Journal of Organometallic Chemistry, 476 (1994) 47–54

Structure and electroreduction of Sb^tBuCl_2. Reactivity and electrochemical behaviour of $(Sb^tBu)_4$

Y. Mourad and A. Atmani

Departement de Chimie, Faculté des Sciences, BP 1796 Atlas-Fes (Morocco)

Y. Mugnier

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (URA 1685), Faculté des Sciences, 6 bd Gabriel, 21000 Dijon (France)

H.J. Breunig and K.H. Ebert

Universität Bremen, Fachbereich 2, Postfach 330440, D-28359 Bremen (Germany)

(Received September 29, 1993)

Abstract

The structure of Sb^tBuCl_2 (**1**) has been determined by single-crystal X-ray diffractometry to be trigonal pyramidal. In the crystals of **1** the Sb^tBuCl_2 molecules associate via Sb ··· Cl contacts of 350.9 pm to form tetramers, where the Sb atoms and four of the Cl atoms occupy the edges of distorted tetragonal cells. These tetrameric units are linked in chains through Sb–Cl distances of 380 pm. The ^tBu groups and half of the Cl atoms are directed outside the $[(Sb–Cl)_4]_x$ framework.

Two-electron reduction of Sb^tBuCl_2 (**1**) in tetrahydrofuran gives $(Sb^tBu)_4$ (**2**). The electrochemical behaviour of **2** has been studied in tetrahydrofuran (THF) and in *N,N*-dimethylformamide (DMF) in the presence of $[Bu_4N][PF_6]$. In THF in cyclic voltammetry at −30°C after two-electron reduction a cleavage of an antimony–antimony bond occurs, initially yielding a dianionic species **3**. At room temperature on the time scale of electrolysis a mixture of anionic and neutral derivatives is obtained. The anionic species reacts slowly with the supporting electrolyte to give $(Sb^tBuBu)_2$. The electrochemical oxidation of **2** in DMF consumes six electrons per mole.

Chemical reactions of **2** with O_2, $(PhTe)_2$, or K occur mainly at the Sb–C bond.

Key words: Tin; X-ray structure; Electrochemistry

1. Introduction

After studies of the synthesis [1] and the chemistry [1–4] of Sb^tBuCl_2 **1** we became interested in the structural and electrochemical characterization of **1**. We wished to compare the product of electrochemical reduction with that of chemical dehalogenation of **1** with Mg in tetrahydrofuran (THF), which gives mainly $(Sb^tBu)_4$ **2** with $(Sb^tBu)_5$ as a byproduct [4]. The same products of electrochemical and chemical synthesis were observed in the case of the reduction of *n*-alkylantimony dibromides [5]. We report here an investigation of the crystal and molecular structure of **1** and a study of the electroreduction of **1** in THF. In addition we report the electrochemical behaviour of the reduction product $(Sb^tBu)_4$ **2** in THF and in DMF and the reactivity of **2** towards O_2, $(PhTe)_2$, and K.

2. Results

2.1. *Crystal structure of Sb^tBuCl_2 (1)*

Single crystals of **1** were obtained by crystallization from the melt. The crystal data are summarized in Table 1. Table 2 contains the atomic coordinates and the equivalent isotropic displacement coefficients. The bond distances and bond angles are given in Table 3.

Correspondence to: Dr. Y. Mourad, Dr. H.J. Breunig.

0022-328X/94/$7.00
SSDI 0022-328X(93)24351-5

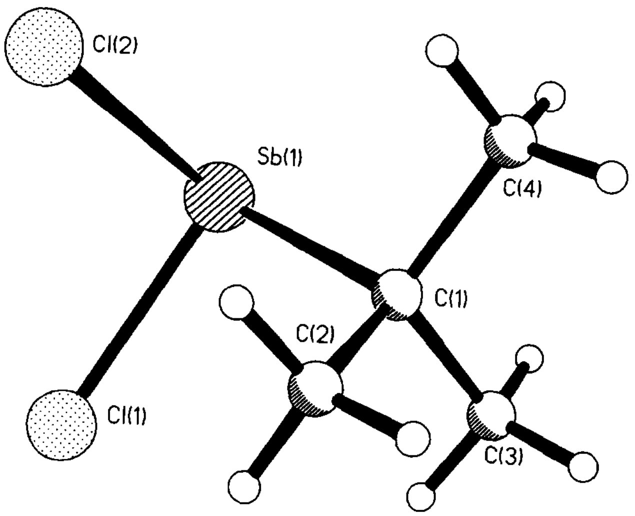


Fig. 1. Structure of the Sb^{t}BuCl$_2$ molecules.

In the crystal structure there are Sb^{t}BuCl$_2$ molecules (Fig. 1) with a trigonal pyramidal coordination at Sb. The bond angles around the antimony (*ca.* 95°) and the bond lengths, (Sb–C 219.0(3), Sb–Cl 237.4(1), and

TABLE 1. Crystal data of **1**

Empirical formula	$C_4H_9Cl_2Sb$
Colour, habit	Colourless needles
Crystal size (mm^3)	0.8×0.6×0.5
Crystal system	Tetragonal
Space group	$P\bar{4}$
Unit cell dimension (Å)	a = 11.386(2) c = 6.161(2)
Volume (Å^3)	798.7(4)
Z	4
Formula weight	249.8
Density (calc.)	2.077 g cm^{-3}
Absorption coefficient	4.020 mm^{-1}
F(000)	472

238.8(1) pm) compare well with the corresponding data from **2** and $SbCl_3$ [6]. The Sb^{t}BuCl$_2$ molecules are associated to give tetramers through secondary Sb ··· Cl bonds with distances of 350.9 pm. In the tetrameric units the Sb atoms and four of the Cl atoms occupy alternate edges of distorted tetragonal cells which are compacted via Sb–Cl distances of 382.1 pm to give a linear arrangement (Fig. 2). The ^{t}Bu groups

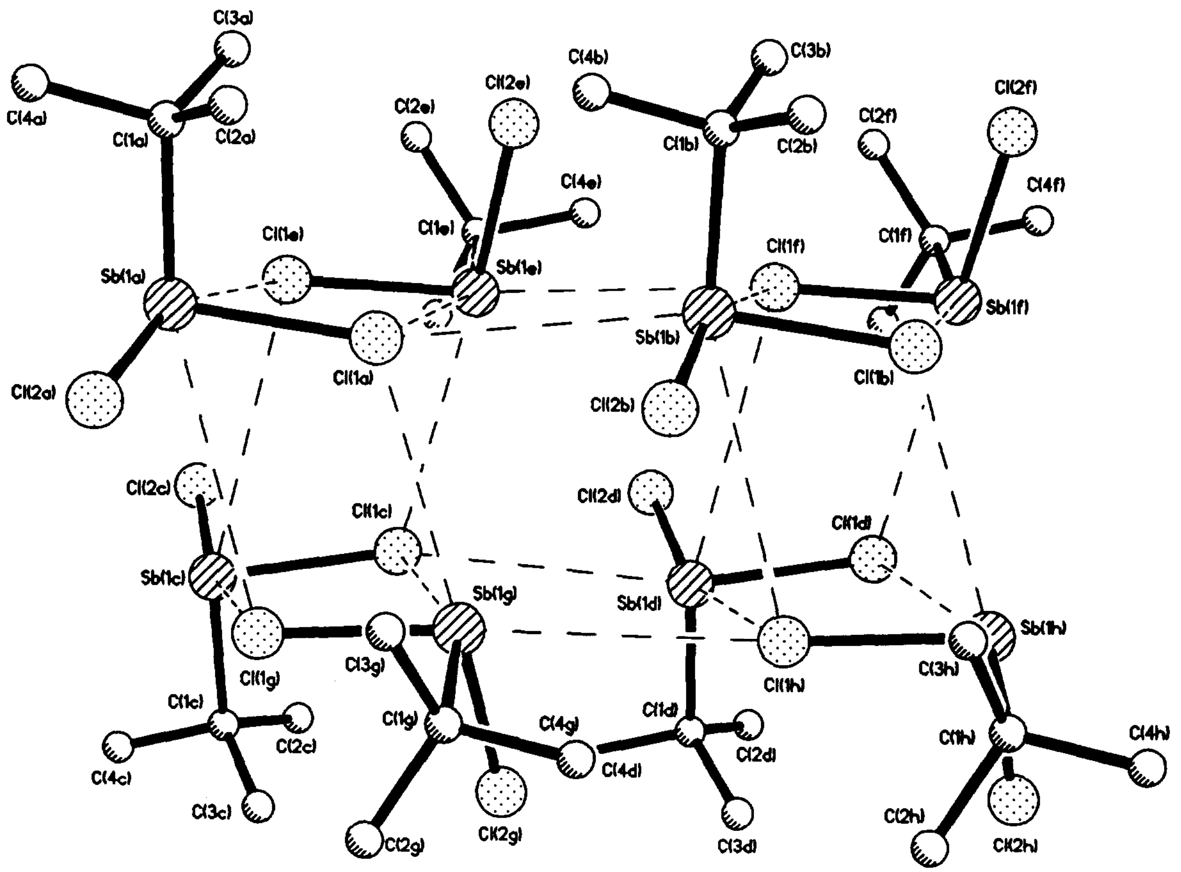


Fig. 2. Arrangement of the Sb^{t}BuCl$_2$ molecules in the crystal of **1**.

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

	x	y	z	U_{eq}
Sb(1)	6569(1)	6688(1)	7293(1)	23(1)
Cl(1)	6262(1)	6803(1)	11121(1)	34(1)
Cl(2)	5692(1)	8529(1)	6497(2)	34(1)
C(1)	8368(3)	7367(3)	7393(6)	21(1)
C(2)	8464(4)	8482(3)	8769(6)	28(1)
C(3)	9133(3)	6381(3)	8341(6)	29(1)
C(4)	8691(3)	7630(4)	5045(7)	28(1)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

and half of the Cl atoms are directed outside this linear framework. Estimates [7–9] give bond orders of 0.9 for the Sb–Cl distances of 238 pm and 0.1 for the 350.9 pm distance. The Sb–Cl distances of 382.1 pm or 399.2 correspond to van der Waals' contacts.

The packing of the Sb^tBuCl_2 molecules in the crystal is different from the arrangement of $SbMeCl_2$ [10] and $SbPhCl_2$ [9], which form polymers of the type $(RSbX_2)_x$.

2.2. *Electrochemical behaviour of 1 and 2*

2.2.1. *Electroreduction of 1 in THF*

The electrochemical behaviour of **1** is similar to that of $SbEtBr_2$, Sb^nPrBr_2 or Sb^nBuBr_2 [5]. An ill-defined reduction wave was observed in THF in the presence of 0.2 M $[Bu_4N][PF_6]$ as supporting electrolyte. After two-electron reduction of **1** at −1.5 V, a red solution which exhibits a polarographic oxidation wave A'_1 ($E_{1/2}$ = −0.5 V *vs.* SCE) was obtained. After evaporation of THF and extraction with toluene, yellow **2** was isolated and characterized by its ^1H-NMR spectrum, which shows a peak at $\delta = 1.56$ ppm [12]. The formation of other rings could not be proven.

TABLE 3. Geometric data for Sb^tBuCl_2 (**1**)

Bond lengths (pm)			
Sb(1)–Cl(1)	238.8(1)	Sb(1)–Cl(2)	237.4(1)
Sb(1)–C(1)	219.0(3)	C(1)–C(2)	153.0(5)
C(1)–C(3)	153.6(5)	C(1)–C(4)	152.3(6)
Bond angles (°)			
Cl(1)–Sb(1)–Cl(2)	95.4(1)	Cl(1)–Sb(1)–C(1)	95.1(1)
Cl(2)–Sb(1)–C(1)	95.0(1)	Sb(1)–C(1)–C(2)	112.1(2)
Sb(1)–C(1)–C(3)	106.5(2)	C(2)–C(1)–C(3)	110.8(3)
Sb(1)–C(1)–C(4)	105.6(2)	C(2)–C(1)–C(4)	110.3(3)
C(3)–C(1)–C(4)	111.5(3)		
Intermolecular distances (pm) [a]			
Sb(1a)–Cl(1e)	350.9		
Sb(1e)–Cl(1a)	399.2		
Sb(1e)–Cl(1c)	350.9		
Sb(1g)–Cl(1a)	350.9		
Sb(1g)–Cl(1c)	399.2		
Sb(1c)–Cl(1g)	350.9		
Sb(1c)–Cl(1e)	399.2		
Sb(1a)–Cl(1g)	399.2		
Sb(1e)–Cl(1f)	382.1		
Sb(1b)–Cl(1a)	382.1		
Sb(1d)–Cl(1c)	382.1		
Sb(1g)–Cl(1h)	382.1		

[a] Symmetry transformations:
Sb(1), Cl(1); e → a, c → e, a → g, g → c: 1–y, x, 2–z
Sb(1), Cl(1); a → e, c → g, e → c, g → a: y, 1–x, 2–z
Sb(1); f → e, a → b, c → d, h → g: y, x, 1+z
Cl(1); e → f, b → a, d → c, g → h: y, x, z–1.

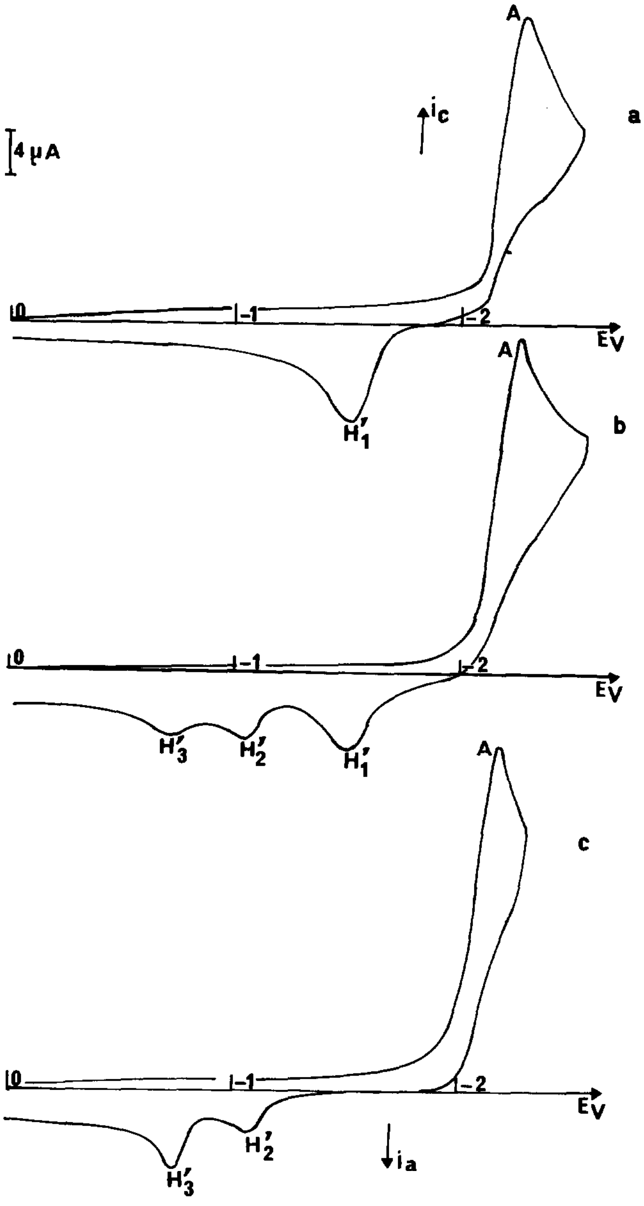


Fig. 3. Cyclic voltammogram of **2** in THF at a platinum electrode. Starting potential 0 V; sweep rate 0.2 V s^{-1} (●) (a) At −30°C; (b) at −15°C; (c) at room temperature. Potential range, 0 V– −2.3 V.

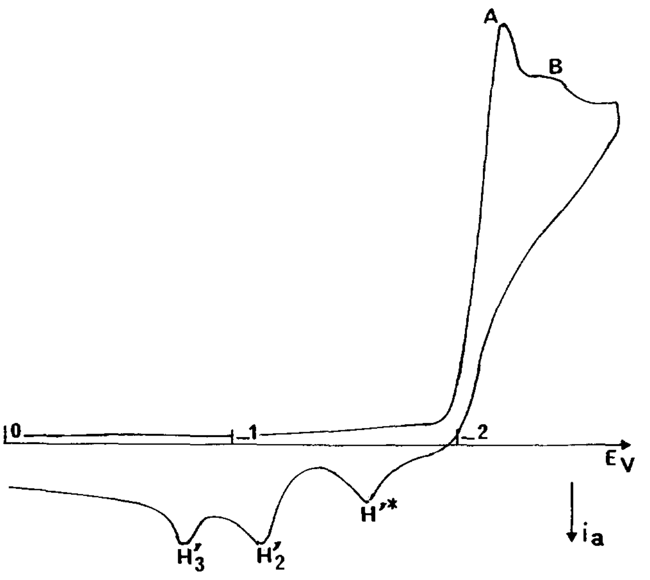


Fig. 4. Cyclic voltammogram of **2** in THF at a platinum electrode at room temperature. Starting potential 0 V; sweep rate 0.2 V s^{-1}; potential range: 0 V– −2.6 V.

2.2.2. *Electrochemical reduction of 2 in THF*

The cyclic voltammogram of **2** in THF at a platinum electrode is shown in Fig. 3. At −30°C an oxidation peak H'_1 is observed when the potential is reversed after reduction peak A (Fig. 3a). When the temperature increases, the following changes are observed: at −15°C three oxidation peaks H'_1, H'_2, H'_3 are obtained (Fig. 3(b)); at room temperature at the same sweep rate the oxidation peak H'_1 disappears (Fig. 3(c)). At more cathodic potentials than A another reduction peak B is observed (Fig. 4). The intensity of this peak increases as the sweep rate decreases. When the potential is reversed after peak B, three oxidation peaks H'^* H'_2 H'_3 are obtained (Fig. 4) (H'^* is situated at approximately the same potential as H'_1).

In polarography **2** exhibits only the reduction wave A ($E_{1/2} = -2.15$ V *vs.* S.C.E.) (Fig. 5(a)). When controlled-potential electrolysis was performed at −2.4 V (plateau of wave A) the current dropped to zero after consumption of 2F, and a red solution was obtained, which exhibits polarographically the oxidation waves H'_2, H'_3 and the reduction wave B (Fig. 5(b)). The relative heights of these waves depend on the concentration of **2** and the temperature). This solution is EPR silent. When the electrolysis was performed at the potential of wave B (−2.6 V), the ill-defined oxidation wave H'^* was obtained after consumption of *ca.* 5F (Fig. 5(c)).

After reoxidation of the red solution at −0.8 V (potential of wave H'_2) and consumption of a quantity of electricity less than one equivalent of electrons, **2**, characterized by its reduction, wave A was obtained, whereas the oxidation wave H'_3 was not changed. When the electrolysis of **2** was performed directly at −2.7 V (potential of wave B) oxidation waves H'^*, H'_2 and H'_3 were observed after consumption of more than 2F, but the coulometry results are not reproducible.

2.2.3. *Electrochemical oxidation of 2*

In THF-$[^nBu_4N][PF_6]$ in the range from −3 V to +1 V at a mercury electrode, no oxidation wave of **2** was observed. Surprisingly, however, the addition of an excess of *N,N*-dimethylformamide (DMF) causes an oxidation wave E′ to appear close to +0.33 V without change of the colour of the solution. In DMF $[Bu_4N][PF_6]$ or DMF $[Bu_4N][ClO_4]$ solution the wave E′ appears at 0 V (Fig. 6(a)).

When the electrolysis of **2** in DMF is performed at +0.2 V a colourless solution is obtained with consumption of an amount of electricity close to 6F (5.8F, 5.7F). A polarographic reduction wave E_1 appears ($E_{1/2} =$ −1,28 V) (Fig. 6(b)). The solution is EPR silent. The wave E_1 was not modified by adding a solution of LiCl in THF. The wave E_1 was also obtained when the

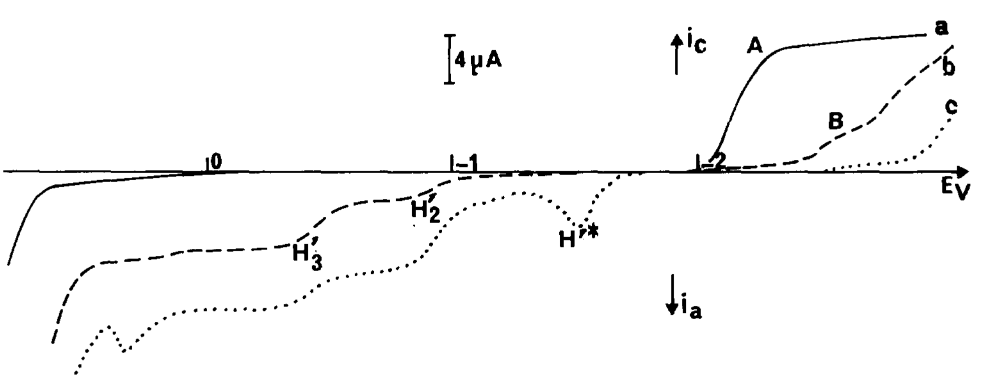


Fig. 5. Polarogram (average current) in THF of **2**. (a) Before electrolysis; (b) after electrolysis at −2.4 V; (c) after electrolysis at −2.6 V.

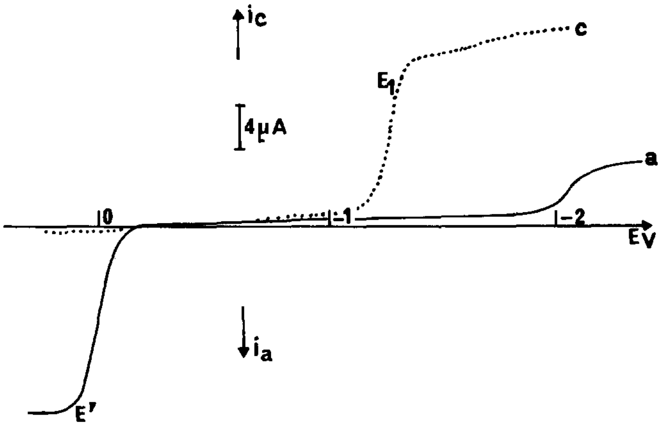


Fig. 6. Polarogram (average current) of 2 in DMF. (a) 2 alone; (b) after electrolysis at +0.2 V.

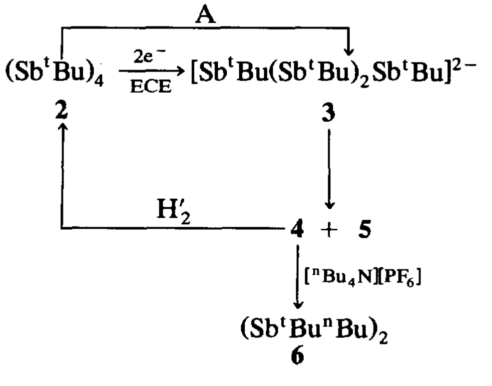
electrolysis was performed with [^{n}Bu$_4$N][ClO$_4$] as supporting electrolyte.

A similar modification of the electrochemical behaviour of 2 in THF was observed after addition of an excess of *N*-methylacetamide, when an oxidation wave E′ appears at $E_{1/2} = +0.38$ V.

3. Discussion

The mechanism of the formation of 2 from two-electron reduction of 1 can be explained with a scheme analogous to that concerning *n*-alkylantimony(I) compounds [5] and the electrochemical reduction of *2* in THF can be rationalized according to Scheme 1.

The two-electron reduction of 2 yields initially a relatively unstable dianionic species which is oxidized at the potential of peak H′$_1$. We suggest that the uptake of two electrons is accompanied by the chemical reaction (ECE or EEC process) which corresponds to cleavage of the antimony–antimony bond with formation of a linear dianionic species 3 formulated as [Sb^{t}Bu(Sb^{t}Bu)$_2$Sb^{t}Bu]$^{2-}$. Analogous behaviour has been described in the electrochemical and chemical reduction of phenylcyclopolyphosphines [13–14]. The cleavage of an antimony–carbon bond is not likely because the oxidation of the dianion 3 regenerates 2. The dianion 3 is unstable at low temperatures on the time scale of cyclic voltammetry. At room temperature 3 decomposes to give two species 4 and 5 which are oxidized at the potential of the peaks H′$_2$ and H′$_3$, respectively. It was not possible to isolate 4 and 5.



Scheme 1.

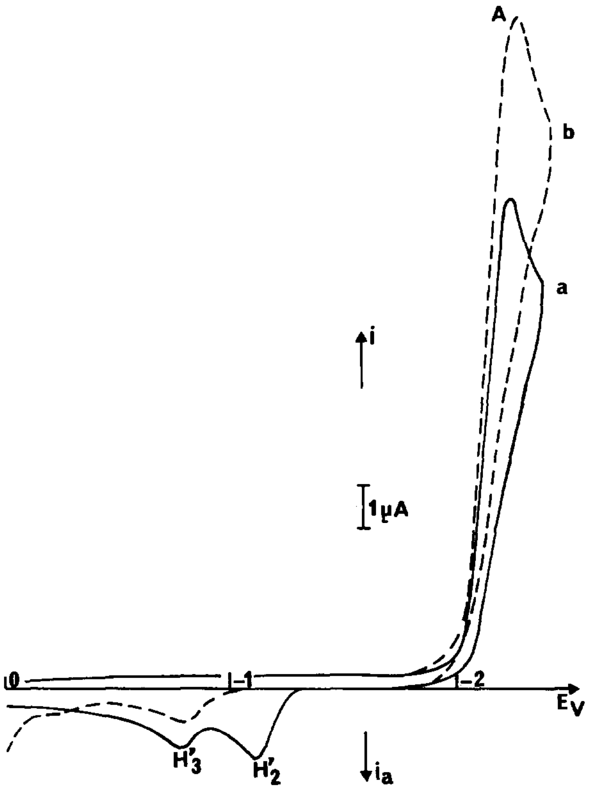


Fig. 7. Cyclic voltammogram of 2 in THF at a platinum electrode. Starting potential 0 V; sweep rate 0.2 V s^{-1}. (a) 2 alone; (b) in the presence of 5 equivalents of ^{n}BuBr.

We suggest that 4 is a dianionic species and 5 a neutral species for the following reasons. (i) Anionic species should be oxidized at higher cathodic potentials than neutral derivatives; (ii) anionic oxidation of 4 at the potential of peak H′$_2$ gives 2; (iii) the wave H′$_2$ disappears when ^{n}BuBr is added to the electrolyzed solution. In the presence of added ^{n}BuBr, the cyclic voltammogram of 2 is changed, peak A increases and the peak H′$_2$ disappears (Fig. 7(b)). This demonstrates the nucleophilic character of 4. Similar behaviour has been observed in the electroreduction of (PhP)$_5$, for which a dianionic trimeric species (PhP)$_3^{2-}$ has been proposed [13]. By analogy, 4 can be formulated (Sb^{t}Bu)$_3^{2-}$. Attempts to synthesize 4 by chemical methods such as reduction of 2 with Na/Hg were not successful. The neutral derivative 5 is possibly an

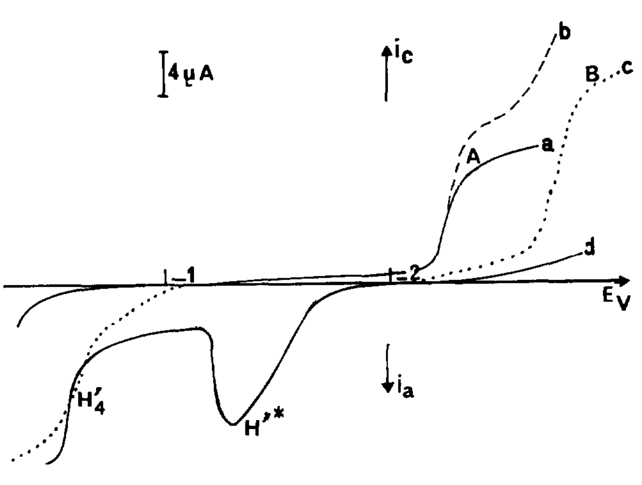
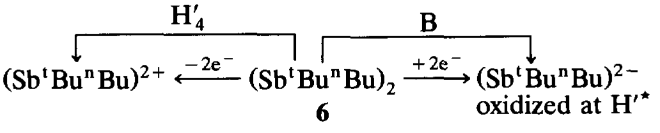


Fig. 8. Polarogram (average current) of **2** in THF. (a) **2** alone; (b) in the presence of 5 equivalents of ^{n}BuBr; (c) after electrolysis at −2.4 V; (d) after electrolysis at −2.7 V.

oligomer of the type Sb^{t}Bu-(Sb^{t}Bu)$_n$-Sb^{t}Bu solvated by THF. The wave H'_3 is at the same potential as wave A'_1 which was obtained after two-electron reduction of **1**.

The product reduced at the potential of peak B is the dimer (Sb^{t}Bu^{n}Bu)$_2$ (**6**) probably formed by slow reaction of the dianion **4** with the supporting electrolyte (see Scheme 1) as the basis of the following data:
i. The electrochemical behaviour of **6** is similar to that of (Ph$_2$Sb)$_2$, [17]. **6** exhibits a polarographic reduction wave B and an oxidation wave H'_4, which are at ($E_{1/2}$ = −2.74 V *vs.* SCE) and ($E_{1/2}$ = −0.56 V *vs.* SCE), respectively; ii. Electrochemical reduction of **2** at −2.7 V consumes more than 2 equivalents of electrons and an oxidation wave H'^* appears in polarography (*vide infra*); iii. Electrolysis of **2** in the presence of ^{n}BuBr consumes 4 equivalents of electrons and the orange solution containing **6** exhibits a reduction wave B and an oxidation wave H'_4 (Fig. 8(c)). The two-electron reduction of **6** yields the anionic species (^{t}BuSb^{n}Bu)$^-$ which is oxidized at the potential of wave H'^* (Fig. 8(d)). The wave H'_4 corresponds to the oxidation of **6** probably yielding the cationic derivative (^{t}BuSb^{n}Bu)$^{2+}$; iv. After appropriate work-up, product **6** was isolated and characterized by mass spectrometry.

$$\underset{\mathbf{2}}{(\mathrm{Sb^tBu})_4} + 4e^- + 4\,^n\mathrm{BuBr} \longrightarrow 2\underset{\mathbf{6}}{(\mathrm{Sb^tBu^nBu})_2} + 4\mathrm{Br}^-$$



$$(\mathrm{Sb^tBu^nBu})^{2+} \xleftarrow{-2e^-} \underset{\mathbf{6}}{(\mathrm{Sb^tBu^nBu})_2} \xrightarrow{+2e^-} (\mathrm{Sb^tBu^nBu})^{2-}$$

oxidized at H'^*

Scheme 2.

The formation and the electrochemistry of **6** are summarized in Scheme 2. An intermediate of the reaction of **4** with ^{n}BuBr or the supporting electrolyte could be the chain ^{n}Bu(Sb^{t}Bu)$_3$^{n}Bu. Such tristibane chains have been described recently [15]. They are unstable with respect to distibanes and cyclostibanes. For related reactions of the triphosphide (PPh)$_3^{2-}$ with Me$_3$SiCl see ref [16].

The oxidation of **2** in the presence of DMF occurs at the potential of wave E′. It corresponds to the EC process because the ^{1}H NMR spectra are not changed when DMF is added to a C$_6$D$_6$ solution containing **2**. We suggest that heterolytic cleavage of antimony–antimony bonds occurs in the polar solvent, after the oxidation of **2**.

3.1. Chemical behaviour of 2

To test the value of **2** not only for the electrochemical, but also for chemical synthesis, the reactivity of **2** towards air, (PhTe)$_2$, and K was investigated. The results are disappointing. Oxidation was performed by slow addition of air to a solution of **2** in benzene. Careful analyses of the colourless solution and the white solid product gave only Sb$_4$O$_6$ as the Sb-containing product. The heterocycles (Sb^{t}BuO)$_n$ were not detected. However, they are obtained by hydrolysis of **1** [18]. The reaction of **2** with (PhTe)$_2$ did not proceed as expected. Instead of the ditellurostibane Sb^{t}Bu(TePh)$_2$, only the tellurene TePh(^{t}Bu) was identified unambiguously by ^{1}H-NMR-(δ(C$_6$D$_6$) 1.48 s(9H)C$_4$H$_9$) $J(^1\mathrm{H}-^{125}\mathrm{Te}) = 23$ Hz; 6.9m, 7.1m; 7.9m (5H)C$_6$H$_5$ and mass spectroscopy ($m/e = 264$ PhTe^{t}Bu$^+$, 208 PhTeH$^+$). Under analogous conditions, good yields of stable SbEt(TePh)$_2$ were obtained from (SbEt)$_5$ and the ditellurene [19]. The reaction of **2** with K in THF at RT in the presence or absence of 18-crown-6 gives a red solution, and a black solid is formed on the surface of the alkali metal. Attempts to isolate the red species or to characterize the reaction products obtained after addition of Me$_3$SiCl or ^{n}BuBr failed. In our hands, selective cleavage of the Sb–Sb bond by K without affecting the Sb–C bonds was not achieved. After work up, the only well-characterized species containing a ^{t}Bu–Sb bond were the starting material **2** and, sometimes Sb^{t}Bu$_3$.

These results indicate that under our conditions the Sb–C bond of **2** is easily affected and more selective methods have to be developed for chemical syntheses retaining the antimony ring **2**.

4. Experimental section

All manipulations were performed under argon. Tetrahydrofuran was purified by distillation from sodium

TABLE 4. Experimental data for the x ray structure determination of **1**

Data collection	
Diffractometer used	Siemens P4
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Temperature (K)	153
Monochromator	Highly oriented graphite crystal
2θ range	5.0–55.0°
Scan type	$2\theta - \omega$
Scan speed	Variable; 3.97–29.30° per min. in ω
Scan range (ω)	1.20° plus Kα-separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan each for 25.0% of total scan time
Standard reflections	3 measured every 197 reflections
Index ranges	$-5 \leq h \leq 14$, $-1 \leq k \leq 14$, $-8 \leq l \leq 8$
Reflections collected	2056
Independent reflections	1828 ($R_{int} = 1.39\%$)
Observed reflections	1695 ($F > 6.0\sigma(F)$)
Absorption correction	Yes (with program DIFABS [20])
Solution and refinement	
System used	Siemens SHELXTL PLUS (VMS)
Solution	Direct methods
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma w(F_0 - F_c)^2$
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0001F^2$
Number of parameters refined	67
Final R indices (obs. data)	$R = 1.90\%$, $wR = 2.21\%$
R indices (all data)	$R = 2.20\%$, $wR = 2.31\%$
Goodness-of-fit	1.17
Largest and mean Δ/σ	0.008, 0.001
Data-to-parameter ratio	25.3:1
Largest difference peak	0.87 eÅ^{-3}
Largest difference hole	-0.68 eÅ^{-3}

benzophenone. *N,N*-dimethylformamide was purified by passing the solvent through a column packed with alumina previously dried at 120°C; it was deoxygenated by bubbling argon immediately before use. The supporting electrolyte was tetra-*n*-butylammonium hexafluorophosphate (0.2 M), the salt (Fluka) was dried and deoxygenated before use.

Experimental data relating to the X ray structure determination are given in Table 4.

4.1. Instrumental

4.1.1. Electrochemical measurements

Voltammetric analyses were carried out in a standard three-electrode cell with a Tacussel UAP4 unit. The reference electrode was a saturated calomel electrode 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 a saturated calomel electrode as the reference electrode.

4.2. Synthesis procedure

Sb^{t}BuCl$_2$ (**1**) [1] and Sb^{t}Bu$_4$ (**2**) [12] were prepared by published methods.

4.2.1. Electrosynthesis of Sb^{t}Bu$_4$ (2)

Sb^{t}BuCl$_2$ **1** (0.4 g; 1.6 mmol) was added to the cathode compartment of the cell containing 100 ml of a 0.2 M solution of (^{n}Bu$_4$NPF$_6$) THF solution. Electrolysis was stopped after consumption of two equivalents of electron per mol of **1**. The solvent was removed *in vacuo* and the orange product was extracted with toluene to give yellow (Sb^{t}Bu)$_4$ characterized by its ^{1}H-NMR spectrum in benzene, (δ) = 1.56 ppm.

4.2.2. Electrosynthesis of (Sb^{t}Bu)$_2$ (6)

(Sb^{t}Bu)$_4$ **1** (0.4 g; 0.56 mmol) and ^{n}BuBr (0.38 g, 2.8 mmol) were added to the cathode compartment containing 100 ml of a 0.2 M solution of [^{n}Bu$_4$N PF$_6$] in THF. The electrolysis was stopped after consumption of 4 equivalents of electron per mol of **2**. The solvent was removed *in vacuo* and the orange product was extracted with toluene to give (Sb^{t}Bu^{n}Bu)$_2$ (**6**) characterized by its mass spectrum. (100°C, 70 eV) [m/z (%) assignment] 472(1) Bu$_4$Sb$_2^+$, 415(1) Bu$_3$Sb$_2^+$, 358(2) Bu$_2$Sb$_2^+$, 292(10) Bu$_3$Sb$^+$, 57(100)Bu$^+$.

Acknowledgments

The authors gratefully acknowledge financial support from the EDF (Novelec Bourgogne) and the Fonds der Chemischen Industrie. They thank Mrs. M.T. Compain for technical assistance.

References

1 H.J. Breunig and W. Kanig, *Chemiker-Zeitung, 102* (1978), 263.
2 H.J. Breunig and H. Kischkel, *Z. Naturforsch., 36b* (1981) 1105.
3 H.J. Breunig and T. Severengiz, *Z. Naturforsch., 37b*, (1982) 395.
4 H.J. Breunig and H. Kischkel, *Z. Anorg. Allg. Chem., 502* (1983) 175.
5 Y. Mourad, Y. Mugnier, H.J. Breunig and M. Ates, *J. Organomet. Chem., 406* (1991) 323.
6 A.F. Wells, *Structural Inorganic Chemistry*, 4th ed, Clarendon, Oxford, 1975, p. 706.
7 L. Pauling, *Die Natur der Chemischen Bindung*, 3rd edn. Verlag Chemie, Weinheim, 1976.
8 M. Hall, M. Nunn, M.J. Begley and D.B. Sowerby, *J. Chem. Soc., Dalton Trans.*, (1986) 1231.

9 O. Mundt, G. Becker, H. Stadelmann and H. Thurn, *Z. Anorg. Allg. Chem., 617* (1992) 59.
10 M. Denker, Diplomarbeit, Bremen 1993.
11 H.J. Breunig, K.H. Ebert and S. Güelec, *J. Organomet. Chem., 427* (1992) 39.
12 H.J. Breunig, W. Kanig and H. Kischkel, in R.B. King and J.J. Eisch (eds), *Organometallic Syntheses,* Volume 3, Elsevier, Amsterdam, 1986, p. 621.
13 J. Dupont and J. Mills, *Inorg. Chem., 12* (1973) 2487.
14 K. Issleib and K. Krech, *Chem. Ber., 99* (1966) 1310.
15 M. Ates, H.J. Breunig, K. Ebert, S. Güelec, R. Kaller and M. Dräger, *Organometallics, 11* (1992) 145.
16 M. Baudler, G. Reuschenbach, D. Koch and B. Carlsohn, *Chem. Ber., 113* (1980) 1264.
17 Y. Mourad, Y. Mugnier, H.J. Breunig and M. Ates, *J. Organomet. Chem., 388* (1990) C9.
18 H.J. Breunig and H. Kischkel, *Z. Naturforsch., 36b,* (1981) 1105.
19 H.J. Breunig, S. Güelec and R. Kaller, *Phosphorus, Sulfur and Silicon, 67* (1992) 33.
20 N. Walker and D. Stuart, *Acta Crystallogr., A39* (1983) 158.