Electrochemistry of 1,1,2,2,3,3-hexa(2,6-diethylphenyl)cyclotristannane. The first examples of electrochemical generation of a stannylene radical anion and a tristannane radical cation

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The radical anion of di(2,6-diethylphenyl)stannylene (Ar_2Sn) has been generated by the electrochemical reduction of cyclotristannane cyclo-(Ar_2Sn)₃, and the electrochemical oxidation of cyclo-(Ar_2Sn)₃ resulted in Sn–Sn bond cleavage with the formation of the radical cation of tristannane.

Significant and exciting progress has been achieved in the chemistry of small rings containing the atoms of Group 14 elements.¹ Data on the electrochemistry of cyclotrisilanes² and cyclotrigermanes³ are available, but this area is still poorly investigated. Here, we report on the electrochemical and simultaneous electrochemical–electron spin resonance (SE–ESR) study of a cyclotristannane [1,1,2,2,3,3-hexa(2,6-diethylphenyl)cyclotristannane 1] and the first example of the electrochemical generation of a stannylene radical anion from $1.^{\dagger}$

The cyclic voltammogram (CV) of the reduction of compound 1 [20 °C, in THF, 0.1 M Bu_4NCIO_4 as a supporting electrolyte, glassy carbon electrode, all potentials are *vs*. Ag[AgCl]aq. KCl (sat.)] exhibits one cathodic peak at –2.0 V (one electron, peak A) and one anodic peak at –0.72 V (A') on the reverse scan (Figure 1).

A great difference between the forward, A, and reverse, A', peak potentials implies that peak A' corresponds to the oxidation of a secondary product arising from the fragmentation of the primary radical anion of **1**, formed at -2.0 V. The nature of this product was revealed using the SE–ESR technique. Upon the electrochemical reduction of **1** at -2.0 V (20 °C, in THF, 0.1 M Bu₄NClO₄ as a supporting electrolyte, Pt electrode) with the simultaneous measurement of the ESR spectrum, a singlet with a set of ^{117,119}Sn sattelites was detected. Its parameters



Figure 1 Cyclic voltammogram of cyclotristannane **1** (10^{-3} M) in THF, at 20 °C, 0.1 MBu₄NClO₄ as a supporting electrolyte, glassy carbon electrode, scan rate of 200 mV s⁻¹.

The electrochemical cell for SE–ESR was described elsewhere.⁷

The ESR spectra were recorded using a Bruker EMX 6-1 spectrometer. Cyclotistannane 1 was synthesised according to the published procedure.⁸ $[g = 2.015, a(^{117,119}Sn) = 151 G and \tau_{1/2} \sim 2 min]$ correspond to those of stannylene radical anion 2.⁴ Radical anion 2 was detected earlier during the chemical reduction of 1 by lithium.⁴ Thus, one can safely assign peak A' to the oxidation of stannylene radical anion 2. The following mechanism of the electrochemical reduction of 1 can be suggested:

$$\begin{array}{c} \begin{array}{c} SnAr_{2} & +e^{-} \\ Ar_{2}Sn - SnAr_{2} \end{array} \xrightarrow{+e^{-}} \left[Ar_{2}Sn - SnAr_{2} \\ Ar_{2}Sn - SnAr_{2} \end{array} \right]^{\bullet -} \\ \begin{array}{c} 1 \\ Ar = 2, 6 \text{-diethylphenyl} \end{array} \xrightarrow{+e^{-}} \left[Ar_{2}Sn - SnAr_{2} \\ Ar_{2}Sn^{\bullet -} + Ar_{2}Sn = SnAr_{2} \\ 2 \\ \end{array} \right]$$

diam agnetic properties

The single oxidation peak at +0.54 V (one electron, peak B) is observed in a CV curve for the oxidation of 1 when the potential was scanned from E = 0 V to the anodic site. On a reverse scan, there is a peak (B') at -0.69 V corresponding to the reduction of the product of fragmentation of the radical cation of cyclotristannane 1. The ESR spectrum of the products of oxidation of 1 at +0.54 V (20 °C, in THF, 0.1 M Bu₄NClO₄ as a supporting electrolyte, Pt electrode) reveals two singlets from two paramagnettic species (Figure 2). One singlet [g = 2.020, $a_1(^{117,119}\text{Sn}) = 394 \text{ G}, a_2(^{117,119}\text{Sn}) = 112 \text{ G}]$ was assigned to radical cation 3, the open form of the radical cation of 1. Indeed, there are two sets of satellites corresponding to the coupling of an unpaired electron with terminal (a_1) and central (a_2) tin atoms. To our knowledge, radical cation 3 is the first radical cation of a tristannane reported so far. Nevetheless, we can compare the $a_1^{(117,119}$ Sn) value in **3** with that reported for the radical cation of Me₃Sn–SnMe₃ [$a_{\parallel}^{(117,119}$ Sn) = 238 G, $a_{\perp}^{(117,119}$ Sn) = 100 G, measured at 77 K in a CFCl₃ matrix⁵]. Both values are of the same order of magnitude.

Another singlet [g = 2.022, $a(^{117,119}Sn) = 250$ G] observed upon the oxidation of **1** was tentatively assigned to stannylene radical cation **4**.



Figure 2 (a) ESR spectrum of radical cations 3 and 4. Singlets corresponding to sattelites of 3 are marked by *, those of 4 are marked by \bullet . (b) ESR spectrum of 3 and 4 at higher gain.

[†] Cyclic voltammetry was performed on a PI-50-1.1 potentiostat or a home-made potentiostat interfaced with an IBM PC. The working electrode was a glassy carbon disk (\emptyset 1.8 mm); the reference electrode was Ag|AgCl|KCl (aq., sat.). The measurements were carried out in THF in the presence of 0.1 M Bu₄NClO₄ as a supporting electrolyte in an argon atmosphere.

The following oxidation mechanism of 1 can be suggested:



Radical cations **3** and **4** are short-living species (lifetimes of about 2 to 3 min); therefore, we were unable to detect spectroscopically the transformation of **3** into **4**. In fact, the open form of the radical cation of cyclotrisilane (similar to **3**) is formed during the chemical oxidation of cyclotrisilane with tetracyanoethylene, as proposed on the basis of its trapping by ethanol.⁶

Thus, using the SE–ESR technique, the radical anion of stannylene 2 and the open form of the radical cation of cyclotristannane were detected, and the formation of the radical cation of stannylene (radical cation 4) upon the electrochemical oxidation of 1 was suggested. This technique opens new opportunities to the electrochemical generation and detection of radical ions of Group 14 element derivatives. This work was supported by the Russian Foundation for Basic Research (grant nos. 00-15-97387 and 02-03-32148), INTAS (grant no. 97-30344), the Ministry of Science of the Russian Federation and the Russian Academy of Sciences (grant no. 1-20).

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