

Division of Synthetic Chemistry – Organoelement Chemistry –

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Prof
TOKITOH, Norihiro
(D Sc)



Assoc Prof
SASAMORI, Takahiro
(D Sc)



Assist Prof
MIZUHATA, Yoshiyuki
(D Sc)



Techn
HIRANO, Toshiko



Proj Res*
AGOU, Tomohiro
(D Sc)



PD
MORIKAWA, Satoshi
(D Eng)



PD
TSURUSAKI, Akihiro
(D Sc)



PD
MIYAKE, Hideaki
(D Sc)

* Assist Prof of
Pioneering
Research Unit for
Next Generation

Students

MIEDA, Eiko (D3)
KANEKO, Yoshikazu (D2)
SATO, Takahiro (D2)

SUGAMATA, Koh (D2)
SAKAGAMI, Michiyasu (D1)
MIYAMOTO, Hisashi (M2)

NODA, Naoya (M2)
SHIMIZU, Tomohiro (M2)
EGAWA, Yasunobu (M1)

Visitors

Prof MUGESH, Govindasamy
Prof APELOIG, Yitzhak
Prof ANG, How Ghee

Indian Institute of Science, India, 23–25 December 2009
Israel Institute of Technology, Israel, 23–25 April 2010
Nanyang Technological University, Singapore, 9–10 December 2010

Scope of Research

Organic chemistry has been developed as that of second-row elements such as carbon, oxygen, and nitrogen so far, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds have been one of "dreams" 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 not only fundamental chemistry but also opening the way to more extensive application of main group chemistry.

Selected Publications

Han JS, Sasamori T, Mizuhata Y, Tokitoh N: Reactivity of an Aryl-Substituted Silicon—Silicon Triple Bond: Reactions of a 1,2-Diaryldisilyne with Alkenes, *J. Am. Chem. Soc.*, **132**, 2546-2547 (2010).
Sato T, Mizuhata Y, Tokitoh N: 1,2-Dialkynyldisilenes: Silicon Analogues of (*E*)-Enediyne, *Chem. Commun.*, **46**, 4402-4404 (2010).
Tsurusaki A, Nagahora N, Sasamori T, Matsuda K, Kanemitsu Y, Watanabe Y, Hosoi Y, Furukawa Y, Tokitoh N: Synthesis, Structures, and Reactivity of Kinetically Stabilized Anthryldiphosphene Derivatives, *Bull. Chem. Soc. Jpn.*, **83**, 456-478 (2010).
Tanabe Y, Mizuhata Y, Tokitoh N: Synthesis and Structure of a Heavier Congener of Biphenyl: 1,1'-Disila-4,4'-biphenyl, *Organometallics*, **29**, 721-723 (2010).

KEYWORDS

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



Characteristic Reactivity of a Diaryl-substituted Disilyne

Recently, we have reported the synthesis and isolation of the first stable 1,2-diaryldisilyne, $\text{Bbt-Si}\equiv\text{Si-Bbt}$, along with its unique properties. Reaction of the disilyne with alkenes afforded compounds having several unique skeletons depending on the kind of alkenes. Moreover, the disilyne showed high reactivity with alkynes, and both polar and non-polar alkynes reacted with it to give the corresponding 1,2-disilabenzenes as the major product. Crystal structure analysis showed that the central ring of the 1,2-disilabenzene was almost planar, and most notably, the Si-Si bond has significant *trans*-bent character. Evidence supporting its aromatic structure was collected by both experimental and theoretical means.

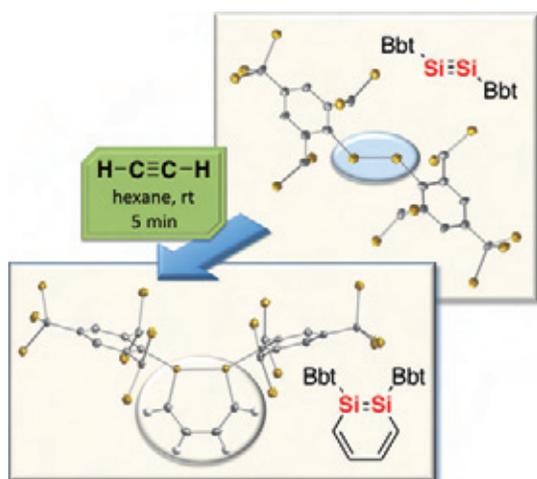
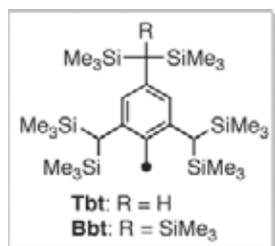


Figure 1. Generation of 1,2-Disilabenzene by the Reaction of a Disilyne with Acetylene.

Synthesis and Properties of 1,1'-Disila-4,4'-biphenyl

The 1,1'-disila-4,4'-biphenyl, the first molecule bearing directly connected two sila-aromatic rings, was synthesized by utilizing the steric protection afforded by Tbt groups and characterized by its spectroscopic and X-ray crystallographic data. Its two SiC_3 rings are twisted with respect to each other with a dihedral angle of ca. 41° . The parent biphenyl has a coplanar structure due to packing forces in the crystalline state, and its dihedral angles in solution or in the gas phase are ca. 45° . In the case of the disilabiphenyl, extremely bulky Tbt groups prevent intermolecular interactions between the disilabiphenyl units, resulting in the retention of a distorted structure even in the solid state. Its UV-vis spectrum showed not only a red shift but also a 6-fold increase in absorbance of the longest absorption

maximum in its electronic spectra in comparison with those of Tbt-substituted silabenzene, indicating that the concept of conjugation through the single bond connecting two aromatic rings is applicable even in the sila-aromatic systems.

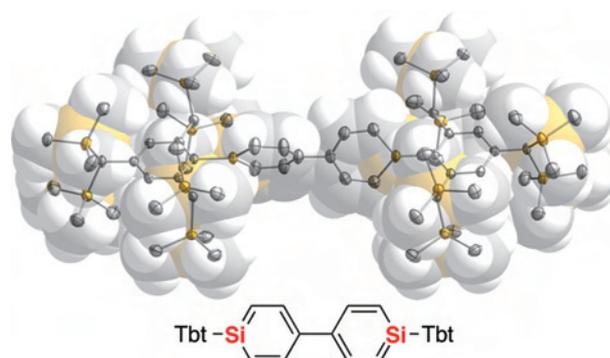


Figure 2. Structure of 1,1'-Disila-4,4'-biphenyl.

Synthesis and Properties of 1,2-Dialkynyldisilenes

Recently, several new disilene ($>\text{Si}=\text{Si}<$) systems have been designed and investigated to evaluate the conjugation between the Si=Si unit and the connected aryl sp^2 -carbon conjugated systems. Although those disilenes exhibited optically and electrochemically unique properties, such π -conjugated systems are structurally limited. Therefore, the synthesis and isolation of the alkynyl-substituted disilenes, the silicon analogues of enedynes, are attractive from the viewpoint of elucidation of the conjugation between the Si=Si and sp-carbon units. We synthesized and isolated the first stable 1,2-dialkynyldisilenes and elucidated their structures using X-ray crystallography. In their UV-vis spectra, the absorption maximum of phenylethynyl-substituted disilene was more red-shifted than that of trimethylsilylethynyl-substituted one, indicating the π -conjugation between the Si=Si bond and phenyl groups through the $\text{C}\equiv\text{C}$ bonds. Notwithstanding the different energy levels of p-orbitals between Si=Si and $\text{C}\equiv\text{C}$ bonds, these findings showed that conjugation was possible between Si=Si and $\text{C}\equiv\text{C}$ units.

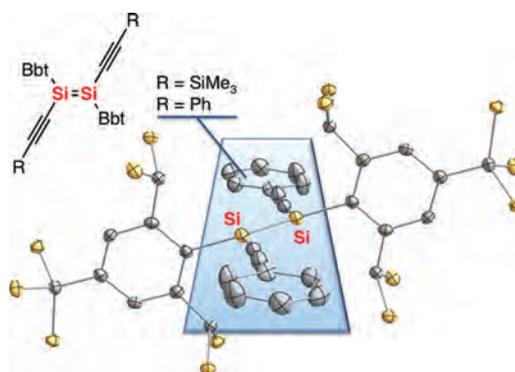


Figure 3. Structure of 1,2-Dialkynyldisilene.