



Transformations of spirogermabifluorene upon reduction with alkali metals

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ABSTRACT

Spirogermabifluorene ($C_{24}H_{16}Ge$, **1**) and the anionic products of its reduction with alkali metals were prepared and investigated by single-crystal X-ray diffraction. A monoanionic intermediate product of the reduction, formed upon the cleavage of a Ge–C bond and proton abstraction from the solvent, was isolated in the form of the cesium salt, $[Cs^+(diglyme)(C_{12}H_8GeC_{12}H_9)]$ (**2**). Structural investigation of **2** revealed the presence of a tricoordinated germanium center and complexation of the cesium cation by two aromatic moieties. The reduction of **1** with an excess of alkali metals leads to the cleavage of the second Ge–C bond with subsequent elimination of biphenyl to give the $C_{12}H_8Ge^{2-}$ dianion which was crystallized as the sodium adduct, $[Na^+(THF)]_2(C_{12}H_8Ge^{2-})$ (**3**). The structural elucidation for complex **3** shows η^3 - and η^5 - coordinations of the sodium ions to the π -system of dianions. The resulting $Na\cdots C$ and $Na\cdots Ge$ contacts along with the $Na\cdots O_{THF}$ interactions lead to the formation of the zigzag polymeric chains in the crystal lattice of **3**.

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1. Introduction

The substantial interest in the chemistry of spirobifluorenes is attributed to their photophysical properties which can be used for applications in organic light-emitting diodes and dye-sensitized solar cells [1–3]. Organometallic analogs of spirobifluorene, having a central sp^3 -hybridized heteroatom, also demonstrate potentially useful optoelectronic properties and electron transport effects [4–6]. Various compounds with a spirosilabifluorene core have been prepared and their fluorescent properties studied [7]. The charging of spirobifluorene and their analogs with additional electrons should result in significant perturbation of electron density within the aromatic system and alteration of chemical and physical properties compared to neutral compounds; however, the number of corresponding reports is limited [8–10].

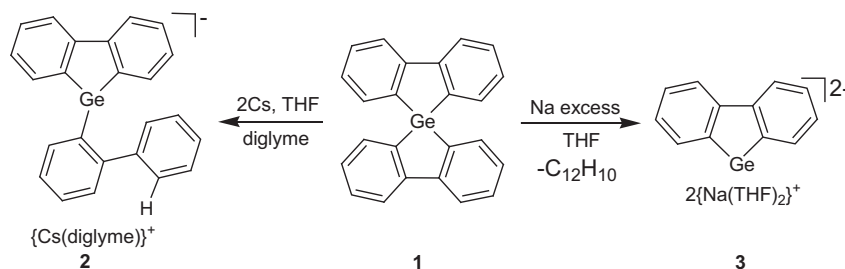
The lithium reduction of spirosilabifluorene in DME led to the formation of an anion with a hypervalent silicon atom – $[C_{24}H_{16}Si-CH_3]^-$ [11]. Recently, we found that spiroilabifluorene upon the reduction with heavier alkali metals in THF can take up and delocalize up to two electrons without any cleavage or rearrangement of the bonds in the resulting anionic products [12]. Herein, we report the investigation of the reduction products for related spirogermabifluorene (**1**, Scheme 1).

2. Results and discussion

The preparation of spirogermabifluorene **1** was reported in 1958; however, the molecular structure of **1** was not investigated [13,14]. Crystals of **1**, suitable for single-crystal X-ray studies, were obtained by sublimation *in vacuo*. Compound **1** crystallizes from the vapor phase in the $P4_12_12$ space group with the germanium atom residing on a crystallographic two-fold axis (Fig. 1). The germanium atom shows a distorted tetragonal environment. The value of the angle between two fluorene planes in **1** ($82.571(3)^\circ$) is very close to that measured in its isostructural silicon analog ($82.52(2)^\circ$) [7]. The C–C bond lengths within the six-membered rings in **1** fall in much narrower range (1.387(4)–1.411(3) Å) than for spirogermabifluorene with an extended π -system (1.363(4)–1.440(4) Å) [15]. The C6–C7 bond connecting two benzene rings is significantly elongated (1.492(3) Å) compared to the other C–C bonds.

Spirogermabifluorene **1** can be irreversibly reduced in THF with alkali metals under ambient conditions. In contrast to the reversible stepwise reduction of spiroilabifluorene [12], compound **1** can cleave up to two Ge–C bonds with subsequent proton abstraction from the solvent molecules [16] during the treatment with alkali metals (Scheme 1). 1H and ^{13}C NMR monitoring of the reduction of **1** with an excess of sodium or cesium showed the formation of a transient diamagnetic monoanion $C_{12}H_8GeC_{12}H_9^-$, which is completely converted into 9-germafluorenyl dianion, $C_{12}H_8Ge^{2-}$, at the last reaction step. Exposure of the reaction mixture to air

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Scheme 1. Preparation of 1–3.

followed by extraction of the products into hexane gave neutral biphenyl $\text{C}_6\text{H}_5\text{--C}_6\text{H}_5$.

The controlled reaction of **1** with two equivalents of cesium produced a solution of the yellow monoanion $\text{C}_{12}\text{H}_8\text{GeC}_{12}\text{H}_9^-$ which was crystallized in the presence of diglyme as salt **2**, $[\text{Cs}^+(\text{diglyme})(\text{C}_{12}\text{H}_8\text{GeC}_{12}\text{H}_9^-)]$. A single-crystal X-ray study of **2** shows the formation of a contact ion pair (Fig. 2). The anionic fragment of **2** contains a tricoordinated germanium atom surrounded by 1,1'-biphenyl-2,2'-diyl and 1,1'-biphenyl-2-yl ligands. The C1--Ge1--C12 angle in **2** ($84.36(5)^\circ$) is smaller than the related angle in **1** ($89.97(9)^\circ$). The Ge1--C bonds are elongated in the anionic product **2** ($1.9962(14)\text{--}2.0339(13)$ Å) compared with **1** ($1.938(2)$ and $1.945(2)$ Å). Cleavage of one Ge--C bond leads to an increased angle between the two benzene planes in 1,1'-biphenyl-2-yl moiety to $46.71(6)^\circ$.

The shortest $\text{Ge}\cdots\text{Cs}$ distance in **2** is $3.7885(9)$ Å, indicating the absence of a significant interaction between the germanium atom and cesium cation. The Cs^+ ion in **2** is located between two six-membered rings of 9-germafluorene and 1,1'-biphenyl-2-yl groups. The corresponding $\text{Cs}\cdots\text{C}_{6(\text{centroid})}$ distances for these unsymmetric η^6 -contacts ($3.4658(10)$ Å and $3.5481(11)$ Å) are close to the related contacts observed in the cesium adducts of polyarene-anions [17–20]. The chemical shift of the cesium ion in the ^{133}Cs NMR spectrum was observed at $\delta = -25$ ppm (THF- d_6 , 25°C). This high-field shift illustrates that the binding of the alkali-metal ion to the π -system of the counterion, observed in the crystal of **2**, persists in a solution. The coordination sphere of the cesium cation is completed by three O-donor functionalities of the chelating diglyme molecule ($\text{Cs}\cdots\text{O}$ $3.0880(12)\text{--}3.2142(14)$ Å).

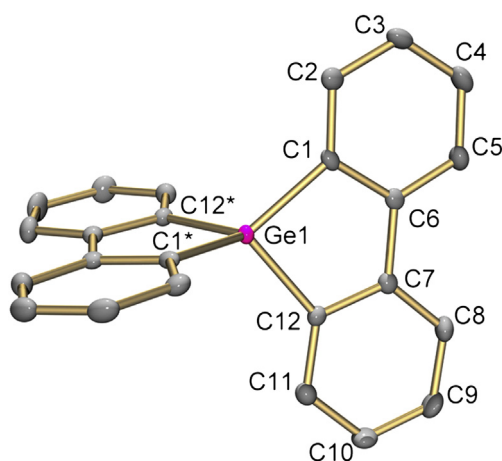


Fig. 1. Molecular structure (50% probability level) of **1** with all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [$^\circ$]: Ge1--C1 $1.938(2)$, Ge1--C12 $1.945(2)$, C1--C2 $1.387(3)$, C1--C6 $1.411(3)$, C2--C3 $1.393(3)$, C3--C4 $1.389(4)$, C4--C5 $1.387(4)$, C5--C6 $1.394(3)$, C6--C7 $1.492(3)$; C1--Ge1--C1^* $117.22(14)$, C1--Ge1--C12 $89.97(9)$.

The 9-germafluorenyl dianion was crystallized with the sodium counterions from the THF solution as the $[\{\text{Na}^+(\text{THF})_2\}(\text{C}_{12}\text{H}_8\text{Ge}^{2-})]$ (**3**) salt according to X-ray diffraction (Fig. 3, left). The planar $\text{C}_{12}\text{H}_8\text{Ge}^{2-}$ dianion shows geometrical parameters in the sodium adduct **3** close to those previously reported for the potassium adduct [21]. The Ge1--C bonds in the dianion ($1.9480(18)$ and $1.9625(18)$ Å) are slightly shorter than in the $\text{C}_{12}\text{H}_8\text{GeC}_{12}\text{H}_9^-$ monoanion ($1.9962(14)\text{--}2.0339(13)$ Å) and almost equidistant to the related separations found in compound **1**. The peripheral C2--C3 , C4--C5 , C8--C9 , and C10--C11 bonds in the dianion are notably shorter ($1.374(2)\text{--}1.381(2)$ Å) than other C--C bonds within the six-membered rings ($1.410(2)\text{--}1.451(2)$ Å). The central C6--C7 bond between six-membered rings is shorter in the dianion ($1.444(2)$ Å) than in **2** and **1** ($1.4795(18)$ Å and $1.492(3)$ Å, respectively).

The sodium Na1 and Na2 cations are coordinated to the aromatic system of the dianion with a substantial shift of alkali-metal ions towards the central five-membered ring. The Na1 ion is η^3 -bound to the C11 , C12 and Ge1 atoms with the corresponding $\text{Na1}\cdots\text{C}$ and $\text{Na1}\cdots\text{Ge1}$ separations of $2.618(2)/2.837(2)$ Å and $3.0244(19)$ Å, respectively. The Na2 cation is attached in an η^5 -mode to the central five-membered ring of the dianion ($\text{Na2}\cdots\text{C}$

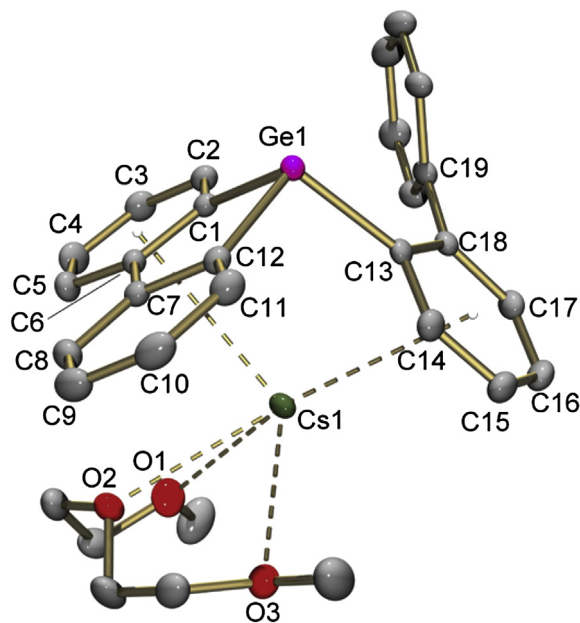


Fig. 2. Molecular structure (50% probability level) of **2** with all hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [$^\circ$]: Ge1--C1 $2.0082(14)$, Ge1--C12 $1.9962(14)$, Ge1--C13 $2.0339(13)$, C1--C2 $1.4010(19)$, C1--C6 $1.4151(17)$, C2--C3 $1.395(2)$, C3--C4 $1.392(2)$, C4--C5 $1.386(2)$, C5--C6 $1.4004(18)$, C6--C7 $1.4795(18)$, C8--C9 $1.491(2)$, Cs1--O1 $3.2142(14)$, Cs1--O2 $3.0880(12)$, Cs1--O3 $3.1755(15)$, $\text{Cs1}\cdots[\text{C1C2C3C4C5C6}]_{\text{centroid}}$ $3.4658(10)$, $\text{Cs1}\cdots[\text{C13C14C15C16C17C18}]_{\text{centroid}}$ $3.5481(11)$; C1--Ge1--C12 $84.36(5)$, C1--Ge1--C13 $99.43(5)$, C12--Ge1--C13 $98.86(5)$.

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