

# Synthesis of $(p\text{-TolSb})_n$ by reaction of $\text{Cp}_2\text{Co}$ with $p\text{-TolSbCl}_2$ , crystal structure of $[\text{Cp}_2\text{Co}][p\text{-TolSbCl}_3]$ , and electroreduction of $p\text{-TolSbCl}_2$

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## Abstract

The reaction of  $\text{Cp}_2\text{Co}$  with  $p\text{-TolSbCl}_2$  in THF gives  $(p\text{-TolSb})_n$  and  $[\text{Cp}_2\text{Co}][p\text{-TolSbCl}_3]$ . <sup>1</sup>H NMR experiments show that this method is also useful for the syntheses of the rings  $(\text{ArSb})_n$  (Ar = Ph, *o*-Tol, *m*-Tol, *p*-Tol). The structure of  $[\text{Cp}_2\text{Co}][p\text{-TolSbCl}_3]$  has been determined by single crystal X-ray diffraction. It contains a centrosymmetric double chlorine-bridged dimeric anion. The two-electron reduction of  $p\text{-TolSbCl}_2$  gives  $(p\text{-TolSb})_n$ .

**Keywords:** Antimony; Cobalt; X-ray structural analysis; Electrochemistry; Cyclopentadienyl

## 1. Introduction

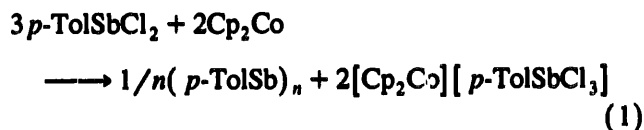
Phenyl- and tolylantimony rings have been synthesized by the reaction of  $\text{PhSbH}_2$  with styrene [1] or by slow air oxidation of arylbis(trimethylsilyl)stibines [2,3]. Both methods require starting materials that are not easy to prepare or handle. A simple attractive alternative would be the dehalogenation of arylantimony dihalides. Earlier attempts to synthesize  $(\text{RSb})_n$  (R = Ph, Tol) by reaction of  $\text{RSbX}_2$  (X = Cl, Br) with Mg [4], or alkali metals [5] gave black polymers of the type  $\text{X}(\text{RSb})_n\text{X}$  instead of rings. We report here the syntheses of *p*-tolyl and related aryl antimony rings by dehalogenation reactions with  $\text{Cp}_2\text{Co}$  and the electrochemical reduction of  $p\text{-TolSbCl}_2$ . For a preliminary communication of some of these results see Ref. [6]. Cobaltocene has been employed before for the syntheses of distibines [7].

## 2. Results and discussion

### 2.1. Reaction of $\text{RSbCl}_2$ (R = Tol, Ph) with $\text{Cp}_2\text{Co}$

The reaction of  $p\text{-TolSbCl}_2$  with cobaltocene in tetrahydrofuran (THF) in a 2:3 molar ratio gives a

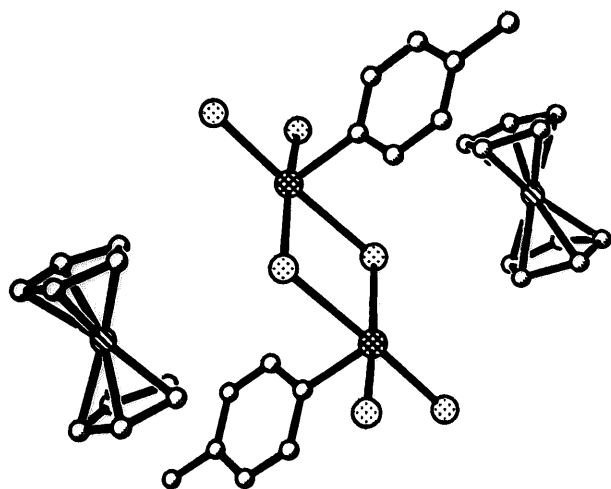
solution containing  $(p\text{-TolSb})_n$  and a yellow precipitate of  $[\text{Cp}_2\text{Co}][p\text{-TolSbCl}_3]$ .



$(p\text{-TolSb})_n$  is obtained in 47% yield as a yellow solid when the solution is stored for several days at  $-23^\circ\text{C}$ . The product was identified by comparison of the <sup>1</sup>H NMR spectra with a sample that had been synthesized and characterized according to the procedure described in the literature [3]. In solutions of  $(p\text{-TolSb})_n$  there is an equilibrium between pentamers and tetramers [3].

The salt  $[\text{Cp}_2\text{Co}][p\text{-TolSbCl}_3]$  has been characterized by various methods. The <sup>1</sup>H NMR spectra in DMSO show the expected ratio of intensities for the signals of the *p*-Tolyl protons and for the Cp groups. Mass spectra have been obtained with the fast atom bombardment (FAB) technique. They show signals for both the  $\text{Cp}_2\text{Co}$  cation and the  $p\text{-TolSbCl}_3$  anion. The composition is confirmed by the elemental analysis. The crystal structure consists of  $[\text{Cp}_2\text{Co}]^+$  cations and  $[p\text{-TolSbCl}_3]_2^{2-}$  anions. The packing of the ions is shown in Fig. 1. The structure of the anion is depicted in Fig. 2. Important distances and angles are listed in Table 1. Table 2 contains the atomic coordinates and the equiva-

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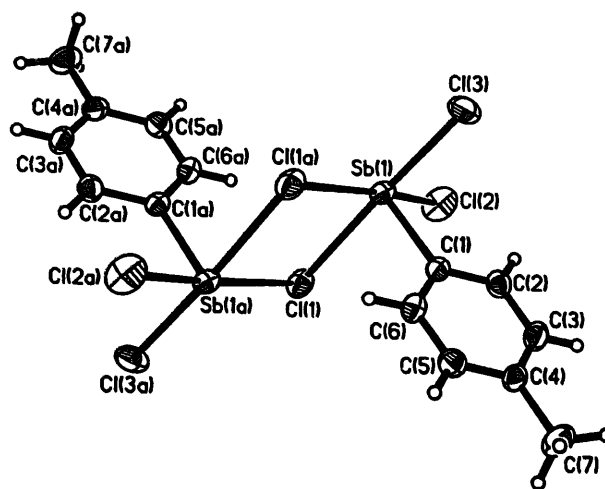
Fig. 1. Unit cell of  $[\text{Cp}_2\text{Co}][p\text{-TolSbCl}_3]$ .

lent isotropic displacement coefficients. The anions consist of  $p\text{-TolSbCl}_2$  units bridged by two chloride ions. The Sb–Cl bond lengths lie between 245 and 300 pm. They are longer than the sum of covalent radii ( $\Sigma r_{\text{cov. Sb,Cl}} = 242$  pm [8]) but shorter than van der Waals contact distances ( $\Sigma r_{\text{v.d.w. Sb,Cl}} = 390\text{--}410$  pm [8]). The geometry around the Sb atoms is distorted tetragonal pyramidal with the tolyl groups in apical positions trans to the  $\text{Sb}_2\text{Cl}_6$  planes. When the lone pairs of electrons are taken into account the coordination of the antimony atoms may be described as pseudo octahedral. The structure is similar to the various salts containing anions of the type  $(\text{RSbCl}_3)_2^{2-}$  [9–11].

The reaction between  $\text{Cp}_2\text{Co}$  and arylantimony dichlorides is a general method for the syntheses of aryl antimony rings. Experiments in NMR tubes in  $\text{C}_6\text{D}_6$  were carried out by adding excess  $\text{Cp}_2\text{Co}$  to solutions of  $\text{PhSbCl}_2$ ,  $o\text{-TolSbCl}_2$  or  $m\text{-TolSbCl}_2$  at room temperature in the absence of light. The reactions were completed by exposing the sealed tubes to ultrasound for 15 min. In the  $^1\text{H}$  NMR spectra of the solutions the characteristic signals of  $(\text{PhSb})_n$ ,  $(o\text{-TolSb})_n$  or  $(m\text{-TolSb})_n$  [3] appeared after the reactions.

## 2.2. Electroreduction of $p\text{-TolSbCl}_2$

In THF, with 0.2 M  $[\text{Bu}_4\text{N}][\text{PF}_6]$  as supporting electrolyte,  $p\text{-TolSbCl}_2$  exhibits a reduction wave at  $-1.7$

Fig. 2. The structure of the anions  $[p\text{-TolSbCl}_3]_2^{2-}$ .

V vs. saturated calomel electrode (SCE) in polarography. The electrolysis of  $p\text{-TolSbCl}_2$  at a mercury cathode consumes 2 equivalents of electrons and a red solution is formed, which exhibits a wave at  $-0.4$  V in polarography. This wave corresponds to the oxidation of intermediates of the type  $\text{Cl}(\text{RSb})_n\text{Cl}$  ( $\text{R} = p\text{-Tol}$ ). A similar behaviour has been observed in the case of the electroreduction of  $\text{RSbX}_2$  ( $\text{R} = \text{Et, Pr, }^n\text{Bu, }^t\text{Bu; X} = \text{Cl, Br}$ ) [12,13]. After concentration of this red solution a reduction wave appears at  $-2.15$  V which indicates the formation of  $(p\text{-TolSb})_n$ . The cyclovoltammogram of  $(p\text{-TolSb})_n$  is shown in Fig. 3. When the potential is reversed after peak  $\text{B}_2$  three oxidation peaks  $\text{H}'_1$ ,  $\text{H}'_2$ , and  $\text{H}'_3$  were observed. The cyclovoltammogram of  $(p\text{-TolSb})_n$  is analogous to that of  $(\text{RSb})_n$  ( $\text{R} = \text{Et, Pr, }^n\text{Bu, }^t\text{Bu; X} = \text{Cl, Br}$ ) [12,13]. Attempts to isolate  $(p\text{-TolSb})_n$  in a pure state from the electrolyzed solutions of  $p\text{-TolSbCl}_2$  were not successful.

## 3. Experimental

All the experiments were done in an argon atmosphere, using dried solvents distilled under argon. The  $^1\text{H}$  NMR spectra were recorded in  $\text{C}_6\text{D}_6$  on a Bruker WH 360 instrument operating at 360 MHz. The mass spectra were recorded on a Finnigan MAT 8222 instrument. The elemental analysis was performed by Mikroanalytisches Laboratorium Beller in Göttingen.

Table 1  
Bond distances (pm) and angles (deg) in  $[\text{Cp}_2\text{Co}][p\text{-TolSbCl}_3]$

Sb(1)–C(1)	215.5(3)	Sb(1)–Cl(2)	245.06(9)
Sb(1)–C(3)	254.05(9)	Sb(1)–Cl(1)	277.12(9)
Sb(1)–Cl(1a)	300.4	Cp(1)–Co(1)	163.2
Cp(2)–Co(1)	163.2		
C(1)–Sb(1)–Cl(2)	92.06(8)	C(1)–Sb(1)–Cl(3)	88.25(7)
Cl(2)–Sb(1)–Cl(3)	93.17(4)	C(1)–Sb(1)–Cl(1)	87.27(7)
Cl(2)–Sb(1)–Cl(1)	89.96(4)	Cl(3)–Sb(1)–Cl(1)	174.62(3)
Cl(2)–Sb(1)–Cl(1a)	174.0	Cp(1)–Co(1)–Cp(2)	178.2

Voltammetric analyses were carried out in a standard three-electrode cell with a Tacussel UAP4 unit. The reference electrode was an SCE separated from the solution by a sintered glass disk. The auxiliary electrode was a platinum disk electrode. For polarograms, a three-electrode Tacussel Tipol polarograph was used. Controlled potential electrolysis was performed with an Amel 552 potentiostat coupled to an Amel 721 electronic integrator. Electrolysis was performed in a cell with three compartments separated by fritted glass of medium porosity. A mercury pool was used as the cathode, a platinum plate as the anode, and an SCE as the reference electrode.

### 3.1. Preparation of *p*-tolylantimony and bis(cyclopentadienyl)cobalt trichloro(*p*-tolyl)antimonate

A solution of 0.3 g (1.6 mmol) of  $\text{Cp}_2\text{Co}$  in 20 ml of THF was added dropwise in the dark to a solution of 0.68 g (2.4 mmol) of  $p\text{-TolSbCl}_2$  in 20 ml of THF. Stirring the mixture for 0.5 h resulted in the formation of a red solution and a yellow solid. Recrystallization of the solid from a 1:1 water-ethanol mixture at  $-23^\circ\text{C}$  gave 0.4 g (50%) of  $[\text{Cp}_2\text{Co}][p\text{-TolSbCl}_2]$  as light yellow crystals suitable for X-ray investigations (m.p.  $195^\circ\text{C}$ ).  $^1\text{H NMR}$  ( $\text{DMSO-d}_6$ ):  $\delta$  2.30 (s, 3H,  $\text{CH}_3$ ), 5.35 (s, 10H, Cp), 7.29–7.31, 7.99–8.10 (m, 4H,  $\text{C}_6\text{H}_4$ ) ppm. MS (FAB)  $m/z$  (%) 189 (100)  $\text{Cp}_2\text{Co}$ , 317 (22)  $\text{TolSbCl}_3^-$ . Anal. Found: C, 39.43; H, 3.62.  $\text{C}_{17}\text{H}_{17}\text{Cl}_3\text{CoSb}$ . Calc. C, 40.15; H, 3.34. The solution

Table 2

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{pm}^2 \times 10^{-1}$ )

	x	y	z	$U(\text{eq})^a$
Sb(1)	3915(1)	1499(1)	4648(1)	26(1)
Cl(1)	5733(1)	104(1)	3899(1)	38(1)
Cl(2)	3728(1)	2653(1)	3370(1)	49(1)
Cl(3)	2418(1)	2797(1)	5449(1)	41(1)
C(1)	5666(3)	2421(2)	5162(2)	23(1)
C(2)	5886(3)	3518(2)	4904(2)	30(1)
C(3)	7020(3)	4111(2)	5216(2)	33(1)
C(4)	7963(3)	3644(2)	5809(2)	30(1)
C(5)	7741(3)	2563(2)	6073(2)	30(1)
C(6)	6613(3)	1956(2)	5759(2)	28(1)
C(7)	9207(3)	4290(3)	6151(2)	48(1)
Co(1)	9412(1)	1357(1)	2991(1)	24(1)
C(10)	8808(4)	-35(3)	2341(2)	48(1)
C(11)	9169(4)	-298(3)	3192(2)	43(1)
C(12)	10542(4)	14(3)	3372(3)	48(1)
C(13)	11033(4)	474(3)	2635(3)	54(1)
C(14)	9978(5)	446(3)	2003(2)	56(1)
C(20)	8307(4)	2217(3)	3800(2)	48(1)
C(21)	9668(4)	2584(3)	3854(3)	55(1)
C(22)	9959(4)	2973(3)	3052(3)	60(1)
C(23)	8783(5)	2848(3)	2518(3)	59(1)
C(24)	7780(4)	2376(3)	2991(3)	52(1)

<sup>a</sup> Equivalent isotropic  $U(\text{eq})$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

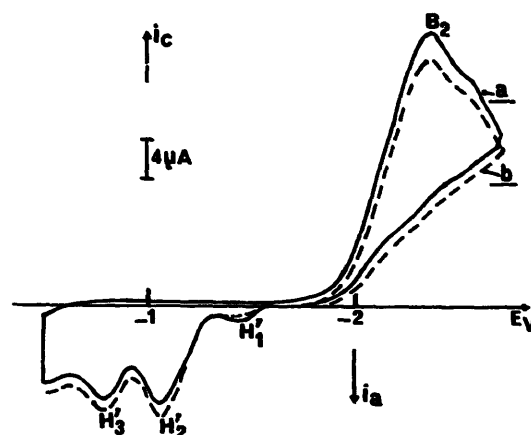


Fig. 3. Cyclic voltammogram of  $(p\text{-TolSb})_n$  in THF on platinum electrode, starting potential  $-0.5\text{ V}$ , sweep rate  $0.2\text{ V s}^{-1}$ .

was separated by decantation and cooled to  $-23^\circ\text{C}$ . After 3 days at this temperature 0.08 g (47%) of  $(p\text{-TolSb})_n$  had formed as a yellow solid (m.p.  $172^\circ\text{C}$ ).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  2.03 (s, 6H,  $\text{CH}_3$ ), 2.06 (s, 6H,  $\text{CH}_3$ ), 2.08 (s, 3H,  $\text{CH}_3$ ), 6.80–6.85, 6.88–6.91, 6.92–6.93 (AA'XX' spin systems, 20H,  $\text{C}_6\text{H}_4$ ) ( $p\text{-TolSb}$ )<sub>5</sub>; 2.07 (s, 3H,  $\text{CH}_3$ ), 6.90–6.95, 7.75–7.79 (m, 4H,  $\text{C}_6\text{H}_4$ ) ( $p\text{-TolSb}$ )<sub>4</sub> ppm. Ref. [3] identical data.

### 3.2. Formation of $(\text{RSb})_n$ ( $R = \text{Ph}, o\text{-Tol}, m\text{-Tol}$ )

Samples of 10 mg (0.05 mmol) of  $\text{Cp}_2\text{Co}$  were added to solutions of 0.09 mmol of  $\text{RSbCl}_2$  ( $R = \text{Ph}$ , 24 mg;  $R = o\text{-Tol}, m\text{-Tol}$ , 26 mg) in 1.5 ml  $\text{C}_6\text{D}_6$  in NMR tubes. The tubes were exposed to ultrasound for 15 min and sealed under argon.  $(\text{PhSb})_n$ :  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ),  $\delta$  6.8–7.2 (m, 15H), 7.4–7.5 (m, 4H), 7.85–7.90 (2H), 7.91–7.95 (4H) ( $\text{PhSb}$ )<sub>5</sub>; 6.7–7.1, 7.73–7.77 (m) ( $\text{PhSb}$ )<sub>4</sub> ppm. ( $o\text{-TolSb}$ )<sub>n</sub>:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ),  $\delta$  2.03 (s, 6H,  $\text{CH}_3$ ), 2.10 (s, 3H,  $\text{CH}_3$ ), 2.29 (s, 6H,  $\text{CH}_3$ ), 6.8–7.1, 7.8–8.0, 8.5–8.6 (m, 20H,  $\text{C}_6\text{H}_4$ ), ( $o\text{-TolSb}$ )<sub>5</sub>; 2.12 (s, 3H,  $\text{CH}_3$ ), 8.2–8.4 (m, 4H,  $\text{C}_6\text{H}_4$ ) ( $o\text{-TolSb}$ )<sub>4</sub>. ( $m\text{-TolSb}$ )<sub>n</sub>:  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ),  $\delta$  1.97 (s, 6H,  $\text{CH}_3$ ), 2.01 (s, 6H,  $\text{CH}_3$ ), 2.07 (s, 3H,  $\text{CH}_3$ ), 6.8–7.1, 7.2–8.0 (m, 20 H,  $\text{C}_6\text{H}_4$ ) ( $m\text{-TolSb}$ )<sub>5</sub>; 2.03 (s, 3H,  $\text{CH}_3$ ), 6.8–8.0 (m, 4H,  $\text{C}_6\text{H}_4$ ) ( $m\text{-TolSb}$ )<sub>4</sub>. Ref. [3] identical data.

### 3.3. Crystal structure determination

#### 3.3.1. Crystal data

$\text{C}_{17}\text{H}_{17}\text{Cl}_3\text{CoSb}$ ,  $M$  508.34, monoclinic,  $a = 980.7(2)\text{ pm}$ ,  $b = 1198.7(2)\text{ pm}$ ,  $c = 1586.4(3)\text{ pm}$ ,  $\beta = 93.98(3)^\circ$ ,  $V = 1.8604(6)\text{ nm}^3$ ,  $Z = 4$ ,  $D_c = 1.8604(6)\text{ nm}^3$ ,  $\mu = 2.767\text{ mm}^{-1}$ ,  $F(000) = 992$ , space group  $P2_1/n$ , crystal size  $0.60 \times 0.60 \times 0.50\text{ nm}^3$ .

#### 3.3.2. Structure determination

Data were collected on a Siemens P4 four-circle diffractometer at  $173(2)\text{ K}$  with  $\text{Mo K}\alpha$  radiation,

$\lambda = 71.073$  pm for 5045 reflections in the  $2\theta-\omega$  mode, of which 4271 were independent reflections ( $R_{\text{int.}} = 3.76\%$ ) and 4271 were used in the full matrix least squares refinement with the SHELXL-93 [14] program system. The structure was solved by direct methods for antimony and the difference Fourier synthesis revealed the positions for the other non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were calculated as a riding model with isotropic  $U$  thermal parameters. The final  $R$  values are  $R_1 = 2.95\%$  and  $wR_2 = 7.10\%$  ( $R_1 = 3.68\%$  and  $wR_2 = 7.60\%$  for all data), goodness-of-fit 0.955. Refined values of the atomic coordinates are given in Table 2. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposit number CSD-404143, the names of the authors and the journal citation.

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