

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



Selected Publications

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

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

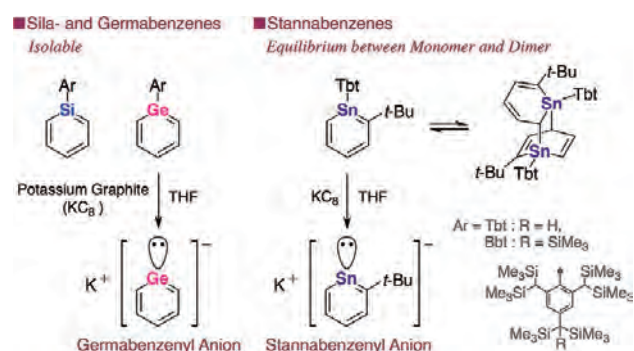
Fujimori, S.; Mizuhata, Y.; Tokitoh, N., A Mixed-anion System Consisting of a Germyl Anion and Anions Delocalized on Conjugated Carbon Ring Skeletons, *Chem. Eur. J.*, **25**, 6284-6289 (2019).

Yanagisawa, T.; Mizuhata, Y.; Tokitoh, N., Additive-free Conversion of Internal Alkynes by Phosphanylaluminanes: Production of Phosphorus/Aluminum Frustrated Lewis Pairs, *ChemPlusChem*, **85**, 933-942 (2020).

Kunzmann, R.; Omatu, Y.; Schnakenburg, G.; Espinosa Ferao, A.; Yanagisawa, T.; Tokitoh, N.; Streubel, R., A Synthetic Equivalent for Unknown 1,3-Zwitterions? – A K/OR Phosphinidenoid Complex with an Additional Si–Cl Function, *Chem. Commun.*, **56**, 3899-3902 (2020).

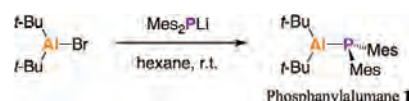
Heavy Phenyl Anion Species

“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 germa- and stannabenzenyl anions, the heavier Group 14 element ($\text{E} = \text{Ge}, \text{Sn}$) analogues of phenyl anion as an isolable compound by the reaction of the corresponding isolated neutral germa- or stannabenzene having a Tbt group on the germanium or tin atom with potassium graphite (KC_8). These germa- and stannabenzenyl anions are expected to be a useful reagent to introduce a heavy benzene skeleton, and we have already succeeded in the synthesis of several types of new germabenzenyl derivatives. The findings of this research are expected to contribute to the design and development of novel functional molecules incorporating a germabenzene ring.



Novel Phosphanylalumanes

The bonding between group 13 (E) and group 15 (Pn) elements formulated as $\text{R}_2\text{E}-\text{PnR}_2$ have attracted much attention due to their relationship, including the vacant p orbital on E and the lone-pair electrons on Pn. In this study, we have reported synthesis and reaction of novel λ^3, λ^3 -phosphanylalumane **1**, Al–P single-bond species, by the reactions of aluminum monohalides [$(t\text{-Bu})_2\text{AlBr}$] with Mes_2PLi .



In the reaction of **1** with phenylacetylene, deprotonation reaction proceeded, demonstrating the high Lewis basicity of **1**. In the reaction with internal alkynes on heating, **1** achieved the activation of internal alkynes. In addition, we found the reversible addition reaction to alkenes by the P–Al σ -bond species for the first time. In other words, the P–Al σ -bond of **1**, an P(III)–Al(III) compound, was cleaved by the addition to terminal alkenes ($\text{RCH}=\text{CH}_2$) in the case of the relatively small substituents ($\text{R}^1 = \text{H}, \text{Me},$ and $n\text{-Bu}$) to afford alkene-adducts **2**, and the P–Al bond of **1** is regenerated by the elimination of the alkenes on heating in the case of $\text{R}^1 = \text{Me}$ and $n\text{-Bu}$. The exposure of **2** ($\text{R}^1 = \text{H}$) to a CO_2 atmosphere afforded compound **3** with elimination of ethylene. We demonstrated the reactivity of **2** ($\text{R}^1 = \text{H}$) as a new C_2 -vicinal P/Al-based FLP.

