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New Titanacycles with Chelating Polychalcogenide Ligands¹

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NEW TITANACYCLES WITH CHELATING POLYCHALCOGENIDE LIGANDS ¹

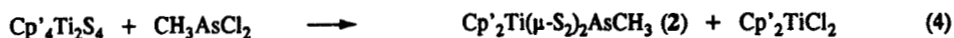
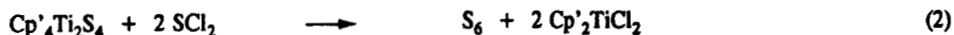
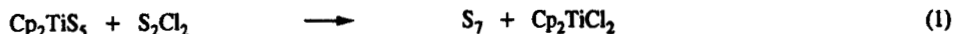
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Abstract The dinuclear titanocene complex $\text{Cp}'_4\text{Ti}_2\text{S}_4$ ($\text{Cp}' = \text{CH}_3\text{C}_5\text{H}_4$) reacts with CH_3AsCl_2 in a molar ratio of 1:1 to give the novel metallacycles $\text{Cp}'_2\text{Ti}(\mu\text{-S})_2\text{AsCH}_3$ and $\text{Cp}'_2\text{Ti}(\mu\text{-S})(\mu\text{-S}_3)\text{AsCH}_3$. $\text{Cp}'_2\text{Ti}(\mu\text{-Se})_2\text{AsCH}_3$ is accessible by reaction of $\text{Cp}'_4\text{Ti}_2\text{Se}_4$ with 1 equivalent of CH_3AsCl_2 . With 2 equivalents of CH_3AsCl_2 five-membered rings $(\text{CH}_3\text{As})_2\text{CH}_3$ rather than $(\text{CH}_3\text{As})_2\text{CH}_4$ ($\text{Ch} = \text{S}, \text{Se}$) are obtained. The new phosphorus-containing titanacycle $\text{Cp}'_2\text{Ti}(\mu\text{-S})(\mu\text{-S}_3)\text{P}(\text{S})\text{C}_6\text{H}_5$ has been isolated from the reaction of $\text{Cp}'_4\text{Ti}_2\text{S}_4$ with $\text{C}_6\text{H}_5\text{PCl}_2$.

INTRODUCTION

$\text{Cp}'_4\text{Ti}_2\text{S}_4$ has been used as a sulfur-transfer reagent like Cp_2TiS_5 (eq. 1,2) and as an excellent precursor to generate metallacycles with inorganic chelating ligands (eq. 3,4)¹⁻⁴.



X-Ray structural analyses and ¹H NMR data show that 1 and 2 contain six-membered metallacycles. The methyl group on arsenic of compound 2 is in an axial position ^{4,5}. The reaction of $\text{Cp}'_4\text{Ti}_2\text{S}_4$ with 2 equivalents of CH_3AsCl_2 yields elemental sulfur (S_8) and $\text{CH}_3\text{As}(\mu\text{-S})(\mu\text{-S}_2)\text{AsCH}_3$, a five-membered heterocycle; the formation of the expected $(\text{CH}_3\text{As})_2\text{S}_4$ has not been observed ⁶.

REACTIONS AND PRODUCTS

From reaction mixtures according to equation 4 two more compounds have now been isolated in low yield. One of them is titanocene pentasulfide (1). The other compound has been identified as another titanocene complex containing arsenic (3). Analytical data (MS; C,H; ^1H NMR) revealed that 3 is isomeric to 2^{4,6}.

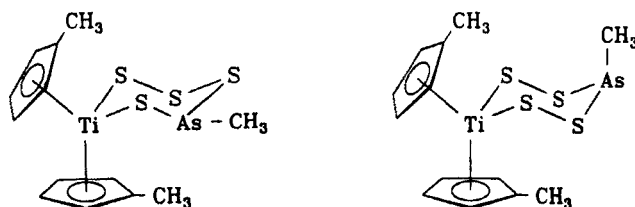
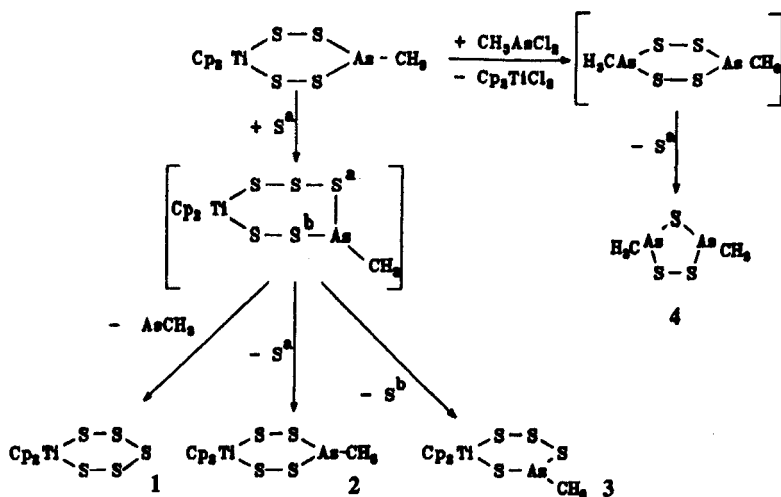


FIGURE 1 Molecular structures of 2 (right) and 3 (left)

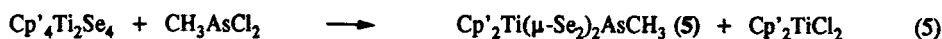
^1H NMR spectrum of 3	6.25 q (1)	6.22 q (2)	6.19 q (1)	Cp
(20°C, CDCl_3) [ppm]:	6.16 m (2)	6.12 q (1)	5.89 q (1)	Cp
	2.26 s (3)	2.03 s (3)	1.87 s (3)	methyl

Since the metallacycle of 3 is of lower symmetry than that of 2 the ^1H NMR spectrum of 3 shows three singlets and eight quartets (two of them are of identical energy) which is in accord with spectra of other titanacycles holding non-symmetrical chelate ligands^{6,7}. The formation of $\text{Cp}'_2\text{TiS}_5$ and 3 is explained in Figure 2⁶.

When reaction 4 is carried out in an equimolar ratio small amounts of 1,3- $(\text{CH}_3\text{As})_2\text{S}_3$ (4) are detected in addition. 4 seems to be responsible for the formation of $\text{Cp}'_2\text{TiS}_5$ and 3. The formally splitted off highly reactive S^a may attack compound 2 (probably in a bimolecular reaction). The resulting seven-membered metallacycle is unstable and rearranges to more stable six-membered species. Actually there are three possible pathways to reduce the ring size. If the same sulfur atom S^a is eliminated 2 is restored. Elimination of S^b results in the formation of the isomeric compound 3. If $\text{Cp}'_2\text{Ti}(\mu\text{-S}_2)(\mu\text{-S}_3)\text{AsCH}_3$ expells the " AsCH_3 " unit $\text{Cp}'_2\text{TiS}_5$ is generated.

FIGURE 2 Formation of $\text{Cp}'_2\text{TiS}_5$ and 3

The analogous reaction of $\text{Cp}'_4\text{Ti}_2\text{Se}_4$ with CH_3AsCl_2 leads to $\text{Cp}'_2\text{Ti}(\mu\text{-Se}_2)_2\text{AsCH}_3$ (5). Satisfactory analytical data (^1H NMR; C,H; HPLC) have been obtained for 5⁸.



^1H NMR data show that 5 contains a symmetrical chelate ligand. The aromatic part of the spectrum shows just 4 triplets for 8 H atoms. 5 reacts with CH_3AsCl_2 to give 1,3-(CH_3As)₂Se₃ and elemental selenium⁸.

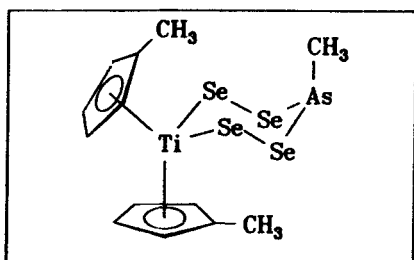


FIGURE 3 Molecular structure of 5

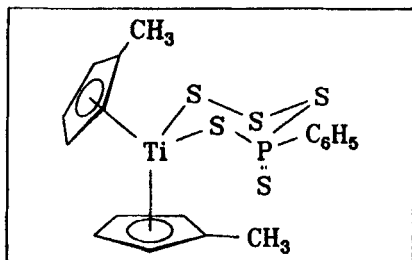
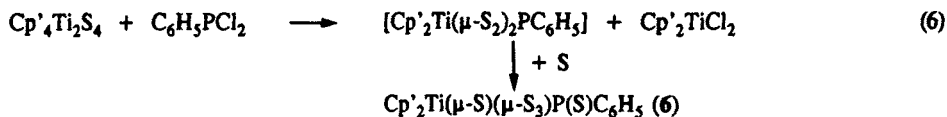
^1H NMR spectrum (20°C, CDCl_3) [ppm]:

6,33 t (2)	6,09 t (2)	Cp
5,86 t (2)	5,68 t (2)	Cp
2,43 s (3)	1,98 s (3)	methyl
0,57 s (3)		methyl

$\text{Cp}'_2\text{Ti}(\mu\text{-S})(\mu\text{-S}_3)\text{P}(\text{S})\text{C}_6\text{H}_5$ (6), a new titanocene complex containing phosphorus, has been obtained from the reaction of $\text{Cp}'_4\text{Ti}_2\text{S}_4$ and $\text{C}_6\text{H}_5\text{PCl}_2$ ⁶. The expected product $\text{Cp}'_2\text{Ti}(\mu\text{-S}_2)_2\text{PC}_6\text{H}_5$ is not observed but rearranges and is oxidized at the phosphorus atom to give 6.

According to the IR spectrum 6 contains a P=S-double bond [$\nu(\text{P}=\text{S}) = 655 \text{ cm}^{-1}$]⁶. ^1H NMR data

revealed that the titanium atom holds a non-symmetrical chelate ligand. All 8 H atoms yield signals at different field strengths ⁶.



¹H NMR data of 6 (20°C, CDCl₃) [ppm]:

8.20-8.12;	7.56-7.50	phenyl
7.31 q (1)	7.00 q (1)	Cp
6.83 q (1)	6.60 q (1)	Cp
6.56 q (1)	6.36 q (1)	Cp
6.18 q (1)	6.00 q (1)	Cp
2.25 s (3)	1.80 s (3)	methyl

FIGURE 4 Likely structure of 6

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