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Electrochemistry of a cyclotrisilane and a cyclotrigermane. The first example of the electrochemical generation of a cyclotrisilane radical anion

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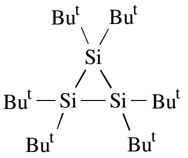
The radical anion of 1,1,2,2,3,3-hexa-*tert*-butylcyclotrisilane has been electrochemically generated in THF at room temperature.

Strained cyclotrimetallanes of Group 14 elements are of great interest because of their intriguing structures and reactivities, and their important role as the precursors of the derivatives of low-coordinated silicon, germanium and tin compounds.[1–3] The chemical properties of these small heterocycles have been intensively studied during the last two decades, but the electrochemistry of cyclotrimetallanes has not been adequately investigated.[1–4] In particular, the reduction potentials of cyclotrimetallanes have not been reported. At the same time, information on the redox potentials and the reversibility of electron attachment (detachment) processes is very important for the elucidation of the energy of frontier orbitals of cyclotrimetallanes and for the better understanding of their reactivity. The nature of radical ions generated upon electrochemical oxidation (reduction) can be studied using simultaneous electrochemical–ESR (SE–ESR) techniques,[5] which were successfully used in the study of paramagnetic intermediates of the electrochemical oxidation (reduction) of a cyclotristannane.[6]

Here we report on an electrochemical and SE–ESR study of Group 14 element cyclotrimetallanes, 1,1,2,2,3,3-hexa-*tert*-butylcyclotrisilane **1** and 1,1,2,2,3,3-hexamesitylcyclotrigermane **2**.



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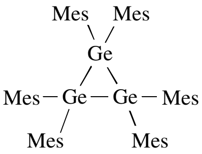

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According to cyclic voltammograms (CV), both of the compounds exhibit low oxidation and high reduction potentials (Table 1). The oxidation and reduction of cyclotrisilane **1** are quasi-reversible processes. A peak at 0.65 V ($i_{pc}/i_{pa} = 0.45$, peak A) on the reverse scan of a CV curve for oxidation and a peak at –2.27 V ($i_{pa}/i_{pc} = 0.42$, peak B) on the reverse scan of the CV curve for the reduction of **1** can be seen in Figure 1. Great differences between the direct and reverse peak potentials (360 mV for oxidation and 320 mV for reduction) suggest that, in fact, the reverse peaks can correspond to the reduction (peak A) or oxidation (peak B) of secondary products arising after the fragmentation of the primary radical ions.

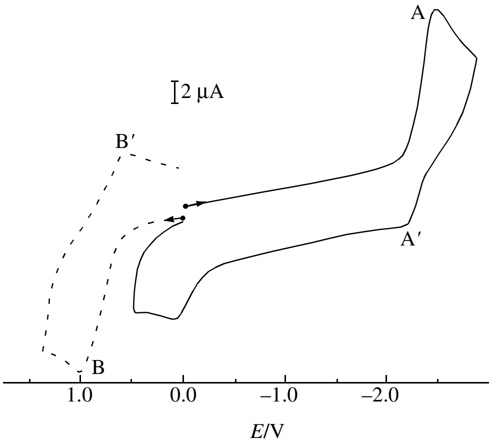

Figure 1 Cathodic (solid line) and anodic (dotted line) CV curves for cyclotrisilane **1** (10^{-3} M) in THF, at 10 °C, 0.1 M Bu_4NClO_4 as a supporting electrolyte; glassy carbon electrode; scan rate 0.5 V s^{-1}.

Table 1 Peak potentials for oxidation and reduction of compounds **1** and **2** (20 °C, THF, 0.1 M Bu_4NClO_4 as a supporting electrolyte; glassy carbon electrode; scan rate 200 mV s^{-1}, Ag | AgCl | aq KCl (sat.) as a reference electrode).

Compound	E^p_{ox}	E^p_{red}
1	1.01 (1e)[a]	–2.59 (1e)[a]
2	0.88 (1e)	–2.76 (1e)

[a] Quasi-reversible.

To detect the primary radical ions, compound **1** was studied by SE–ESR.† Upon the reduction of **1** at –2.59 V (in THF, 0.1 M Bu_4NClO_4 as a supporting electrolyte; Pt electrode; 20 °C) in the cavity of an ESR spectrometer, we detected the ESR spectrum of a paramagnetic species, $g = 2.0039$ (Figure 2). This spectrum is in good agreement with the simulated spectrum for the radical anion of **1**, in which the unpaired electron is coupled with three equivalent silicon atoms with $a(^{29}Si) = 6.9$ G. This value is close to that (7.0 G) reported[1] for the radical anion of **1** generated by chemical reduction of **1** at < 200 K. At room temperature, the radical anion of **1** has a lifetime of about 1 min.

Despite the quasi-reversible oxidation of **1** at 1.01 V, we failed to detect any primary or secondary paramagnetic species

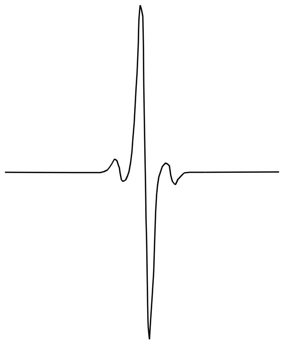

Figure 2 ESR spectrum of the radical anion of cyclotrisilane **1** electrochemically generated in THF at 20 °C.

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† The electrochemical (cyclic voltammetry) experiments were carried out on a PI-50-1.1 potentiostat or a home-made potentiostat interfaced to an IBM PC. The working electrode was a glassy carbon disk (∅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 Bu_4NClO_4 as a supporting electrolyte in an argon atmosphere.

The electrochemical cell for SE–ESR measurements was described elsewhere.[5]

The ESR spectra were recorded using a Bruker EMX 6-1 spectrometer.

Cyclotrisilane **1** and cyclotrigermane **2** were synthesised according to published procedures.[7,8]

by SE–ESR techniques both at room temperature and at 200 K. Thus, the lifetime of the radical cation of **1** (in its cyclic or opened form) is too short. Note that sterically hindered 2,6-diethylphenyl (Dep) substituents can increase the lifetime of the radical cation; therefore, the open form of the radical cation of $(Dep_2Sn)_3$ can be detected by ESR spectroscopy.[6]

The oxidation and reduction of cyclotrigermane **2** are irreversible processes at 20 °C. This fact suggests very short lifetimes of the corresponding radical ions. Indeed, we were unable to detect any paramagnetic species upon the electrochemical oxidation of **2** at 0.88 V or on the reduction of **2** at –2.76 V directly in the cavity of the ESR spectrometer both at room temperature and at 200 K.

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