Division of Synthetic Chemistry
- Organoelement Chemistry -

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Visitor

Prof JUTZI, Peter University of Bielefeld, Germany, 23 October–26 November 2007

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 reactivity 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 2007)

Publications

Sasamori T, Matsumoto Te, Takeda N, Tokitoh N: Synthesis and Properties of a Rhodium Complex Having a Novel *β*-Ketophosphenato Ligand, a Heavier Congener of a *β*-Ketoiminato Ligand, *Organometallics*, **26**, 3621-3623 (2007).

Nagahora N, Sasamori T, Watanabe Y, Furukawa Y, Tokitoh N: Kinetically Stabilized 1,1'-Bis[(*E*)-diphosphenyl]ferrocenes; Syntheses, Structures, Properties, and Reactivity, *Bull. Chem. Soc. Jpn.*, **80**, 1884-1900 (2007).

Presentations

Synthesis and Characterization of the First Stable Stannanetellone, Tokitoh N, The 10th International Conference on the Chemistry of Selenium and Tellurium (ICCST-10), Łódź, Poland, 24 June 2007 (invited).

Recent Progress in the Chemistry of Multiply Bonded Germanium and Tin Compounds, Tokitoh N, Mizuhata Y, Sugiyama Y, Tajima T, Inamura K, Sasamori T, The 12th International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin and Lead (ICCOC-GTL-12), Galway, Ireland, 13 July 2007 (invited).

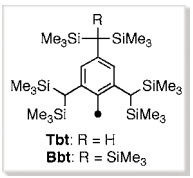
Grants

Tokitoh N, Sasamori T, Nagahora N, Mizuhata Y, The Chemistry of Unsaturated Compounds of Heavier Main Group Elements: Pursuit of Novel Properties and Functions, Grant-in-Aid for Creative Scientific Research, 1 April 2005–31 March 2009.

Sasamori T, Construction of Novel Extended π-Electron Conjugated Systems Containing Heavier Main Group Elements, Grant-in-Aid for Young Scientists (B), 1 April 2006–31 March 2008.

Sasamori T, Construction of Novel d-π Electron Conjugated Systems Containing Heavier Main Group Elements and Transition Metals and Elucidation of their Properties. Grant-in-Aid for Science Research on Priority Areas

Synthesis of Bis[(*E*)-diphosphenyl]ferrocenes



Low-coordinated species of heavier group 15 elements have attracted much interest due to their low-lying π* levels compared with diazenes (–N=N–) from two reasons: (i) their electrochemical properties and (ii) coordination ability toward transition metals. We have already reported the synthesis and isolation of many examples of "heavy" diazenes (–P=P–, –Sb=Sb–, –Bi=Bi–, and so on) by taking advantage of efficient steric protection groups, Tbt and Bbt, and revealed their unique characters based on their molecular structures, spectroscopic properties, and reactivities. Recently, we have succeeded in the syntheses, structural characterization, and properties of the first 1,10-bis[(*E*)-diphosphenyl]ferrocenes **1** kinetically stabilized by Tbt or Bbt groups. The ligand-exchange reactions of **1** with group 6 metal carbonyl complexes resulted in the formation of complexes **2** along with unique *E*-to-*Z* isomerization of the diphosphene moieties.

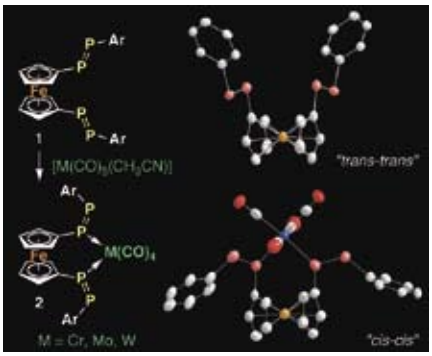


Figure 1. Complexation of **1** and the structures of **1** and **2** (M = W).

Generation of Silabenzene Anion Radical

The chemistry of aromatic compounds containing a heavier group 14 element, *i.e.*, "heavy aromatics," is important to understand the concept of "aromaticity", which has been one of the fascinating topics in organic chemistry. We have succeeded in the synthesis and isolation of kinetically stabilized sila-, germa-, and stannaaromatic compounds stabilized by Tbt group, and revealed their considerable aromaticity based on their molecular structures, spectroscopic properties, and reactivities. The comparison of redox properties between heavy aromatics and the corresponding aromatic hydrocarbons and the structural features of the corresponding radical species of heavy aromatics should be of great interest and importance in terms of their unique properties. An electrochemical study of kinetically stabilized silabenzene **3** revealed that the reduction potential of **3** is –2.96 V (vs. Cp_2Fe/Cp_2Fe^+) and lower than that of naphthalene. The anion radical species **4** was generated by the one-electron reduction using lithium naphthalenide and characterized by ESR spectroscopy.

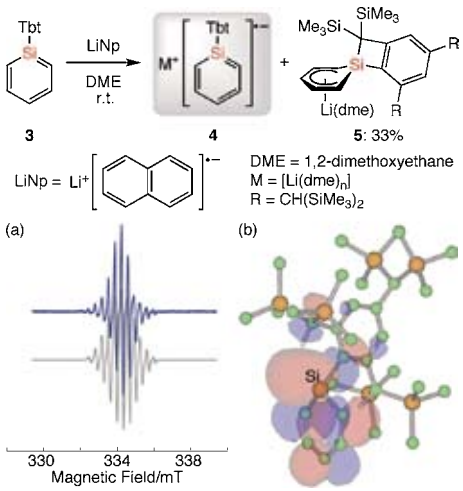


Figure 2. Generation of silabenzene anion radical **4**. (a) Observed (up) and simulated (below) ESR spectra of **4**. (b) Optimized structure of **4** and its SOMO.

"Synergy of Elements", 1 April 2007–31 March 2008.

Nagahora N, Study on Development of Novel Molecular Devices Bearing Metallocene and Double Bonds between Heavier Group 15 Elements, Kinki Invention Center, 1 April 2007–31 March 2008.

Mizuhata Y, Grant-in-Aid for Young Scientists (Kyoto Univ.), Synthesis and Properties of Novel Stannaaromatic Compounds by Taking Advantages of Kinetic Stabilization, 1 April 2006–31 March 2007.

Awards

Matsumoto Ta, The Best Poster Award, 2007 KAIST-Kyoto University Chemistry Symposium, 27 January 2007.

Mizuhata Y, Inoue Research Award for Young Scientists, 5 February 2007.

Sasamori T, Daiichi-Seiyaku Award in Synthetic Organic Chemistry, Japan, 22 February 2007.

Tanabe T, The Student Lecture Award, The 87th Annual Meeting of the Chemical Society of Japan, May 2007.

Hamaki H, The Student Lecture Award, The 87th Annual Meeting of the Chemical Society of Japan, May 2007.

Tanabe T, OMCOS Poster Prize in Organometallic Chemistry, The 14th IUPAC Symposium on Organometallic Chemistry Directed towards Organic Synthesis, 4 August 2007.

Nagahora N, Sasamori T, Tokitoh N, BCSJ Award (The Best Article of the Month), 15 October 2007.