

Division of Synthetic Chemistry - Organoelement Chemistry -

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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. Organic synthesis mediated by biocatalysts is also studied.

Research Activities (Year 2004)

Presentations

Synthesis, Structures and Reactivities of Kinetically Stabilized Germaaromatic Compounds, Tokitoh N, Nakata N, Takeda N, The 11th International Conference On the Coordination and Organometallic Chemistry of Germanium, Tin and Lead, 27 June - 2 July 2004, Santa Fe, New Mexico, U.S.A.

Synthesis of Polythioethers Tethered with Bulky Aryl Groups and Their Complexation with Late-transition Metals, Tokitoh N, Shimizu D, Takeda N, Sasamori T, The 21st International Symposium on the Organic Chemistry of Sulfur, 4 - 9 July 2004, Madrid, Spain.

Synthesis of Silylboranes by the Reactions of a Bulky Silylene with Boron Compounds and Their Application to the Synthesis of a Borylsilyl Anion, Takeda N, Kajiwara T, Sasamori T, Tokitoh N, Heron Island Conference on Reactive Intermediates & Unusual Molecules, 17 - 23 July 2004, Queensland, Australia.

Syntheses and Properties of Transition Metal Complexes of Kinetically Stabilized Metallaaromatic Species of

Heavier Group 14 Elements, Tokitoh N, The 36th International Conference on Coordination Chemistry, 18 - 23 July 2004, Merida, Mexico.

Generation and Reactions of Overcrowded Dimetal-lastannane Derivatives, Tajima T, Takeda N, Sasamori T, Tokitoh N, The 7th International Conference on Heteroatom Chemistry, 20 - 25 August 2004, Shanghai, P. R. China.

Grants

Tokitoh N, Studies on the synthesis, structure, properties, and functions of novel aromatic compounds containing heavier group 14 elements, Grant-in-Aid for Scientific Research (A)(2), 1 April 2002 - 31 March 2005.

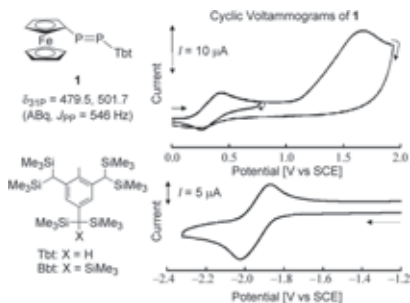
Tokitoh N, Synthesis of dynamic complexes containing heteroatoms by taking advantage of kinetic stabilization, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2002 - 31 March 2006.

Tokitoh N, Synthesis of metallacyclopentadienes derivatives by using bulky substituents and the elucidation of their properties, Grant-in-Aid for Exploratory Research, 1

Synthesis of the First Stable Ferrocenyl-diphosphene and Elucidation of its Redox Behavior

A number of examples of kinetically stabilized diphosphenes (RP=PR), and diarsenes (RAS=AsR) have been isolated and characterized. In addition, we have reported the synthesis of novel doubly bonded systems between heavier group 15 elements, i.e., distibene (RSb=SbR), dibismuthene (RBi=BiR), etc. by taking advantage of efficient steric protection groups, Tbt and Bbt groups. Recently, much attention has been paid to redox-active species containing a diphosphene unit in the field of molecular electronics and switches. Although generation of a ferrocenyl diphosphene, Mes*P=PFC (Fc = ferrocenyl, Mes* = 2,4,6-tri-*t*-butylphenyl), has been reported by Pietschnig and Niecke, detailed studies have not been fully accomplished due to its instability in solution. Recently, we succeeded in the synthesis of a new ferrocenyl diphosphene TbtP=PFC and revealed its unique multi-switchable electrochemical properties.

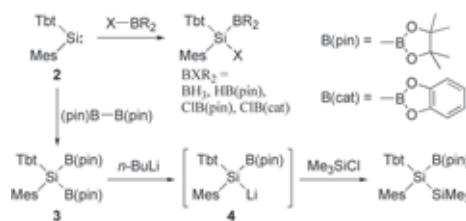
Diphosphene **1** was synthesized by the dehydrochlorination reaction of Tbt-P(H)-P(Cl)-Fc with DBU. In sharp contrast to Mes*P=PFC, **1** is very stable in the solid state and even in solution. The molecular structure of **1** was confirmed by NMR spectra and X-ray crystallographic analysis, which evidenced the P=P double-bond character



of **1**. The cyclic voltammograms of **1** showed the reversible reduction and oxidation couples at -1.91 and $+0.34$ V vs. SCE, respectively. The electrochemical results for **1** were reasonably supported by the DFT calculations, which suggested that the LUMO and HOMO orbitals should be mainly π^* orbital of the diphosphene moiety and d orbitals of the iron(II) atom, respectively.

Unprecedented Insertion Reaction of a Silylene into a B-B Bond and Generation of a Novel Borylsilyl Anion

Borylsilyl anions, i.e., silicon analogues of boron-stabilized carbanions, have been completely unprecedented species. We have recently developed a novel synthetic method for silylboranes derivatives based on the unique insertion reactions of an overcrowded silylene **2** [Tbt(Mes)Si:] into B-X (X = H or halogen) bonds. In addition, the synthesis of a diborylsilane, Tbt(Mes)Si[B(pin)]₂ (**3**, pin = pinacolato) was achieved via the insertion reaction of **2** with bis(pinacolato)diboron. These reactions are quite important from the standpoints of development on a new synthetic method for borylsilanes and elucidation of reactivities of silylenes. Furthermore, the reaction of **3** with *n*-BuLi resulted in the generation of borylsilyl anion **4**, which could be trapped by chlorotrimethylsilane. It is noteworthy that the formation of **4** is the first example for the generation of a borylsilyl anion and that a diborylsilane is shown to be a possible precursor for a borylsilyl anion.



April 2003 - 31 March 2004.

Kawai Y, Development of methods for the determination of the absolute configuration of chiral compounds using a novel crystalline agent, Grant-in-Aid for Scientific Research (C)(2), 1 April 2003 - 31 March 2005.

Takeda N, Synthesis of double bond species between group 10 metals and chalcogens and the elucidation of their properties, Grant-in-Aid for Young Scientists (B), 1 April 2003 - 31 March 2005.

Sasamori T, Synthesis of novel π electron conjugated systems containing heavier group 14 and 15 elements and the elucidation of their properties, Grant-in-Aid for Young

Scientists (B), 1 April 2004 - 31 March 2006.

Nagahora N, Syntheses, structure, and properties of novel low-coordinated species of heavier main group elements, Grant-in-Aid for JSPS Fellows, 1 April 2003 - 31 March 2005.

Awards

Kajiwaru T, Shinohara A, The Best Oral Presentation Award, The 84th Annual Meeting of the Chemical Society Japan, 27 April 2004.

Sugiyama Y, The Best Poster Award, The 17th Symposium on Fundamental Organic Chemistry, 25 September 2004.