

# Division of Synthetic Chemistry – Organoelement Chemistry –

<http://boc.kuicr.kyoto-u.ac.jp/www/index-e.html>



Prof  
TOKITOH, Norihiro  
(D Sc)



Assoc Prof  
SASAMORI, Takahiro  
(D Sc)



Assist Prof  
MIZUHATA, Yoshiyuki  
(D Sc)



Assist Prof  
AGOU, Tomohiro  
(D Sc)



Techn Staff  
HIRANO, Toshiko



PD  
GUO, Jing-Dong  
(Ph D)



PD  
MAJHI, Paresh Kumar  
(Ph D)

## Students

MIYAMOTO, Hisashi (D3)  
NAGATA, Koichi (D3)  
AWANE, Hiroyuki (D2)  
HIRANO, Koki (D2)  
SUZUKI, Yuko (D1)

FUJIMORI, Shiori (M2)  
SUGAHARA, Tomohiro (M2)  
HONJO, Kazuma (M1)  
NAKANO, Tomohiro (M1)  
YANAGISAWA, Tatsuya (M1)

## Guest Scholars

KYRI, Andreas  
FAßBENDER, Jan

University of Bonn, Germany, 30 April-31 August  
University of Bonn, Germany, 23 August-4 September

## Guest Res Assoc

STREUBEL, Rainer  
MAYER, Ulrich F. J.

University of Bonn, Germany, 6 June-11 June  
Mayer Scientific Editing, Germany, 19 May-13 June

## 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 more extensive application of main group chemistry.

### KEYWORDS

Steric Protection    Kinetic Stabilization    Low-coordinated Species  
Heteroatom        Transition Metal Complexes



## Selected Publications

Sasamori, T.; Sugahara, T.; Agou, T.; Sugamata, K.; Guo, J.-D.; Nagase, S.; Tokitoh, N., Reaction of a Diaryldigermynes with Ethylene, *Chem. Sci.*, **6**, 5526-5530 (2015).

Agou, T.; Wasano, T.; Sasamori, T.; Guo, J.-D.; Nagase, S.; Tokitoh, N., Ring Expansion to 1-Bromo-1-alumacyclonona-2,4,6,8-tetraene by Insertion of Two Alkyne Molecules into the Al-C Bonds, *Angew. Chem. Int. Ed.*, **54**, 9568-9571 (2015).

Sasamori, T.; Sugahara, T.; Agou, T.; Guo, J.-D.; Nagase, S.; Streubel, R.; Tokitoh, N., Synthesis and Characterization of a 1,2-Digermabenzene, *Organometallics*, **34**, 2106-2109 (2015).

## Reactions of Diaryldigermynes with Ethylene and Acetylene

Recently, divalent or multiple-bonded compounds of heavier group 14 elements have received much attention as potential transition metal-free catalysts. We have investigated the reactivity of stable Ge–Ge triple-bond compounds, digermynes, with small molecules and reported their unique and transition metal-free transformations with ethylene and acetylene.

Reaction of the digermine BbtGe≡GeBbt (**1a**, Bbt = 2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-4-[C(SiMe<sub>3</sub>)<sub>3</sub>]-C<sub>6</sub>H<sub>2</sub>) with ethylene initially afforded the corresponding 1,2-digermacyclobutene **2**. Depending on the reaction conditions applied, further reaction of **2** with ethylene furnished two different reaction products: 1,4-digermabicyclo[2.2.0]hexane **3** or a bis(germiranyl)ethane **4**. Combined experimental and theoretical results suggested that **3** and **4** are the thermodynamic and kinetic reaction products, respectively.

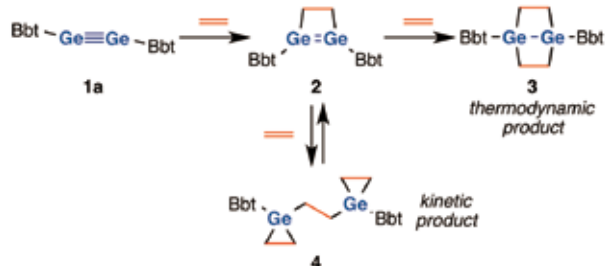


Figure 1. Reactions of digermine **1a** with ethylene.

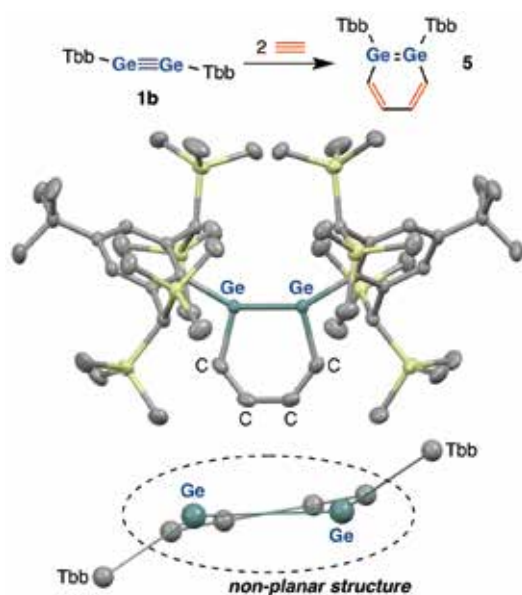


Figure 2. Reaction of digermine **1b** with acetylene and the structure of **5** (overhead and side views).

The reaction of the digermine TbbGe≡GeTbb (**1b**, Tbb = 4-*t*-Bu-2,6-[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>) with two equivalents of acetylene gave the 1,2-digermabenzene **5** as a stable, crystalline compound via a formal [2 + 2 + 2] reaction. The [Ge<sub>2</sub>C<sub>4</sub>] ring of **5** exhibited a nonplanar structure, wherein six π electrons are partially delocalized. Despite its non-planar structure, theoretical calculations suggested aromaticity for **5**, comparable to that of 1,2-disilabenzene.

## Formation of an Alumacyclononatetraene by Insertion of Two Alkyne Molecules into the Al–C Bonds of an Alumacyclopentadiene

The reaction of heteroles with compounds containing carbon–carbon multiple bonds, such as alkynes, is a useful method to construct new heterocyclic skeletons with specific structures and properties. Treatment of 1-bromo-2,3,4,5-tetraethylalumole (**6**) with 3-hexyne afforded the corresponding ring-expansion product 1-bromo-1-alumacyclonona-2,4,6,8-tetraene (**7**), accompanied by the formation of hexaethylbenzene. Compound **6** is, to our knowledge, the first example of structurally characterized, stable group 13 element-containing cyclononatetraene derivative. The AlC<sub>8</sub> nine-membered ring of **6** exhibited a highly twisted, nearly C<sub>2</sub>-symmetric structure both in the crystalline state and in solution. Deuterium-labeling experiments and DFT calculations on the reaction of **6** with 3-hexyne suggested that 1-bromo-1-alumacyclohepta-2,4,6-triene (**8**), which is formed by the insertion of one molecule of 1-hexyne into the Al–C bond of alumole **6**, is the key intermediate for the generation of **7** as well as hexaethylbenzene.

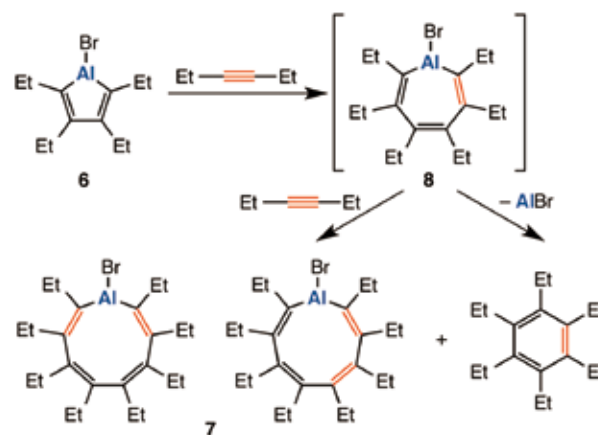


Figure 3. Reaction of bromoalumole **6** with 3-hexyne.