

Division of Synthetic Chemistry – Organoelement Chemistry –

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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



Recent Selected Publications

Garcia, J. A.; Yasui, Y.; Yukimoto, M.; Mizuhata, Y.; Tokitoh, N., Synthesis of a Kinetically Stabilized 2,2-Dihydrosilene, *Chem. Lett.*, **51**, 898-901 (2022).

Jun-i, Y.; Mizuhata, Y.; Tokitoh, N., Convergent Synthesis of *E*-Disilene by the Reduction of Diastereomerically Separable 1,2-Dichlorodisilanes, *Eur. J. Inorg. Chem.*, **2022(5)**, e202100962 (2022).

Oshiro, T.; Mizuhata, Y.; Tokitoh, N., 2-Germaazulene: Synthesis and Properties of 2-Heteraazulene Containing a Germanium Atom as a Skeletal Element, *Chem. Lett.*, **51**, 312-316 (2022).

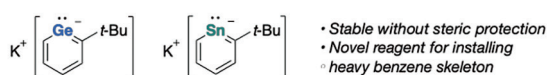
Fujimori, S.; Mizuhata, Y.; Tokitoh, N., Stannabenzylpotassium: The First Isolable Tin-Containing Benzene Derivative, *Chem. Eur. J.*, **24**, 17039-17045 (2018).

Mizuhata, Y.; Fujimori, S.; Sasamori, T.; Tokitoh, N., Germabenzylpotassium: A Germanium Analogue of a Phenyl Anion, *Angew. Chem. Int. Ed.*, **56**, 4588-4592 (2017).

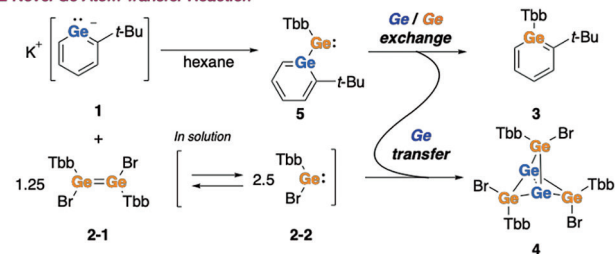
Novel Germanium-Atom-Transfer Reaction Using Germabenzenyl Anion

“Single atom” is regarded as the simplest building block of all molecules. Although its potential high versatility, limited generation method and extremely high reactivity prevent its application to organic synthesis. In recent years, the synthesis and isolation of “metallylone” which can be described as a central E(0) atom with Lewis bases have been reported. Some of the compounds are expected to be utilized as the synthon of group 14 elements. We have successfully synthesized the germa- and stannabenzenyl anions, the heavier Group 14 element (E = Ge, Sn) analogues of phenyl anion as an isolable compound. These germa- and stannabenzenyl anions can be used to introduce a heavy benzene skeleton, and we have already succeeded in the synthesis of several types of new germabenzenyl derivatives. Additionally, when germabenzenyl potassium **1** was reacted with dibromodigermene **2-1**, the novel germanium-atom-transfer reaction was observed. In the reaction, germa-benzene **3** and pentagerma[1.1.1]propellane **4** were obtained. According to the various additional experiments and quantum chemical calculations, it was revealed that the reaction underwent the Ge atom exchange on the germabenzenyl ring to the germylene-derived Ge atom and transfer of the extruded Ge atom to bromogermylene **2-2** *via* germabenzenylgermylene **5**. The findings of this research are expected to provide a novel synthetic method of molecular germanium clusters, which attract much attention due to their unique electronic and bonding situation as well as the similarity to the allotrope of elemental germanium.

■ Germa- and Stannabenzenyl Anions



■ Novel Ge Atom Transfer Reaction



Kinetically Stabilized 2,2-Dihydrosilene

Siliconcarbon doubly bonded compounds, also known as “silenes”, are generally difficult to isolate due to the instability caused by the poor 3p(Si)-2p(C) orbital overlap as well as high reactivity towards oligomerization driven by

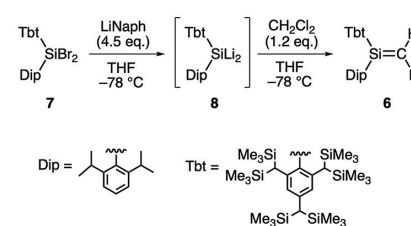
their polar, zwitterionic character ($\text{Si}^{\delta+}=\text{C}^{\delta-}$).

We succeeded in synthesis of 2,2-dihydrosilene **6**. The formation of **6** was confirmed by multinuclear NMR studies and extensive theoretical calculations. Although the successful identification of **6** by X-ray crystallographic analysis was achieved, it was not suitable for discussion because the obtained crystal contained trace amount. of an impurity.

Dibromosilane **7** was treated with 4.5 equiv. of lithium naphthalenide in THF at $-78\text{ }^{\circ}\text{C}$ to give the corresponding dilithiosilane **8**, to which was added 1.2 equiv. of CH_2Cl_2 to afford a crude product containing approximately 36% of **6**, as judged by ^1H NMR. Further purification of the crude product to isolate **6** proves to be extremely challenging at this stage despite several attempts to recrystallize the crude product with various solvents and conditions. Nevertheless, the characteristic NMR signals of **6** were sufficiently determined. ^{29}Si NMR spectrum of **6** showed a sharp resonance at 90.5 ppm, which is characteristic of a doubly bonded silicon atom. Furthermore, a signal at 95.4 ppm ($^1J_{\text{C-H}} = 146\text{ Hz}$) in the ^{13}C NMR was assigned to that of the sp^2 -carbon atom based on DEPT-135 measurement. In the ^1H NMR spectrum, two doublet signals were observed for the two geminal protons at around 4.76 ($^2J_{\text{H-H}} = 9.4\text{ Hz}$) and 4.55 ppm ($^2J_{\text{H-H}} = 9.4\text{ Hz}$). This assignment was further complemented with ^1H - ^{13}C HSQC.

The silene **6** was found to be stable in solution and in the solid state at room temperature for a long period of time, suggesting that the protection used was sufficient. Further investigations towards the properties of **6** as well as its reactivity are currently in progress.

■ Synthesis of 2,2-Dihydrosilene **6**



■ HSQC Spectrum of **6**

