ELSEVIER

Journal of Organometallic Chemistry 483 (1994) 167–172

Journal of Organometallic Chemistry

Redox behaviour and reactions of $(PhCH_2)_3Sb$; syntheses and structures of $[(PhCH_2)_3SbMe]I$ and $[(PhCH_2)_3SbMe]_3Sb_3I_{12}$

H.J. Breunig [a,*], K.H. Ebert [a], R. Kaller [a], Y. Mourad [b], A. Atmani [b], Y. Mugnier [c]

[a] *Universität Bremen, Fachbereich 2, Postfach 330440, D-28334 Bremen, Germany*
[b] *Departement de Chimie, Faculté des Sciences, BP 1796 Atlas-Fes, Morocco*
[c] *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (URA 33), Faculté des Sciences, 6 bd Gabriel, 21000 Dijon, France*

Received 21 February 1994; in revised form 3 April 1994

Abstract

$(PhCH_2)_3Sb$ (1) reacts with MeI to form $[(PhCH_2)_3SbMe]I$ (2). The action of excess I_2 on 2 gives $[(PhCH_2)_3SbMe]_3Sb_3I_{12}$ (3). 3 is synthesized in 78% yield by addition of SbI_3 to 2. The crystal structures of 2 and 3 are reported. The cations of 2 have a distorted tetrahedral coordination at Sb with Sb–C bond distances of 210.5(20)–215.7(20) pm and SbC_2 angles between 103.1° and 121.7°. Sb ⋯ I contacts of 373.3 pm increase the coordination at Sb to distorted trigonal bipyramids with Me and I in the axial positions. The crystals of 3 contain distorted tetrahedral $[(PhCH_2)_3SbMe]^+$ cations and $(Sb_3I_{12})^{3-}$ anions with the approximate structure of two SbI_3 molecules (mean Sb–I bond distances 283.2 pm) capping opposite planes of a SbI_6^{3-} octahedron (mean Sb–I distance 302.4 pm). In addition to the preparative results the electrochemical properties of 1 are communicated and discussed.

Keywords: Antimony; Alkyl complexes; X-ray structural analysis

1. Introduction

Recently we found that Me_4SbI and I_2 react with formation of golden semiconducting crystals of $(Me_4Sb)_3I_8$ [1]. In this compound linear polyiodide chains are stabilized by weak Sb ⋯ I interactions. In this context we became interested in anion cation interactions in less symmetrical and better shielded stibonium iodides and related compounds and chose tribenzylmethylstibonium iodides as our synthetic aim. We report here on the oxidative addition of MeI to $(PhCH_2)_3Sb$ (1) with formation of $[(PhCH_2)_3SbMe]I$ (2) and on the reaction of 2 with I_2 or SbI_3 to form $[(PhCH_2)_3SbMe]_3Sb_3I_{12}$ (3). The crystal structures of 2 and 3 are reported. The preparative results prompted an investigation of the redox behaviour of 1. This work continues our study of the electrochemistry of tertstibines [2] and other organoantimony compounds [3].

2. Results and discussion

2.1. Syntheses and structures of $[(PhCH_2)_3SbMe]I$ (2) and $[(PhCH_2)_3SbMe]_3Sb_3I_{12}$ (3)

Tribenzylstibine (1) reacts with excess MeI according to Eq. (1) with formation of tribenzylmethylstiboniumiodide (2). Air stable colourless crystals of 2 suitable for X ray diffractommetry were obtained in 30% yield by recrystallization from ethanol.

$$\underset{1}{(PhCH_2)_3Sb} + MeI \longrightarrow \underset{2}{[(PhCH_2)_3SbMe]I} \qquad (1)$$

The reaction of 2 with I_2 was carried out in a 2:3 molar ratio in refluxing ethanol. Instead of the expected addition of I_2 to 2 with formation of polyiodides a partial fission of Sb-C bonds occurred and red crystals of $[(PhCH_2)_3SbMe]_3Sb_3I_{12}$ (3) were formed in low yield after recrystallization of the orange initial

0022-328X/94/$07.00
SSDI 0022-328X(94)24700-S

Table 1
Crystallographic data for 2 and 3

	2	3
empirical formula	$C_{22}H_{24}ISb$	$C_{22}H_{24}I_4Sb_2$
formula weight (g/mol)	537.1	1039.1
crystal colour and shape	colourless needles	red plates
crystal size (mm)	0.4 × 0.1 × 0.1	0.8 × 0.4 × 0.1
crystal system	monoclinic	orthorhombic
space group	$P2_1/n$	$Pccn$
unit cell dimension	$a = 1032.3(4)$ pm $b = 941.1(3)$ pm $c = 2214.3(6)$ pm $\beta = 100.27(2)°$	$a = 1531.7(5)$ pm $b = 2291.2(9)$ pm $c = 2443.0(8)$ pm
volume	$2166.8(13)\ 10^6\ \mathrm{pm}^3$	$8573(5)\ 10^6\ \mathrm{pm}^3$
Z	4	12
density (calc.)	$1.685\ \mathrm{g\ cm^{-3}}$	$2.414\ \mathrm{g\ cm^{-3}}$
absorption coefficient	$2.762\ \mathrm{mm^{-1}}$	$6.374\ \mathrm{mm^{-1}}$
$F(000)$	1040	5580
R	7.64%	5.82%
$R = \Sigma \|\|F_o\| - \|F_c\|\| / \Sigma \|F_o\|$		
R_w	8.25%	5.57%
$R_w = (\Sigma_w \|F_o\| - \|F_c\|)^2/\Sigma_w F_o^2)^{1/2}$		
weighting scheme	$w = (\sigma^2(F) + 0.0015F^2)^{-1}$	$w = (\sigma^2(F) + 0.0005F^2)^{-1}$
Max./Min. residual electron density 1.51/ − 1.51 eÅ^{-3}		

product from acetone. These crystals were used for X-ray crystal structure determination. A better way to synthesize 3 is however by the addition of SbI_3 to a solution of 2 in ethanol and acetone (Eq. 2). This method gives 3 as an orange solid in 78% yield.

$$\underset{2}{3[(PhCH_2)_3SbMe]I} + 3SbI_3 \longrightarrow \underset{3}{[(PhCH_2)_3SbMe]_3Sb_3I_{12}} \qquad (2)$$

The crystallographic data of 2 and 3 are summarized in Table 1. Table 2 contains the atomic coordinates and the equivalent isotropic displacement coefficients. Selected bond distances and angles are given in Table 3. Fig. 1 shows the structure of a pair of ions of 2. There are $(PhCH_2)_3SbMe^+$ cations where the Sb atoms are in the centres of distorted tetrahedra formed by the methyl and methylene carbon atoms. The phenyl groups are bent towards the methyl groups forming a basket like arrangement around this substituent. Two of the tetrahedral planes of the cations are capped by the I^- anions with Sb ··· I contact distances of 373.3 pm opposite to the CH_3 groups and 410.8 pm opposite to one of the CH_2 groups. The former distance is substantially smaller than the sum of van der Waals radii of Sb and I that is estimated as 420–430 pm. As each iodide occupies the capping positions of two tetrahedral cations the contacts between the ions lead to a 2:2 coordination and a chain of the type $(\cdots Sb(PhCH_2)_3Me \cdots I \cdots)_x$ in a helical arrangement is formed. A comparison of 2 with the more symmetrical stibonium iodide Me_4SbI reveals major structural differences. The cations of Me_4SbI are perfect tetrahedra with each plane capped y by I^- in an Sb ··· I distance of 405.6 pm [4,5] and a 4:4 coordination of cations and anions. Bicapped tetrahedra and chains formed through anion cation contacts more closely related to 2 are however found in the structure of $(Me_4Sb)_2\ (MeSbI_4)$ [5].

The structure of 3 consists of $(PhCH_2)_3SbMe^+$ cations and $Sb_3I_{12}^{3-}$ anions. The unit cell is shown in Fig. 2. The Sb(4) cations occupy positions on twofold symmetry axes. In these cations the positions of the carbon atoms of the methyl and methylene groups cannot be distinguished. The structure of the Sb(3) cations is similar to that of the $(PhCH_2)_3SbMe^+$ ions

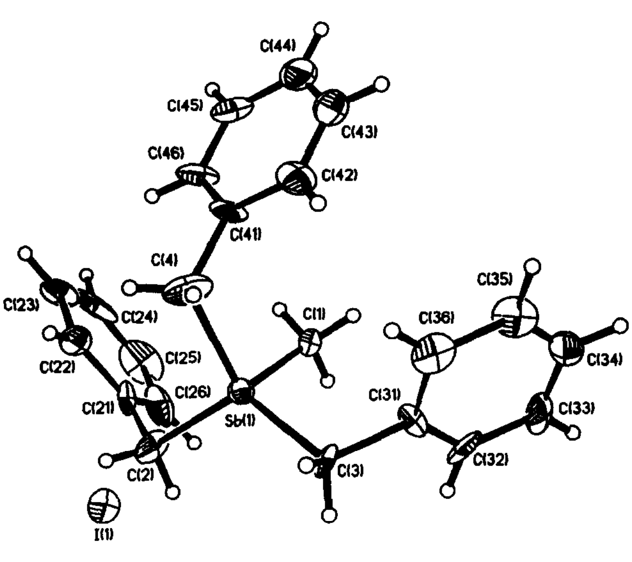

Fig. 1. Structure of 2.

Table 2

Atomic coordinates and equivalent isotropic displacement coefficients

	x	y	z	U_{eq} [a]
2				
I(1)	0.2512(1)	0.3839(1)	0.3340(1)	0.027(1)
Sb(1)	0.0890(1)	0.4865(1)	0.1757(1)	0.021(1)
C(1)	0.0031(19)	0.5570(18)	0.0874(10)	0.031(7)
C(2)	0.2934(18)	0.4774(20)	0.1712(10)	0.033(7)
C(21)	0.3138(16)	0.4125(17)	0.1151(8)	0.018(5)
C(22)	0.3082(19)	0.2665(20)	0.1066(10)	0.031(7)
C(23)	0.3186(19)	0.2045(25)	0.0486(10)	0.036(7)
C(24)	0.3328(19)	0.2935(34)	0.0017(11)	0.051(10)
C(25)	0.3445(24)	0.4423(33)	0.0097(10)	0.054(10)
C(26)	0.3309(18)	0.5003(26)	0.0657(11)	0.042(7)
C(3)	0.0161(19)	0.6289(17)	0.2383(10)	0.032(6)
C(31)	−0.1219(16)	0.6830(21)	0.2109(8)	0.023(6)
C(32)	−0.1318(22)	0.8101(18)	0.1834(10)	0.035(7)
C(33)	−0.2531(22)	0.8620(22)	0.1572(10)	0.039(8)
C(34)	−0.3681(22)	0.7807(27)	0.1602(11)	0.044(8)
C(35)	−0.3563(22)	0.6525(29)	0.1862(12)	0.052(10)
C(36)	−0.2802(21)	0.6004(23)	0.2123(10)	0.037(7)
C(4)	0.0177(21)	0.2724(21)	0.1813(10)	0.040(8)
C(41)	−0.0917(18)	0.2383(20)	0.1281(10)	0.032(7)
C(42)	−0.2227(19)	0.2613(21)	0.1360(10)	0.036(7)
C(43)	−0.3212(22)	0.2295(22)	0.0845(12)	0.047(9)
C(44)	−0.2923(25)	0.1711(22)	0.0307(13)	0.053(10)
C(45)	−0.1590(24)	0.1473(21)	0.0279(13)	0.047(9)
C(46)	−0.0606(19)	0.1782(22)	0.0764(10)	0.035(7)
Sb(1)	0.2500	0.2500	0.1059(1)	0.026(1)
I(1)	0.3873(1)	0.2512(1)	0.0212(1)	0.037(1)
I(2)	0.2655(1)	0.1187(1)	0.1115(1)	0.030(1)
I(3)	0.3965(1)	0.2587(1)	0.1933(1)	0.031(1)
3				
Sb(2)	0.4740(1)	0.1589(1)	0.1176(1)	0.029(1)
I(4)	0.5154(1)	0.0592(1)	0.0507(1)	0.045(1)
I(5)	0.6400(1)	0.2100(1)	0.1004(1)	0.048(1)
I(6)	0.5154(2)	0.0978(1)	0.2126(1)	0.066(1)
Sb(3)	0.7431(1)	0.5119(1)	0.0255(1)	0.037(1)
C(1)	0.6154(17)	0.5460(10)	0.0129(9)	0.061(10)
C(2)	0.7761(15)	0.4593(11)	−0.0444(7)	0.055(10)
C(21)	0.7055(17)	0.4152(10)	−0.0554(9)	0.042(9)
C(22)	0.7107(20)	0.3645(10)	−0.0307(8)	0.052(10)
C(23)	0.6367(32)	0.3270(16)	−0.0363(12)	0.098(20)
C(24)	0.5758(34)	0.3408(17)	−0.0665(15)	0.128(25)
C(25)	0.5650(18)	0.3919(17)	−0.0942(15)	0.100(16)
C(26)	0.6379(20)	0.4335(13)	−0.0900(10)	0.067(12)
C(3)	0.8224(18)	0.5840(11)	0.0513(8)	0.057(10)
C(31)	0.7916(17)	0.6041(12)	0.1057(8)	0.050(9)
C(32)	0.8308(18)	0.5793(12)	0.1519(10)	0.065(11)
C(33)	0.8014(28)	0.5996(16)	0.2045(10)	0.092(17)
C(34)	0.7444(31)	0.6382(19)	0.2124(18)	0.117(22)
C(35)	0.7041(21)	0.6643(13)	0.1642(15)	0.087(14)
C(36)	0.7312(18)	0.6441(12)	0.1137(11)	0.069(11)
C(4)	0.7368(16)	0.4522(10)	0.0926(7)	0.045(8)
C(41)	0.6431(15)	0.4472(8)	0.1134(7)	0.032(7)
C(42)	0.6076(16)	0.4856(11)	0.1519(7)	0.043(9)
C(43)	0.5223(19)	0.4774(12)	0.1716(8)	0.059(11)
C(44)	0.4725(16)	0.4301(11)	0.1527(10)	0.057(10)
C(45)	0.5075(16)	0.3930(10)	0.1151(8)	0.047(9)
C(46)	0.5912(17)	0.4002(9)	0.0966(8)	0.040(8)
Sb(4)	0.2500	0.7500	0.2448(1)	0.038(1)
C(5)	0.3388(17)	0.7031(12)	0.1923(11)	0.064(10)
C(51)	0.3853(28)	0.7406(17)	0.1557(15)	0.079(17)
C(52)	0.4802(23)	0.7474(17)	0.1680(13)	0.061(13)
C(53)	0.5462(42)	0.7864(22)	0.1401(14)	0.145(28)
C(54)	0.5089(27)	0.8220(18)	0.0984(15)	0.072(16)
C(55)	0.4206(35)	0.8189(19)	0.0830(19)	0.102(23)
C(56)	0.3572(28)	0.7815(18)	0.1141(18)	0.086(18)
C(6)	0.3226(23)	0.8148(12)	0.2885(9)	0.096(14)
C(61)	0.3310(13)	0.8678(7)	0.2509(6)	0.039(8)
C(62)	0.4049	0.8769	0.2186	0.066(15)
C(63)	0.4121	0.9275	0.1872	0.118(19)
C(64)	0.3456	0.9690	0.1881	0.085(19)
C(65)	0.2718	0.9600	0.2204	0.102(19)
C(66)	0.2645	0.9094	0.2519	0.119(21)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor (10^{-4} pm^2).

in **2**. The angles and distances in the anions support a description as SbI^{3-} octahedra capped on two opposite planes by SbI$_3$ molecules. A stereochemical influence of the lone pairs at Sb^{III} is not indicated by the geometric data of the central octahedron but may be discussed for the six coordinated antimony atoms in the capping positions. Recently a similar structure has been determined for the anion of [K(15-crown-5)$_2$]$_3$Sb$_3$I$_{12}$ [6]. The interactions between the anions and the cations in **3** are weaker than in **2**. Two iodine atoms of different anions are in capping positions above tetrahedral planes of the cations at Sb ··· I distances of 409 and 416 pm.

The results of this synthetic and structural work confirm the expectation that the number of Sb ··· I contacts between organostibonium ions and iodides decreases when methyl substituents are replaced by the sterically more demanding benzyl groups. For further studies on stibonium polyiodides however organic groups with stronger Sb–C bonds should be chosen.

2.2. Electrochemical behaviour of (PhCH$_2$)$_3$Sb (1)

In tetrahydrofuran (THF) in presence of 0.2 M Bu$_4$NPF$_6$ as supporting electrolyte the polarogram of **1** exhibits a well defined oxidation wave E′ ($E_{1/2} = 0.4$ V) and a reduction wave A ($E_{1/2} = -2.75$ V) (Fig. 3a). The height of wave E′ is smaller than that of wave A ($h_A/h_{E'} = 1.5$). The cyclic voltammogram for **1** suggests a reversible one electron transfer process (system E/E′, Fig. 4a) with peak current ratios, peak potential separations and dependance on scan rates typical for a diffusion controlled process (ΔEp = 80 mV at 100 mVs^{-1}, $ip_{E'}/ip_E = 1.13$). For the reduction, the corresponding peak A is obtained and during the reverse scan a peak A$'_1$ is observed at −1.5 V (Fig. 4b). At the time scale of electrolysis the coulometry data depend on the experimental conditions, in particular on the temperature. At 0°C the oxidation of **1** on a mercury pool electrode at the potential of wave E′ consumes a quantity of electricity near to 0.6 equivalents of elec-

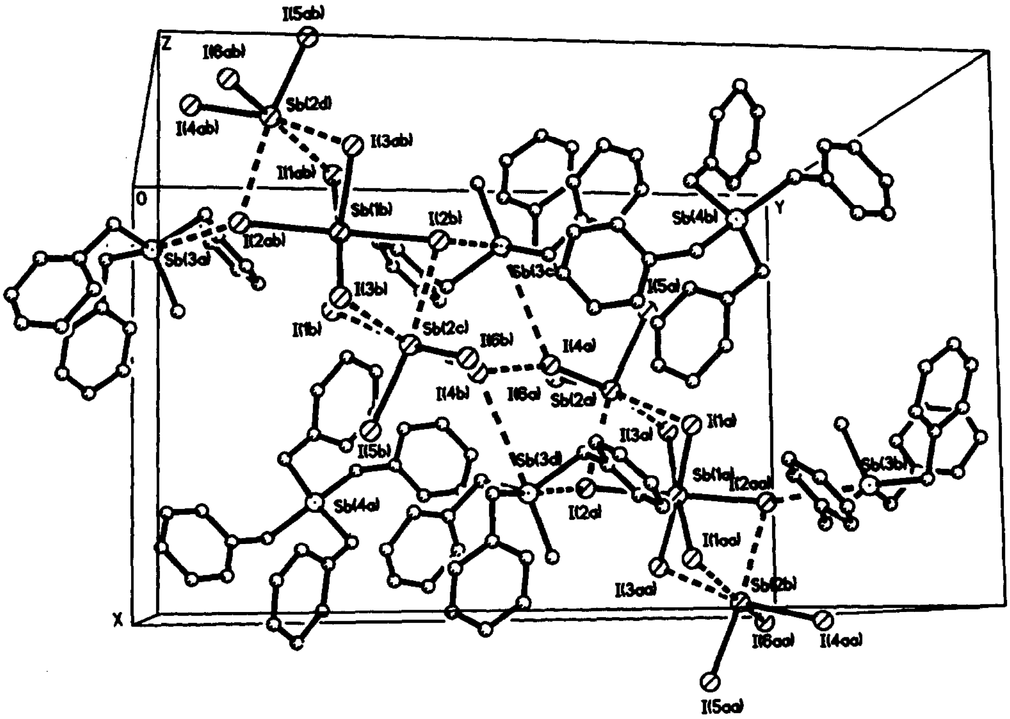

Fig. 2. Unit cell of **3**. For disorder at Sb(4) see text.

trons and a colourless solution was obtained. No signal was detected by ESR spectroscopy. The polarogram of this electrolyzed solution exhibits two reduction waves, E* and A*. The height of wave A* is nearly the same as that of the initial wave A (Fig. 3b). When the temperature of this solution increases from 0°C to 20°C, the reduction wave E* disappears and the oxidation wave E′ and two reduction waves E_1 and E_2 appear (Fig. 3c). The same reduction waves E_1, E_2 and A (see Fig. 3c) were obtained when the electrolysis of **1** was performed at room temperature with consumption of one equivalent of electron. No ESR signal was observed.

At the time scale of voltammetry the one electron oxidation of **1** yields the paramagnetic cation $(PhCH_2)_3Sb^+$ (**1a**) which is reducible at the potential of peak E. Radical cations of this type are very unstable [7]. As the oxidation process consumes less than one equivalent of electrons at 0°C we suggest that **1a** reacts with **1** to form a diamagnetic dicationic derivative **1b** formulated as $[(PhCH_2)_3Sb]_3^{2+}$. This assumption is based on the following results:

i The reduction of **1b** at the potential of wave E* (see Fig. 3b) gives **1** according to the reaction (3):

$$\underset{\mathbf{1b}}{[(PhCH_2)_3Sb]_3^{2+}} + 2e^- \longrightarrow \underset{\mathbf{1}}{3(PhCH_2)_3Sb} \qquad (3)$$

ii **1b** was formed by a 0.66 electron oxidation of **1** (experimental result: n = 0.6 e^-).

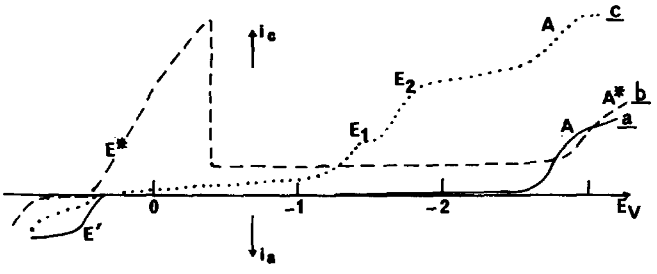

Fig. 3. Polarogram of **1** in THF, (a) before electrolysis, (b) after electrolysis at 0.5 V at 0°C (consumption of 0.6 Faraday mol^{-1}), (c) after evolution at RT.

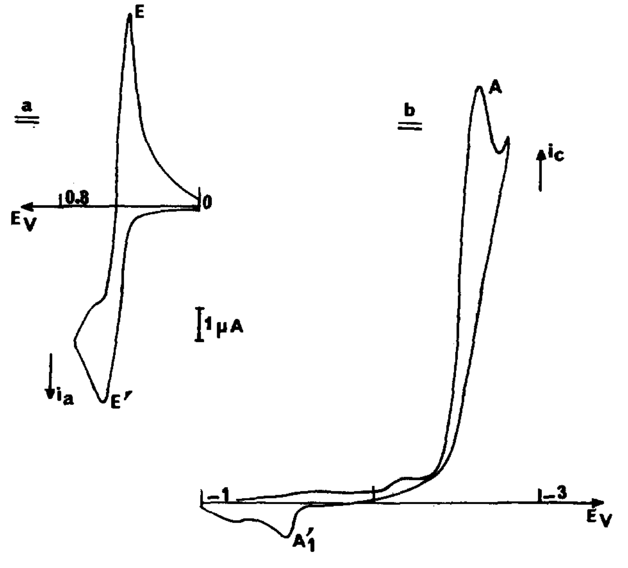

Fig. 4. Cyclic voltammogram of **1** in THF on hanging mercury electrode, sweep rate 0.05 V s^{-1}. (a) anodic scan, (b) cathodic scan. Starting potential: 0 V (a), −1 V (b).

Table 3
Selected distances and angles of **2** and **3**

distances [pm]		bond angles [°]	
2			
Sb(1)–C(1)	210.5(20)	C(2)–Sb(1)–C(1)	103.1(8)
Sb(1)–C(2)	213.1(20)	C(3)–Sb(1)–C(1)	105.3(7)
Sb(1)–C(3)	215.8(20)	C(3)–Sb(1)–C(2)	121.1(7)
Sb(1)–C(4)	215.7(20)	C(4)–Sb(1)–C(1)	104.9(7)
		C(4)–Sb(1)–C(2)	108.4(8)
		C(4)–Sb(1)–C(3)	112.4(8)
Sb(1)···I(1)	373.3	I(1)–Sb(1)–C(1)	176.4
Sb(1)···I(1e)	410.8	I(1)–Sb(1)–C(2)	75.6
		I(1)–Sb(1)–C(3)	72.9
		I(1)–Sb(1)–C(4)	78.7
3			
Sb(1)–I(1)	295.1(2)	I(2)–Sb(1)–I(1)	89.1(1)
Sb(1)–I(2)	302.0(2)	I(3)–Sb(1)–I(1)	88.1(1)
Sb(1)–I(3)	310.2(2)	I(3)–Sb(1)–I(2)	88.7(1)
Sb(1)–I(1a)	295.1(2)	I(1a)–Sb(1)–I(1)	90.9(1)
Sb(1)–I(2a)	302.0(2)	I(1a)–Sb(1)–I(3)	176.7(1)
Sb(1)–I(3a)	310.2(2)	I(2a)–Sb(1)–I(1)	94.5(1)
		I(2a)–Sb(1)–I(2)	174.9(1)
		I(2a)–Sb(1)–I(3)	87.8(1)
		I(3a)–Sb(1)–I(3)	93.1(1)
		I(2)–Sb(1)–I(1a)	94.5(1)
		I(1a)–Sb(1)–I(2a)	89.1(1)
		I(1)–Sb(1)–I(3a)	176.7(1)
		I(2)–Sb(1)–I(3a)	87.8(1)
		I(3a)–Sb(1)–I(3a)	88.1(1)
		I(2a)–Sb(1)–I(3a)	88.7(1)
Sb(2)–I(1)	343.3	I(5)–Sb(2)–I(4)	92.6(1)
Sb(2)–I(2)	332.7	I(6)–Sb(2)–I(4)	91.4(1)
Sb(2)–I(3)	317.1	I(6)–Sb(2)–I(5)	97.3(1)
Sb(2)–I(4)	288.0(2)	I(4)–Sb(2)–I(3)	170.2
Sb(2)–I(5)	283.2(2)	I(5)–Sb(2)–I(3)	97.2
Sb(2)–I(6)	278.3(2)	I(6)–Sb(2)–I(3)	87.8
		I(1)–Sb(2)–I(3)	79.1
		I(2)–Sb(2)–I(3)	82.3
		I(1)–Sb(2)–I(4)	100.6
		I(1)–Sb(2)–I(5)	89.4
		I(1)–Sb(2)–I(6)	165.9
		I(2)–Sb(2)–I(4)	88.1
		I(2)–Sb(2)–I(5)	165.9
		I(2)–Sb(2)–I(6)	96.7
		I(2)–Sb(2)–I(1)	76.6

Attempts to isolate **1b** failed. The compound is unstable at room temperature and reacts with (residual) water to regenerate **1** (yield 30% determined by polarography) and to form unknown species which are reduced at the potential of the waves E_1 and E_2. These species are also formed by one-electron oxidation of **1** at room temperature.

With this background it is interesting to compare the electrochemical behaviour of **1** with the electrooxidation of Ph_3P in acetonitrile [8–10] giving Ph_3P^+, that reacts with water to give Ph_3PO and Ph_3PH^+. A similar reactivity is ruled out here because of the following results.

(i) The regeneration of **1** indicates that no proton is obtained during the chemical process because we have verified by polarography that upon addition of H^+ (HPF_6) on **1** the oxidation wave E′ disappears immediately and an ill-defined wave at −1.18 V appears which can be attributed to the reduction of $(Ph_2CH_2)_3SbH^+$.

(ii) We have prepared $(Ph_2CH_2)_3SbO$ [11] by chemical oxidation (air) of **1** and characterized by mass spectroscopy. In polarography. $(Ph_2CH_2)_3SbO$ exhibits two reduction waves at −1.31 V and −1.94 V respectively, the height of the former wave being smaller than of the latter. The waves E_1 and E_2 appear when $(Ph_2CH_2)_3SbO$ is reacted with HPF_6. A preliminary study of the reaction of $(Ph_2CH_2)_3SbO$ with HPF_6 by spectroscopic techniques (NMR, MS) revealed however that it is rather complex and various products form.

3. Experimental part

Manipulations with the air sensitive compound **1** were carried out under Ar in dry oxygen free solvents. **1** was synthesized according to literature procedures [11] and was characterized by ^1H NMR spectroscopy (C_6D_6), 2.58 (s, 6H, CH_2) 6.84–6.87, 6.93–6.98 (m, 15H, C_6H_5) and mass spectroscopy (EI, 70 eV, 135°C . *m/z* (rel. int. %) 394 (2) M^+, 303 (27) $(PhCH_2)_2Sb^+$, 212 (11) $PhCH_2Sb^+$, 91 (100). The oxidation of **1** in the air was performed as described [11] giving $(PhCH_2)_3SbO$ (mass spectrum: EI, 70 eV, 200°C ; *m/z* (rel. int. %) 410 (1) M^+, 394 (1) $(PhCH_2)_3Sb$, 319 (4) $(PhCH_2)_2SbO$, 303 (20) $(PhCH_2)_2Sb^+$, 91 (100).

Experimental data of the crystal structure determination are given in Table 4. The following spectrometers were used: MS, CH 7A. Varian MAT, 8222 Finnigan MAT; NMR, Bruker WH 360, 360 MHz. The MS data refer to ^{121}Sb. Voltammetric analyses were carried out in a standard three elctrode cell with a Tacussel UAP4 unit. The reference electrode was a saturated calomel electrode separated from the solution by a

Table 4
Experimental data for the X ray structure determination of **2** and **3**

Diffractometer used: Siemens P_4; radiation Mo Kα (= 0.71073 Å), graphite monochromator, scan type 2 $\theta - \omega$;
3 reference reflections, solution and refinement, direct methods, (full matrix, least squares, Sb, I, and C anisotropic, H atoms: riding model, system used: Siemens SHELXTL PLUS (VMS) [12].
2: temperature 153 K, 2 θ range 5–53°, index ranges $-1 \leqslant h \leqslant 12$, $-1 \leqslant k \leqslant 11$, $-27 \leqslant l \leqslant 27$, reflections collected 6294, independent reflections 4373 ($R_{int.} = 0.0962$, observed reflections 2226 ($F > 4.0\ \sigma(F)$), absorption correction with program DIFABS [13]
3: temperature 173 K, 2 θ range 5–50°, index ranges $0 \leqslant h \leqslant 18$, $0 \leqslant k \leqslant 27$, $0 \leqslant l \leqslant 29$, reflections collected 8441, independent reflections 7597 ($R_{int.} = 0.0085$, observed reflections 3934 ($F > 4.0\ \sigma(F)$), absorption correction with program DIFABS [13]

sintered glass disk. The auxiliary electrode was a platinum disk electrode. For polarograms a three electrode Tacussel Tipol polarograph was used. The controlled potential electrolyses were performed with an Amel 552 potentiostat coupled to an Amel 721 electronic integrator. Electrolyses were performed in a cell with three compartments seperated with fritted glass of medium porosity. A mercury pool was used as the cathode, a platinum plate as the anode and a saturated calomel electrode as the reference electrode.

3.1. *Tribenzylmethylstiboniumiodide (2)*

An excess of 4.1 g (28.9 mmol) MeI was added to 1.31 g (3.3 mmol) of **1** and the mixture was heated for 2 h under reflux. After the elimination of the volatile components a colourless air stable solid was obtained. Recrystallization from ethanol gave 0.53 g (30%) of **2** as colourless crystals (melting point 138–140°C) suitable for X-ray diffractommetry. MS (FAB pos., matrix nitrobenzylalcohol, *m/z* (%) 409 (100) $(PhCH_2)_3SbMe^+$, 318 (4), 227 (31), 91 (98), ^{1}HNMR (360 MHz) δ (DMSO-d_6) 0.70 (s, 3H, Me), 3.68 (s, 6H, $-CH_2-$), 6.94–6.97 7.18–7.32 (m, 15H, C_6H_5). Found C 49.27, H. 4.52; C_{22} $H_{24}SbI$ calc. C, 49.20 H 4.50%.

3.2. *Tris(tribenzylmethylstibonium) dodecaiodotriantimonate (3)*

a) by reaction of **2** with I_2. 20 ml ethanol were added to 0.5 g (0.93 mmol **1** and 0.34 g (1.36 mmol) I_2 and the mixture was boiled under reflux for 30 min. A dark red solution formed. Cooling of the solution to 5°C gave **3** as an orange solid. Recrystallization from acetone gave 0.02 g (4%) of red crystals (m.p. 124–125°C) that were used for X-ray diffractommetry. MS (FAB pos., matrix nitrobenzylalcohol, *m/z* (%) 409 (100) $(PhCH_2)_3SbMe^+$, 318 (4), 227 (31), 91 (100), ^{1}HNMR (360 MHz) δ (DMSO-d_6) 0.70 (s, 3H, Me), 3.68 (s. 6H, $-CH_2-$), 6.94–6.98 7.19–7.31 (m, 15H, C_6H_5). Found C 25.65, H 2.42; $C_{56}H_{72}Sb_6I_{12}$ calc. C, 25.42 H 2.32%.

b) by reaction of **2** with SbI_3. To a solution of 0.42 g (0.78 mmol) of **2** in 5 ml ethanol and 5 ml acetone, 0.39 g (0.78 mmol) SbI_3 was added. An orange solid precipitated and was isolated by filtration and dried in the air. The yield was 0.63 g (78%) with a m.p. of 123–124°C. Found C 25.38 H 2.56; $C_{66}H_{72}I_{12}$ calc. C 25.42 H 2.32%.

Acknowledgement

We grateful acknowledge financial support from Electricité de France (Novelect Bourgogne and Club d'Electrochimie Organique) and the Fonds der Chemischen Industrie.

References

[1] U. Behrens, H.J. Breunig, M. Denker and K.H. Ebert, *Angew. Chem., 106* (1994) 1023; *Angew. Chem., Int. Ed. Engl. 33* (1994) 987.

[2] Y. Mourad, Y. Mugnier, H.J. Breunig and M. Ates, *J. Organomet. Chem., 398* (1990) 85.

[3] Y. Mourad, Y. Mugnier, H.J. Breunig and M. Ates, *J. Organomet. Chem., 406* (1991) 323.

[4] G. Burbach, S.Q. Dou, A. Weiss and B. Bunsenges, *Phys. Chem. 93* (1989) 1302.

[5] H.J. Breunig, K.H. Ebert, S. Gülec, M. Dräger, D.B. Sowerby, M.J. Begley and U. Behrens, *J. Organomet. Chem., 427* (1992) 39.

[6] B. Borgsen, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem., 596* (1991) 55.

[7] A.S. Romankhin, E.V. Nikitin, O.V. Parakin, Y.A. Ignatev, B.S. Mironov and Y.M. Kargin, *J. Gen. Chem., 56* (1986) 2298; *Zh. Obsh. Khim., 56* (1986) 2597.

[8] G. Schiavon, S. Zecchin, G. Cogoni and G. Bontempelli, *J. Electroanal. Chem., 48* (1973) 425.

[9] S. Gilberto, Z. Sandro and C. Gianni, *Electroanal. Chem., 48* (1973) 425.

[10] H. Ohmori, S. Nakai and M. Masui, *J. Chem. Soc., Perkin Trans., I* (1978) 1333.

[11] I.P. Tsukervanik and D. Smirnov, *Zh. Obshch. Khim., 7* (1937) 1527.

[12] Siemens SHELXTL PLUS. Release 4.0 for Siemens R3 Crystallographic Research Systems, Siemens Analytical X-ray Instruments, Madison, WI, 1989.

[13] N. Walker and B. Stuart, *Acta Crystallogr., A 39* (1983) 158.