

Division of Synthetic Chemistry – Organoelement Chemistry –

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SCHMER, Alexander Universität Bonn, Germany, 1 May–30 June

VOLK, Niklas Universität Bonn, Germany, 1 June–31 July

Scope of Research

Organic chemistry has mainly developed with the use of second-row elements such as carbon, oxygen, and nitrogen, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds has been a dream for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of fundamental chemistry, and open the way to the more extensive application of main group chemistry.

KEYWORDS

Steric Protection

Kinetic Stabilization

Low-coordinated Species

Heteroatom

Transition Metal Complexes



Selected Publications

Sugahara, T.; Guo, J.-D.; Sasamori, T.; Nagase, S.; Tokitoh, N., Regioselective Cyclotrimerization of Terminal Alkynes Using a Digermyne, *Angew. Chem. Int. Ed.*, **57**, 3499-3503 (2018).

Fujimori, S.; Mizuhata, Y.; Tokitoh, N., Ru-Complexes of an Anionic Germabenzenyl Ligand, *Chem. Commun.*, **54**, 8044-8047 (2018).

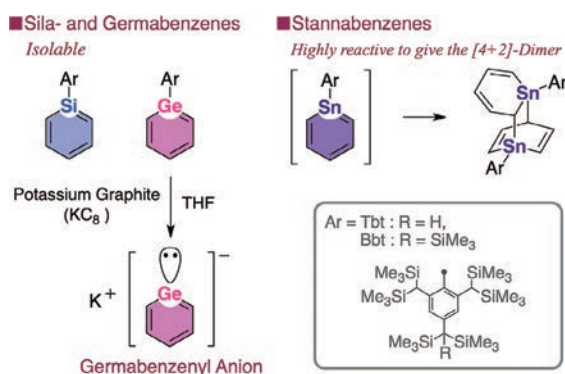
Sugahara, T.; Sasamori, T.; Tokitoh, N., 2,5-Digermaselenophenes: Germanium Analogues of Selenophenes, *J. Am. Chem. Soc.*, **140**, 11206-11209 (2018).

Mizuhata, Y.; Fujimori, S.; Noda, N.; Kanesato, S.; Tokitoh, N., Generation of Stannabenzene and Their Monomer-Dimer Equilibration, *Dalton Trans.*, **47**, 14436-14444 (2018).

Fujimori, S.; Mizuhata, Y.; Tokitoh, N., Stannabenzenylpotassium: The First Isolable Tin-containing Benzene Derivative, *Chem. Eur. J.*, **24**, 17039-17045 (2018).

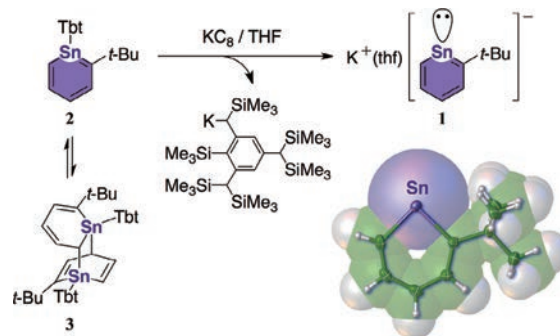
Stannabenzeyl Anion: Heavy Phenyl Anion

“Heavy benzenes” in which the carbon atom(s) of the benzene ring is replaced by high-period group 14 element(s), *that is*, “heavy element” (silicon, germanium, tin, and lead), have attracted much attention from the interest of its aromaticity experimentally and theoretically. However, these compounds are extremely high-reactive species, *e.g.*, silabenzene (HSiC_5H_5) in which one of the skeletal carbon atom of the benzene ring is replaced by a silicon atom, is known to decompose by self-oligomerization reaction even at very low temperature of $-200\text{ }^\circ\text{C}$. We have already succeeded in the synthesis and isolation of sila- and germabenzenes as stable compounds even at room temperature by taking advantage of kinetic stabilization afforded by a very bulky substituent, Tbt group, to prevent the self-oligomerization. These compounds are found to have “aromaticity” and unique electronic state. In addition, recently, we successfully synthesized the germabenzenyl anion as an isolable compound by the reaction of the corresponding isolated neutral germabenzene having a Tbt group on the germanium atom with potassium graphite (KC_8). However, in the tin case, stannabenzene having a Tbt or Bbt group on the tin atom are extremely reactive and lead to the formation of the [4+2] dimer of stannabenzene.



In this study, utilizing the successful method of synthesis of the germabenzenyl anion, we have reported the isolation and characterization of stannabenzeyl anion **1**. For the synthesis and isolation of a stable stannabenzene, we have introduced an additional substituent (*t*-butyl group) on the carbon atom adjacent to the tin atom. As the result of introducing *t*-butyl group, the equilibrium mixture of stannabenzene **2** and the corresponding dimer **3** could be obtained. We reasoned that the equilibrium mixture of the monomeric stannabenzene **2** and its dimer **3** would be a suitable precursor to gain the corresponding stannabenzeyl anion. The reaction of the equilibrium mixture with 2.1 equivalents of potassium graphite (KC_8) in THF successfully gave the first stable tin-containing phenyl anion de-

rivative, stannabenzeylpotassium $\text{K}^+(\text{thf})\cdot\mathbf{1}$. The properties revealed by X-ray crystallographic analysis, NMR, UV/Vis spectroscopy, and theoretical calculations showed the monomeric nature of **1** reflecting intermolecular electronic repulsion around the stannabenzeyl anion. It should be noted that this new stabilization strategy utilizing electronic repulsion is a promising method for isolating highly reactive species and that the stannabenzeyl anion is a potential intermediate for new organostannyl species.



Germanium Analogues of Selenophenes

We have reported the synthesis of 2,5-digermaselenophene **5** as purple crystals by the reaction of 1,2-digermacyclobutadiene **4**, which was obtained by the reaction of the stable digermene $\text{TbbGe}\equiv\text{GeTbb}$ with diphenylacetylene, with an equimolar amount of $(\text{Me}_2\text{N})_3\text{P}=\text{Se}$ in C_6D_6 at room temperature. X-Ray crystallographic analysis revealed that 2,5-digermaselenophene **5** exhibits a nonplanar structure with a *trans*-pyramidalized geometry of the five-membered $[\text{SeGe}_2\text{C}_2]$ ring. The UV/vis spectrum of **5** in hexane showed a strong absorption at $\lambda_{\text{max}} = 536\text{ nm}$ (ϵ 7800), which was assigned to the HOMO–LUMO transition based on TDDFT calculations (533.6 nm; $f = 0.2164$). Such an absorption at longer wavelength suggests that 2,5-digermaselenophenes could serve as promising building blocks for optoelectronic materials. Further investigation on the electrochemical properties of such digermaselenophenes is currently in progress.

