A new method for the generation of stable phenoxyl radicals by the reaction of $[(Me_3Si)_2N]_2E$ (E = Ge, Sn) with sterically hindered phenols

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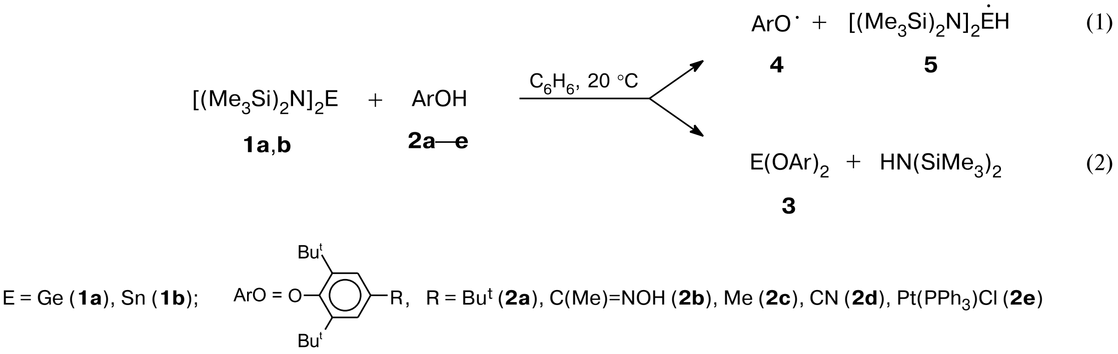
An unusual reaction of diaminogermylene and diaminostannylene with sterically hindered phenols which leads to the formation of stable phenoxyl radicals in high concentrations was found. The reaction mechanism was proposed. Amides $[(Me_3Si)_2N]_2E$ (E = Ge, Sn) were investigated electrochemically.

Key words: diaminogermylene, diaminostannylene, sterically hindered phenols, deprotonation reaction, ESR.

Divalent germanium and tin amides occupy a particular place among carbene analogs. This is due to the presence of two reaction centers, *viz.*, a two-coordinated germanium or tin atom and labile polar bonds Ge(Sn)—N, which can easily be cleaved by sufficiently acidic reagents (for example, NH- and OH- acids). Thus, depending on the structure of reagents, Ge^{II} and Sn^{II} amides can undergo reactions typical of both carbene analogs (insertion into σ-bonds, addition to multiple bonds, complexation reaction)[1] and Ge^{IV} and Sn^{IV} amides playing a role of metallation agents[2—4] and leading to new germylenes (stannylenes). For the metallation reactions, stable monomeric carbene analogs of the type $[(Me_3Si)_2N]_2E$ (E = Ge (**1a**), Sn (**1b**)) were found to be the most convenient. Particularly, reaction of amides **1** with sterically hindered phenols ArOH (**2**) afford stable compounds $(ArO)_2E$ (**3**)[2]. For the first time it was found that this metallation reaction (20 °C, C_6H_6) is accompanied by the formation of high concentrations of phenoxyl radicals $ArO^{\bullet}$ (**4**) (Scheme 1).

The stable radicals **4** were identified by ESR spectroscopy. ESR spectra of radicals **4** are identical to those described in the literature[5]. The reaction of stannylene **1b** with phenols **2** leads to the formation of radicals **4** in substantially higher concentrations (up to 2 orders of magnitude) than the reaction of **2** with germylene **1a**. The formation of radicals **4** is not connected with the decomposition reaction of carbene analogs **3**, which are the main reaction products of **1** with **2**. Indeed, according to the ^1H NMR data carbene analogs **3** are stable in a solution at room temperature. Besides, ^1H NMR monitoring of the reaction of **1** with **2** did not reveal the formation of

Scheme 1



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any intermediate compounds (for example, products of insertion reaction of **1** into H—O bond of phenols **2**), whose decomposition could lead to radicals **4**.

In order to estimate a possibility of the formation of radicals **4** by a redox reaction of carbene analogs **1** with phenols **2,** we carried out electrochemical investigation of amides **1**. It was shown that both compounds are reduced irreversibly at high cathode potentials (—2.83 (**1a**) and −2.45 V (**1b**)). Therefore, the pathway of formation of phenoxyl radicals **4** by the oxidation of phenols **2** by carbene analogs **1** can be completely excluded. Compounds **1** are oxidized irreversibly at rather low anodic potentials, 0.72 (**1a**) and 1.34 V (**1b**).

In the simultaneous electrochemical — ESR investigations (SE-ESR) of the reduction and the oxidation of compounds **1** we did not manage to observe any paramagnetic species either at room temperature or at lower temperature (200 K), which suggests the short life-times of the initial radical ions of the carbene analog **1**.

Hence, the formation of phenoxyl radicals **4** is not connected with either the decomposition of stable carbene analogs **3** or other intermediates or with the redox reactions of **1** with **2**. The most likely way of the formation of radicals **4** could be hydrogen abstraction from the OH group of phenols **2** under the action of amides **1** (Scheme 1, reaction (1)), which proceeds simultaneously with the main process, *viz.*, metallation of phenols (Scheme 1, reaction (2)). Obviously, the other product of the reaction (1), namely the element-centered radical **5**, is labile and its ESR-signal cannot be observed against a background of the intense signal of stable radical **4**.

The hydrogen abstraction can occur directly or result from the fragmentation of an intermediate donor-acceptor complex between **1** and **2**. It should be noted that the formal abstraction of two hydrogen atoms from cyclo-1,3-diene with the formation of benzene by tin (II) amide is documented[6].

The reaction (1) is apparently specific for carbene analogs **1**. Our attempts to perform it with gemylenes and stannylenes of other structures ($GeMe_2$, $GeCl_2 \cdot$dioxane, $GeCl_2 \cdot PPh_3$, GeI_2, $SnCl_2$, $SnCl_2 \cdot$dioxane, SnI_2, $[Sn(NEt_2)_2]_x$) were unsuccessful. The reaction (1) is the first example of the reaction where carbene analogs with Group 14 elements abstract hydrogen from the reagent.

Experimental

All reactions and measurements were carried out in an atmosphere of dry Ar. Benzene, deuterobenzene, and THF were dried and degassed according to standard procedures[7]. Stable germylene **1a** and stannylene **1b** were synthesised according to the published procedures[8]. Specimens of phenols **2** were kindly provided by E. P. Milaeva.

Electrochemical investigations were carried out using a potentiostate PI-50-1.1. The working electrode was a glassy-carbon rod (diameter 1.8 mm), background electrolyte was 0.1 *M* solution of Bu_4NClO_4 in THF, the reference electrode was Ag/AgCl/KCl (sat.); THF was distilled over benzophenone ketyl in an atmosphere of dry Ar directly to an electrochemical cell. For SE-ESR-experiments, the electrochemical cell designed by A. B. Ilyasov and Yu. M. Kargin was used[9]. This was a Pyrex tube (diameter 5 mm) with the working electrode as a Pt helix (diameter of the Pt wire 0.3 mm), an auxiliary Pt electrode (diameter of the Pt wire 0.3 mm), and an Ag wire (diameter 0.4 mm) as a reference electrode. The cell was supplied with a vacuum valve.

The ESR and NMR spectra were recorded at 20 °C on Bruker EMX 6-1 and Bruker AM-200 instruments, respectively.

Reaction of 1 with phenols 2. Germylene **1a** (61 mg, 0.156 mmol) was placed in an NMR tube and 0.5 mL of dry C_6D_6 was added. Phenol **2a** (35 mg, 0.134 mmol) was added in three equal portions to the solution of **1a**. After addition of the phenol, the solution assumes a green colour. Broadened signals of $(Me_3Si)_2NH$ and phenolate **4a** appear in the ^1H NMR spectrum of the reaction mixture and a signal for phenoxyl radical **4a** appears in the ESR spectrum. Other reactions of amides **1** with phenols **2** were carried out similarly.

SE-ESR investigation of 1. Bu_4NClO_4 (136 mg) and germylene **1a** (stannylene **1b**) (20 mg) were placed into an electrochemical cell for SE-ESR in an atmosphere of dry Ar. THF (2 mL) was distilled from Ph_2CO/Na directly to the cell. The cell was degassed and evacuated. ESR spectra were recorded in the intervals of potentials from 0 to −3.0 V and from 0 to +3.0 V.

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