2S_4$	2.63	$Cp'_4Ti_2Se_4$	3.06
$Cp'_2TiS_4AsCH_3$	3.14	$Cp'_2TiSe_4AsCH_3$	4.25
S_6	3.06		
S_8	4.61		

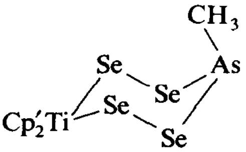
Table 2

^{1}H-NMR shifts of the Cp′ protons in Cp'_2TiSe_5 and $Cp'_2TiSe_4AsCH_3$ (in $CDCl_3$). H_A are the protons neighboring the methyl group

Cp'_2TiSe_5 [12]	$Cp'_2TiSe_4AsCH_3$	Assignment
6.28(2) dd	6.33(2) dd	H_A eq
6.11(2) dd	6.09(2) dd	H_B eq
5.99(2) dd	5.86(2) dd	H_B ax
5.86(2) dd	5.68(2) dd	H_A ax
2.32(3) s	2.43(3) s	CH_3 eq
1.99(3) s	1.98(3) s	CH_3 ax

The identity and composition of **6** are based on its mass and ^{1}H NMR spectra. The mass spectrum (160 °C; 70 eV) does not exhibit a peak for the molecular ion but various characteristic fragment ions such $Cp'_2TiSe_3As^+$ and $CH_3AsSe_2^+$ are present. However, the spectrum also reveals that at 160 °C **6** has already partly decomposed to give Cp'_2TiSe_5 and $(CH_3As)_2Se_3$, which both are observed as molecular ions. These are the same products as were obtained upon decomposition of **6** in solution (see above).

The ^{1}H NMR spectrum of **6** is in accord with the assumption of a rigid six-membered $TiSe_4As$ metallacycle as the central structural unit (Table 2). The methyl group on arsenic shows an unusual low chemical shift (0.57 ppm), indicating an axial position, and this is consistent with the structure of the analogous sulfur compound, $Cp'_2TiS_4AsCH_3$ [11]. The other six lines can be assigned by comparison with the spectrum of Cp'_2TiSe_5 [12] as shown in Table 2. Thus, the spectrum supports a $Cp'_2Ti(\mu\text{-}Se_2)_2AsCH_3$ structure, in keeping with the structure of the analogous sulfur compound:



When 1 mol of $Cp'_4Ti_2Se_4$ (**8**) is treated with 2 mol (rather than 1 mol) of CH_3AsCl_2 the following reaction was expected to take place:

$$Cp'_2Ti(\mu\text{-}Se_2)_2TiCp'_2 + 2\ CH_3AsCl_2 \rightarrow CH_3As(\mu\text{-}Se_2)_2AsCH_3 + 2\ Cp'_2TiCl_2 \qquad (7)$$

When this reaction was carried out at 0 °C in CS_2 and with exclusion of light the HPLC analysis showed that within 2 min the starting complex **8** had disappeared and **6** had been formed as well as Cp'_2TiCl_2. However, **6** then slowly degraded and $(CH_3As)_2Se_3$ was formed together with elemental selenium.

$$CH_3As(\mu\text{-}Se_2)_2AsCH_3 \rightarrow 1,3\text{-}(CH_3As)_2Se_3 + \frac{1}{n}Se_n \qquad (8)$$

No indication of the formation of $(CH_3As)_2Se_4$ was observed. Thus reaction 6 is very fast and the attack of CH_3AsCl_2 on **6** significantly slower. The As-containing product expected from eq. 7 is evidently unstable, and rapidly decomposes even at 0 °C to give the novel five-membered ring $CH_3As(\mu\text{-}Se)(\mu\text{-}Se_2)AsCH_3$ (**7**) and elemental Se according to eq. 8. Compound **7** was identified from its retention time and ^{1}H NMR shift, which were identical to those of a sample prepared from Cp'_2TiSe_5 and CH_3AsCl_2 (see below). The corresponding phenyl derivative 1,3-$(C_6H_5As)_2Se_3$ was known previously [13], and was characterized by X-ray diffraction. The molecules are of C_2 symmetry. Although we have not been able to determine the exact positions of the As atoms in the As_2Se_3 ring of **7** it is likely that the selenium extrusion reaction 8 yields the 1,3-isomer rather than 1,2-$(CH_3As)_2Se_3$.

After the preparation of a selenium-rich As–Se heterocycle according to reaction 7 had failed we tried to prepare CH_3AsSe_5 from **8** and CH_3AsCl_2; eq. 9:

$$Cp'_2TiSe_5 + CH_3AsCl_2 \rightarrow CH_3AsSe_5 + Cp'_2TiCl_2 \qquad (9)$$

This reaction turned out to be slow at 20 ° C in CS_2, since only after 1 h was Cp'_2TiCl_2 observed. After 18 h the precipitate formed, consisting of amorphous red elemental selenium and Cp'_2TiCl_2, was filtered off, the filtrate was evaporated, and the residue extracted with CH_2Cl_2; cooling of the extract gave orange needles of $(CH_3As)_2Se_3$ (**7**) in 4% yield (m.p. 48 ° C):

$$2\ CH_3AsSe_5 \rightarrow (CH_3As)_2Se_3 + 7\ Se \qquad (10)$$

There was no indication of the formation of CH_3AsSe_5. Satisfactory analytical data (C, H, Se) were obtained for **7**, and the mass spectrum exhibited a peak for the molecular ion (65 ° C; EI, 70 eV). The data indicate that this product is identical to the $(CH_3As)_2Se_3$ obtained by reaction 8.

The formation of **7** by reaction 10 is not straightforward and it is obvious that a number of reactive intermediates must be involved in the conversion of CH_3AsSe_5 to **7**. However, similar reactions have been observed for equally reactive selenium-rich selenium sulfide rings, which are also converted rapidly into more stable species in solution. For example, Se_5S in CS_2 at 20 ° C decomposes within 5 h to give Se_7S, Se_6S, and Se_5S_3 [2,12]. Possible mechanisms for this type of reaction have been discussed elsewhere [15].

The number of arsenic–selenium binary heterocycles has so far been rather limited, with As_4Se_3, As_4Se_4, $(PhAs)_2Se_3$, and $(MeAs)_3Se_3$ as the best known examples [16]. It is to be expected that reactions of the novel $Cp'_2TiSe_4AsCH_3$ with sulfur and selenium chlorides will provide new non-metallic heterocyclic compounds containing As–Se bonds.

Experimental

HPLC equipment: Gynkotek High Precision Pump Model 300 C with Gynkotek Loop injector (10 μl), Waters Radial Pak 8C18 reversed-phase column (length 10 cm; inner diameter 8 mm) contained in a compression module; UV absorbance detector (Waters, model 440) operating at 254 nm. Dried ($MgSO_4$), freshly distilled, and degassed methanol was used as eluent. The following spectrometers were used: Bruker WH400 spectrometer for ^{1}H NMR spectroscopy, chemical shifts are given in ppm relative to internal $SiMe_4$; Varian MAT 311A mass spectrometer.

Preparations

$Cp'_2Ti(\mu\text{-}Se_2)_2TiCp'_2$ was made as described by Giolando et al. [9] from Cp'_2TiCl_2 and Li_2Se_2. Anhydrous Li_2Se_2 was prepared as described by Gladysz et al. [14] from elemental selenium by treatment with super hydride ($LiBEt_3H$) in a molar ratio of

1 : 1. Cp'_2TiSe_5 was made by a similar method; the selenium/super hydride ratio was increased to 5 : 2 and the resulting "Li_2Se_5" was treated with Cp'_2TiCl_2. Methyldichloroarsane was not commercially available, and so was made from As_2O_3 as described by Banks et al. [17]. All manipulations described below were carried out with exclusion of light at temperatures between 0 and 20 ° C. Solvents were carefully dried and distilled.

Preparation of $Cp'_2TiSe_4AsCH_3$ *(6)*

To a suspension of 200 mg (0.29 mmol) of **4** in 5 mL of CS_2, a solution of 43.5 mg (0.27 mmol) of CH_3AsCl_2 in 4 mL of CS_2 was added at 0 ° C. After 3 min stirring the mixture was cooled to − 78 ° C for about 1 h. The precipitated Cp'_2TiCl_2 was filtered off and the solution was evaporated to half of its original volume under vacuum, and, if necessary, filtered again. Addition of 2–3 mL of hexane followed by evaporation of CS_2 and cooling to − 78 ° C (18 h) afforded 53.7 mg (10.6%) of black-violet crystals.

$(CH_3C_5H_4)_2TiSe_4AsCH_3$ (**6**): ^{1}H NMR ($CDCl_3$): 6.33 dd; 6.09 dd; 5.86 dd; 5.68 dd (Cp); 2.43 s, 1.98 s (CpMe); 0.57 s (AsMe). EI-MS (T = 160 ° C): m/z 604–602 (1%, $Cp'_2TiSe_5^+$); 520 (0.9%, $Cp'_2TiSe_3As^+$); 444 (19%, $Cp'_2TiSe_3^+$); 418 (12%, $(CH_3As)_2Se_3^+$); 403 (10%, $CH_3As_2Se_3^+$); 365 (12%, $Cp'_2TiSe_2^+$); 286 (18%, $Cp'_2TiSe^+/Cp'_2TiSe_2^+$); 250 (26%, $CH_3AsSe_2^+$); 206 (65%, $Cp'_2Ti^+/Cp'TiSe^+/TiSe_2^+$); 79 (100%, Se^+, Cp'^+) and further signals. Anal. Found: C, 25.29; H, 2.73. $C_{13}H_{17}TiSe_4As$ (611.96) calcd.: C, 25.51; H, 2.81%.

Preparation of $1,3\text{-}(CH_3As)_2Se_3$ *from* Cp'_2TiSe_5

To a slurry of 1.8 g (3 mmol) of Cp'_2TiSe_5 in 60 mL of CS_2 at 20 ° C were added 483 mg (3 mmol) of CH_3AsCl_2. After about 18 h stirring the colour of the solution had changed from dark-violet to red. The precipitate (a mixture of Cp'_2TiCl_2 and polymer selenium, ca. 1.53 g) was filtered off. The orange solution was evaporated. The oily residue obtained was extracted with 40 mL of CH_2Cl_2 for about 3 h. Cooling of the extract to − 78 ° C afforded 52.7 mg (3.7%) of orange crystals. The amount of $1,3\text{-}(CH_3As)_2Se_3$ in solution was determined by reversed-phase HPLC as 8%. The 3 cyclic selenium molecules Se_6. Se_7, and Se_8 were also detected [6,18].

$1,3\text{-}(CH_3As)_2Se_3$ (**7**): ^{1}H NMR ($CDCl_3$): 1.57 s. EI-MS (T = 65 ° C): m/z 418 (65%, $(CH_3As)_2Se_3^+$); 403 (27%, $CH_3As_2Se_3^+$); 325 (8%, $CH_3As_2Se_2^+$); 245 (68%, $CH_3As_2Se^+$); 155 (100%, $AsSe^+$); 89 (12%, $AsCH_3$). Anal. Found: C, 6.16; H, 1.50; Se, 56.82, $C_2H_6Se_3As_2$ (416.80) calcd.: C, 5.76; H, 1.45; Se, 56.83%. IR: cm^{-1} (CsI): 2910–2840 w, 1390 m, 1225 m, 825 s, 560 m s, 250 s.

Reaction of $Cp'_2Ti(\mu\text{-}Se_2)_2TiCp'_2$ *with 2 mol of* CH_3AsCl_2

A solution of 45.1 mg (0.28 mmol) of CH_3AsCl_2 in 4 mL of CS_2 was rapidly added at 0 ° C to a suspension of 100 mg (0.14 mmol) of **4** in 10 mL of CS_2. The progress of the reaction was monitored by reversed-phase HPLC (after 3, 10, 20, 30, 50, 70, and 100 min and 18 h). Compound **4** had completely reacted within 3 min at which time the main components of the mixture were Cp'_2TiCl_2 and **6**, corresponding the treatment of **4** with just one mol of the halide. In addition, a small amount of **7** could already be detected. Subsequently the concentration of **6** decreased, and after 18 h **6** had completely disappeared. Cp'_2TiCl_2, $1,3\text{-}(CH_3As)_2Se_3$, and elemental selenium (in solution appearing as Se_6, Se_7, Se_8 [6,18]) were the final products. The product mixture was not worked up but the concentrations of Cp'_2TiCl_2 and 1,3-$(CH_3As)_2Se_3$ in solution were determined by reversed-phase HPLC after calibration using solutions of known concentrations; taking the volume of the reaction mixture into consideration the concentrations were converted into the mass of each product. The following amounts were observed: Cp'_2TiCl_2: 72 mg (93% of the theoretical yield based on eqs. 7 and 8); 1,3-$(CH_3As)_2Se_3$: 21 mg (35%). ^1H NMR ($CDCl_3$): 1.57 s.

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