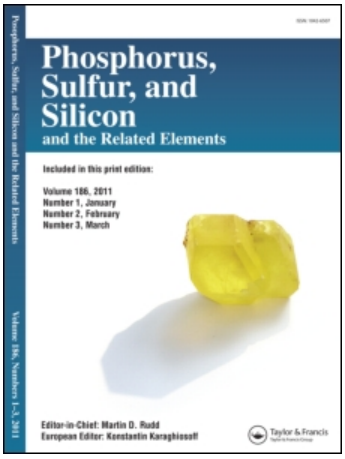

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SYNTHESIS OF METALLACYCLOSULFANES $(RC_5H_4)_2TiS_5$ FROM DIMERIC LOW VALENT ALKYLTITANOCENE CHLORIDE

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The new Ti(III) complexes $[(RCp)_2TiCl]_2$ (R = iPr, tBu; Cp = η^5-C_5H_4) were obtained by chemical reduction (Al/Hg) of the corresponding dichlorides. The further reaction of sulfur powder at room temperature led exclusively to titanacyclohexasulfane $[(RCp)_2TiS_5]$ and alkyltitanocene dichloride. The various new complexes were fully characterized by NMR, mass spectrometry and microanalyses.

Many papers are dealing with the interesting family of metal-chalcogen chelates of the type ME_x (E = S, Se). Some of them for which M is a part of a metallocene species have been reported as metallacyclochalcogenanes during the last fifteen years.[1,2,3] These compounds are usually available from chemically or electrochemically prepared chalcogenide anions and metallocene dichlorides.[2,4-7] They present a real authentic utility. For example $[(\eta^5\text{-}C_5H_4R)_2TiE_5]$ (**1**) (R = H, iPr; E = S, Se) are suitable substrates for Se and S atoms transfer and can serve as a soluble chalcogen reservoir in the synthesis of new chalcogen-containing hydrocarbon molecules and polyheterochalcogen large rings.[4,8-13] However $[(\eta^5\text{-}C_5H_5)_2ME_5]$ complexes exhibit a low solubility which could be detrimental to further organic syntheses. On the other hand, C_5Me_5 ligand which usually makes the solubility improved remains not very easy to prepare.

In a recent paper,[14] we have shown that complexes (1) (R = H, iPr; E = Se) can be obtained chemically from the reaction of Se powder on the corresponding dimer $[(\eta^5\text{-}C_5H_4R)_2TiCl]_2$, or electrochemically by cathodic reduction of the metallocene dichloride in the presence of selenium powder. Besides some syntheses of 1 (R = H; E = S) were reported in the literature.[2,6,15] Shaver[6] found that the size of the metallacyclosulfane ring is greatly dependent of the electron density on the transition metal. Thus only MS_5 rings were isolated for biscyclopentadienyl complexes (M = Ti, Zr, Hf) whereas MS_3 rings were formed with bis-Me_5C_5 ligand.[16]

In the present report, we describe the chemical access to $[(RCp)_2TiS_5]$ (**2**) (R = iPr, tBu; Cp = η^5-C_5H_4), from sulfur powder and the new Ti(III) dimers $[(RCp)_2TiCl]_2$ (**3**) according to the overall process of Equation (2). The spectral characteristics are also reported.[17]

The Ti(III) complexes were prepared using the method described by Coutts[18] consisting with the reduction of the Ti(IV) dichloride by activated aluminium foil in tetrahydrofuranne (Equation 1) prior to the addition of sulfur powder.

$$6[(RCp)_2TiCl_2] + 2Al \rightarrow \underset{\mathbf{3}}{3[(RCp)_2TiCl]_2} + 2AlCl_3 \quad (1)$$

$$\underset{\mathbf{2}}{[(RCp)_2TiCl]_2} + 5/8S_8 \rightleftarrows [(RCp)_2TiS_5] + [(RCp)_2TiCl_2] \quad (2)$$

In our hands the reaction led to the very air sensitive compounds **3** for which the ESR spectra were in accordance with the expected structures but microanalyses were incorrect. This failure is likely due to a particularly low stability but also to a similar solubility for the two products formed in the reaction (1). Some $AlCl_3$ remains in the desired product even after several washings. We tried to take out the Ti(III) complexes from the reaction mixture through a short alumina column chromatography[19] with tetrahydrofuran as eluent. At this time, the microanalysis systematically showed a slight deficit in chlorine accounting, very likely, for the formation of some -oxo complex during the chromatographic separation.

However, in each cases, the Ti(III) complexes **3** thus isolated were perfectly characterized by ESR and mass spectrometry and suited for further experiments. The ESR spectra (THF) ($g = 2.0066 \pm 0.0005$ for R = tBu; $g = 2.0217 \pm 0.0005$ for R = iPr) are very similar to this obtained from $[(Cp_2TiCl)_2]$.[20] The molecular isotopic pattern and characteristic fragmentations clearly appear in mass spectra.

The air stable (solid state) metallacyclosulfanes **2** were obtained by reacting the paramagnetic Ti(III) compounds with octasulfur in THF at room temperature. We found that only MS_5 rings were formed together with Ti(IV) dichloride complexes in a nearly equivalent amount. The by-product was readily separated by flash chromatography. These results are in close accordance with the stoechiometry of the overall reaction (2). However, a small excess of the dichloride is often observed. This anomaly could be due to traces of $AlCl_3$ still present in the starting reagent which cause the cyclosulfane to be slightly decomposed. Usually the overall yield of **2** ranged from 50 to 60%.

Refering to the paper published by Shaver,[6] it is clear, from our results, that the donor effect of the substituents iPr and tBu on the Cp rings does not affect noticeably the electron density at the titanium atom level which remains not very different of that observed for the unsubstituted Cp ligand.

The ^1H NMR spectra of complexes **2** exhibit two different signals for the substituent which are consistent with their non equivalence due to the molecule locked in a chair conformation.[6]

The exact masses determined by high-resolution techniques and the good correspondence between the observed and calculated values confirm the proposed structures. The fragmentation pattern is characteristic for the progressive loss of the sulfur atoms followed by the subsequent fragmentation of the substituted cyclopentadienyl ligands.

The mass spectrum recorded from a solution of **2** (R = tBu) after being left for some hours in air clearly indicates signals at higher values than the molecular pic. The highest signal observed corresponds to m/e: $[M + 50]^+$ (weak 1.5%) taking into account for the evident incorporation of oxygen into the molecule. The m/e: $[M + O]^+$ signal is particularly significant (22.6%). This result contrasts with

those from Rauchfuss[21] stating the great resistance of $[(RCp)_2TiS_5]$ (R = H, CH_3) to a variety of oxo compounds.

EXPERIMENTAL

All the reactions were performed under an argon atmosphere. Solvents are distilled from sodium benzophenone ketyl before use. i-propyl titanocene dichloride[22] and t-butyltitanocene dichloride[23] were prepared according to the literature. Sulfur was freshly sublimated. Elemental analyses were performed by Service Central d'Analyses, CNRS, Lyon. Spectra were recorded by means of the following instruments: ^1H NMR, JEOL FX 100; mass spectra, FINNIGAN 3002 (70eV, direct introduction), m/e values correspond to most abundant isotope.

Bis(η^5-alkylcyclopentadienyl) titanium (III) chloride dimers $[(RCp)_2TiCl]_2$ **(3)** *R = iPr, tBu*

The substituted titanocene dichloride $(RCp)_2TiCl_2$ (1.58 mmol) in freshly distilled THF (40 mL) was reduced overnight at room temperature in the presence of Al/Hg (prepared from aluminium foil (1 g) and $HgCl_2$ (0.32 g) in THF).[18] The supernatent was rapidly filtrated on a fritted glass containing free oxygen alumina (Merck 1077 heated in vacuum before use). The alumina was washed with three portions (10 mL) THF and the solvent distilled off led approximately to 0.55 mmol (35% yield) of the brown-green, highly air-sensitive paramagnetic complexes **3** m/e = 651 (R = tBu); m/e = 595 (R = iPr).

Bis(η^5-t-butylcyclopentadienyl) titana (TiIV) cyclohexasulfane. 0.28 g (0.43 mmol) of **3** in freshly distilled THF (5 mL) was added at room temperature to 0.073 g (0.284 mmol) of freshly sublimated S_8 (5.3 moles S per mole of the dimer). A stirring was maintained during three days. The weight of the crude residue obtained on removal the solvent was close to the calculated value for a quantitative yield. The solid was shown to be a mixture (^1H NMR) containing $[(tBuCp)_2TiCl_2]$ (53%) and $[(tBuCp)_2TiS_5]$ (47%). The latter compound was obtained in a pure state after flash chromatography (silicagel 60 Merck 9385, eluent: hexane-diethyl ether 7/3): 0.088 g (46% from sulfur), m.p. 162°C ^1H NMR ($CDCl_3$) δ 1.16 (s, 9H, tBu), 1.31 (s, 9H, tBu), 5.96 (pt, 2H, C_5H_4), 6.24 (m, 4H, C_5H_4), 6.35 (m, 2H, C_5H_4). Mass spectrum m/e relative intensity: 450, 2.6 (M^+); 418, 3.6 $(M-S)^+$; 386, 25.3 $(M-2S)^+$; 354, 55.2 $(M-3S)^+$; 322, 5.2 $(M-4S)^+$; 290, 27.8 $(M-5S)^+$ and other fragments. $C_{18}H_{26}S_5Ti$ (449.8): Calcd.: C, 47.98; H, 5.81; S, 35.58; Ti, 10.63. Found: C, 47.87; H, 6.04; S, 35.57; Ti, 10.61.

Bis(η^5-i-propylcyclopentadienyl) titana (TiIV) cyclohexasulfane. Similarly to the above process, the proportions observed in reaction mixture were: $[(iPrCp)_2TiCl_2]$(51%) and $[(iPrCp)_2TiS_5]$(49%). The hexasulfane was isolated after chromatography (60%; m.p. 110°C). ^1H NMR ($CDCl_3$) δ 1.05 (d, 6H, iPr), 1.22 (d, 6H, iPr), 2.71 (hp, 1H, CH), 3.01 (hp, 1H, CH), 5.85 (pt, 2H, C_5H_4), 6.20 (m, 6H, C_5H_4). Mass spectrum m/e, relative intensity: 422, 16.3 (M^+), 390, 15 $(M-S)^+$, 358, 67.3 $(M-2S)^+$, 326, 72.6 $(M-3S)^+$, 294, 33 $(M-4S)^+$, 262, 100 $(M-5S)^+$, 219, 42.6 $(M-C_3H_7S_5)^+$ and other fragments. $C_{16}H_{22}S_5Ti$ (421.8): Calcd.: C, 45.48; H, 5.25; S, 37.94; Ti, 11.33. Found: C, 45.57; H, 5.24; S, 37.81; Ti, 11.42.

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