Journal of Organometallic Chemistry 696 (2011) 523–526

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Formation of $[Cp_2TiSbMe_2]_2$, $[Cp_2TiSb(SiMe_3)_2]_2$ and $[Cp_2TiCl]_2 \cdot 2Mes_4Sb_2$

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ARTICLE INFO

Article history:
Received 30 June 2010
Received in revised form
24 August 2010
Accepted 1 September 2010
Available online 15 September 2010

Keywords:
Antimony
Titanium
X-ray diffractometry

ABSTRACT

Reactions of $[Cp_2Ti(btmsa)]$ (btmsa = bis(trimethylsilyl)acetylene) with R_4Sb_2 (R = Me, Me_3Si) give $[Cp_2TiSbMe_2]_2$ (**1**) or $[Cp_2TiSb(SiMe_3)_2]_2$ (**2**) respectively. $[Cp_2TiCl]_2 \cdot 2Mes_4Sb_2$ (**3**) is serendipitously formed from $[Cp_2Ti(btmsa)]$ and Mes_2SbH containing NH_4Cl traces.

1. Introduction

Recently we described the syntheses of the first titanocene complexes with organoantimony ligands: $[Cp_2Ti(Sbdmp)_2]$ (dmp = 2,6-$Mes_2C_6H_3$) [1], $[Cp_2TiSbR_2]_2$ (R = Et), $[(Cp_2Ti)_3(RSb)_3Sb]$ (R = 2-$(Me_2NCH_2)C_6H_4$) and $[(Cp_2Ti)_5(RSb)_2Sb_7]$ (R = Me_3SiCH_2) [2] by reactions of the titanocene source $[Cp_2Ti(btmsa)]$, (btmsa = bis(trimethylsilyl)acetylene, $Me_3SiC{\equiv}CSiMe_3$) with antimony compounds of the type $RSbH_2$ or R_2SbSbR_2. Very few related complexes of Zr and Hf including $[Cp_2Zr(SbPh_2)_2]$ [3], $[CpCp^*HfSbdmp]$ [4], $[CpCp^*Hf(Cl)Sb(H)dmp]$ [5], $[CpCp^*Hf(SbMes_2)_2]$ [6] are known. Analogous compounds with phosphorus or arsenic ligands have been studied more frequently and group 4 metal complexes with R_3E, R_2E, RE, R_3E_3 (E = P, As) ligands have been synthesized [7–14].

We report here on reactions between $[Cp_2Ti(btmsa)]$ and R_2SbSbR_2 (R = Me, Me_3Si) giving the novel Sb–Ti complexes $[Cp_2TiSbMe_2]_2$ (**1**) and $[Cp_2TiSb(SiMe_3)_2]_2$ (**2**) respectively and on the serendipitous formation of $[Cp_2TiCl]_2 \cdot 2Mes_4Sb_2$ (**3**) from $[Cp_2Ti(btmsa)]$ and Mes_2SbH containing NH_4Cl traces.

2. Results and discussion

The distibanes R_4Sb_2 (R = Me, Me_3Si) react with $[Cp_2Ti(btmsa)]$ in benzene at room temperature with exchange of the btmsa ligand and formation of crystalline samples of $[Cp_2TiSbMe_2]_2$ (**1**) or $[Cp_2TiSb(SiMe_3)_2]_2$ (**2**) respectively. The reaction is described in equation (1). The first steps probably are the substitution of btmsa and the insertion of titanocene into the Sb–Sb bond of the distibane with intermediate formation of $[Cp_2Ti(SbR_2)_2]$. In the final step **1** and **2** are obtained by reaction with a second titanocene moiety. **1** is the only isolated product although the 1:1 M ratio of Me_4Sb_2 and $[Cp_2Ti(btmsa)]$ was applied. **1** and **2** can be viewed as being composed of Cp_2Ti^+ and R_2Sb^- and therefore the reaction (1) is a redox process with oxidation of Ti(II) to Ti(III) and reduction of Sb (II) to Sb(I).

$$2[Cp_2Ti(btmsa)] + R_2SbSbR_2 \rightarrow \underset{\substack{\mathbf{1},\mathbf{2}\\ \mathbf{1}:\,R\,=\,Me\\ \mathbf{2}:\,R\,=\,Me_3Si\\ btmsa\,=\,Me_3SiC{\equiv}CSiMe_3}}{[Cp_2TiSbR_2]_2} + 2\ btmsa \qquad (1)$$

The analogous ethyl derivative $[Cp_2TiSbEt_2]_2$ was obtained in a similar way [2]. Also in presence of excess tetramethyldistibane we found no evidence for $[Cp_2Ti(SbMe_2)_2]$, a complex that might be formed not only initially by the insertion reaction of titanocene with tetramethyldistibane but also by addition of the distibane to **1**.

Related to compound **2** is the monomeric phosphorus complex $[Cp_2TiP(SiMe_3)_2]$ that was formed from $[Cp_2TiCl]_2$ and $LiP(SiMe_3)_2$ [15]. It is remarkable that **2** is a dimer in the solid state whereas the analogous phosphorus complex is monomeric. This difference however reflects the steric situation. As a consequence of the increase of the atomic radii from phosphorus (1.1 Å) to antimony

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doi:10.1016/j.jorganchem.2010.09.007

(1.4 Å) the protection by Me_3Si groups is sufficient to prevent the phosphorus monomer from dimerization but not a $[Cp_2TiSb(SiMe_3)_2]$ monomer.

The new complexes are orange (**1**) or red (**2**) air sensitive compounds. Their characterization is based mainly on single crystal X-ray crystallography. Meaningful NMR spectra were not observed and mass spectra showed only ions corresponding to decomposition products. Elemental analyses were not carried out because of the sensitivity of the samples. **2** was isolated as crystalline solid only in reduced quantities. Nevertheless, it is possible that in solution the amount of **2** could have been larger but the identification of the compounds was hindered by its magnetic properties. The molecular structures of **1** and **2** are shown in the Figs. 1 and 2.

The structures of **1** and **2** consist of R_2Sb units between two Cp_2Ti groups forming a planar $(SbTi)_2$ heterocycle. The Sb atoms adopt a distorted tetrahedral geometry with wider Ti–Sb–Ti angles (**1**: 105.32(5), **2**: 103.384(13)°) and smaller C(2)–Sb(1)–C(1) 93.8(6) or Si–Sb–Si (94.51(2)°) angles. Related structural parameters were reported for $[Cp_2TiSbR_2]_2$ (R = Et). The transannular Sb···Sb distances (**1**: 3.4991(11), **2**: 3.7145(4) Å) are shorter than the sum of the van-der-Waals radii of two antimony atoms [Σr.v.d.W (Sb, Sb) = 4.4 Å]. The Sb–Ti-bond lengths in **2** (2.999(4) Å) are larger than in **1** (2.8800(17), 2.8890(18) Å) or $[Cp_2TiSbEt_2]_2$ (molecule 1: 2.8797(11), 2.8917(11); molecule 2: 2.9046(11), 2.9105(11) Å).

The inspection of the ^1H NMR spectra during the synthesis of **1** revealed that the signals of the starting materials $[Cp_2Ti(btmsa)]$ [$\delta = 6.40$ (C_5H_5), 0.33 (CH_3)] and Me_4Sb_2 ($\delta = 0.82$) decreased in intensity during the reaction whereas the signal for non coordinated btmsa ($\delta = 0.14$) increased. However no new signals appeared in the spectra. Also when crystals of **1** or **2** were solved in C_6D_6 no characteristic NMR signals were observed. This absence of NMR signals is not surprising because also the analogous ethyl derivative was found NMR silent and DFT calculations on $[Cp_2TiSbR_2]_2$ (R = Et) had shown that indeed the paramagnetic state with two unpaired electrons at the Ti(III) centers with d^1 configuration is lower in energy than the diamagnetic state with coupled electrons [2]. It can be concluded that **1** and **2** are paramagnetic at room temperature as well.

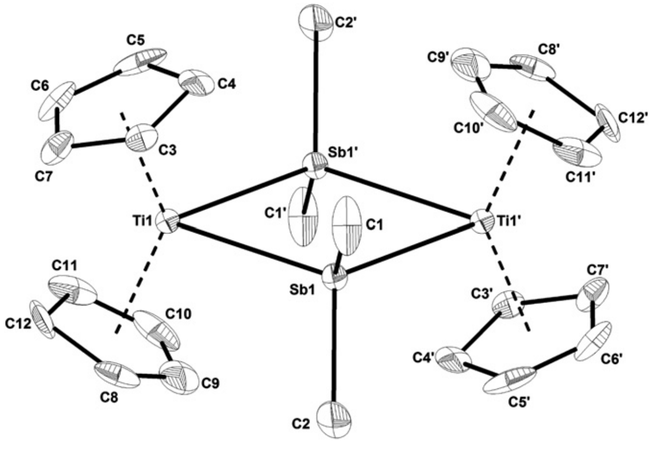

Fig. 1. Thermal ellipsoid (20%) representation of **1**. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and bond angles (°): Sb(1)–Ti(1) 2.881(2), Sb(1)–Ti(1′), 2.889(2), C(1)–Sb(1) 2.163(12), C(2)–Sb(1) 2.154(12), C(2)–Sb(1)–C(1) 94.3(7), Sb(1)–Ti(1)–Sb(1′), 74.66(5) Ti(1)–Sb(1)–Ti(1′) 105.34(5).

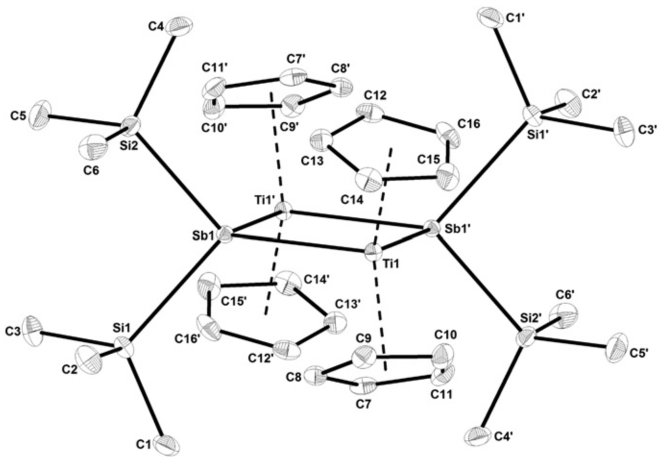

Fig. 2. Thermal ellipsoid (20%) representation of **2**. The hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ti(1)–Sb(1) 2.9994(4), Ti(1′)–Sb(1′) 2.9927(5), Si(1)–Sb(1) 2.5842(6), Si(2)–Sb(1) 2.5824(6), Sb(1)···Sb(1′) 3.7145(4), Ti(1)–Sb(1)–Ti(1′) 103.384(13), Si(1)–Sb(1)–Si(2) 94.51(2), Si(1)–Sb(1)–Ti(1) 114.779(16), Si(2)–Sb(1)–Ti(1) 114.870(16), Sb(1)–Ti(1)–Sb(1′) 76.616(13).

Mass spectra were measured from crystalline samples of **1** or **2** with the EI technique. The spectra showed no signals of the intact Sb–Ti complexes. Instead intense signals of the distibanes, (Me_4Sb_2, $m/z = 304$, M^+; $(Me_3Si)_4Sb_2$, $m/z = 534$, M^+) and of the molecular ion of Cp_2Ti ($m/z = 178$, 100%) were observed. The spectra contain also signals for Cp_nTi_6 ($n = 4$–8) clusters. These results indicate that **1** and **2** decompose under the conditions of mass spectrometry with the formation of the parent distibanes and titanocene monomers and oligomers.

In an attempt to synthesize analogues of **1** and **2** containing dimesitylantimony units we reacted $[Cp_2Ti(btmsa)]$ with Mes_2SbH (Mes = 2,4,6-$Me_3C_6H_2$) in benzene at ambient temperature. After working up the product mixture several crystals of $[(Cp_2TiCl)_2]\cdot 2(Mes_2Sb)_2$ (**3**) were obtained. The source of the chlorine atoms is probably ammonium chloride used during the preparation of Mes_2SbH. In related reactions $(Ph_2P)_2$ and $[(Cp_2TiCl)_2]$ were formed from $Cp_2Ti(btmsa)$ and Ph_2PCl [13]. The crystal structure of **3** was determined by single crystal X-ray diffraction. The structure is shown in Fig. 3.

Crystals of **3** contain the complex $[(Cp_2TiCl)_2]$ and tetramesityldistibane in the ratio 1: 2. The structures of the components of **3** were determined independently several years ago. The geometrical parameters of **3** and the pure compounds $[(Cp_2TiCl)_2]$ [15] and $(Mes_2Sb)_2$ [16,17] are similar. Future work will concentrate on obtaining the analogue of **1** and **2** containing dimesitylantimony unit by the reaction of pure Mes_2SbH with $[Cp_2Ti(btmsa)]$.

3. Conclusion

Reactions between $[Cp_2Ti(btmsa)]$ and substituted distibanes offer a feasible access to dimeric complexes between titanocene and diorganoantimony units. In contrast distibane formation is favoured in reactions between $Cp_2Ti(btmsa)$ and Mes_2SbH with NH_4Cl traces.

4. Experimental

Crystals suitable for X-ray diffraction of **1**–**3** were grown from concentrated benzene solutions in case of **2** and **3** or deuterated benzene solution in case of **1** Table 1. Data were collected at 173(2) K on a Siemens P4 diffractometer using a 0.71073 Å MoKα radiation and corrected for absorption effects using DIFABS [18]. The structures were solved by direct or Patterson methods [19]. Structure solutions and refinements were performed using WinGX software package [20]. The representations of the X-ray structures