Division of Synthetic Chemistry - Organoelement Chemistry -

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Visitors

Prof KOST, Daniel Ben-Gurion University of the Negev, Israel, 15 October 2009 Prof ERKER, Gerhard Westfälische Wilhelms-Universität, Germany, 18 September 2009 Prof GATES, Derek P. University of British Columbia, Canada, 31 August 2009 Prof JONES, William D. University of Rochester, USA, 25-26 August 2009 Prof ARNASON, Ingvar University of Iceland, Iceland, 7 April-22 May 2009

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.

Research Activities (Year 2009)

Publications

Mizuhata Y, Sasamori T, Tokitoh N: Stable Heavier Carbene Analogues, Chem. Rev., 109, 3479-3511 (2009). Yuasa A, Sasamori T, Hosoi Y, Furukawa Y, Tokitoh N:

Synthesis and Properties of Stable 1,2-Bis(metallocenyl)disilenes: Novel d- π Conjugated Systems with a Si=Si Double Bond, Bull. Chem. Soc. Jpn., 82, 793-805 (2009). Tsurusaki A, Sasamori T, Tokitoh N: [4+2] Cycloaddi-

Stable 1,2-Bis(metallocenyl)disilenes: Novel $d-\pi$ Conjugated Systems with a Si=Si Unit

1,2-Bis(metallocenyl)disilenes (metal: Fe or Ru) were synthesized for the first time and were characterized by spectroscopic and X-ray crystallographic analyses. On the basis of cyclic voltammograms, iron derivative was found to be a stable five-electron redox system with four steps, while ruthenium one showed four-step redox couples with four electrons. The UV/vis spectra and theoretical calculations for these disilenes suggested that they should be novel $d-\pi$ conjugated systems containing a disilene unit.

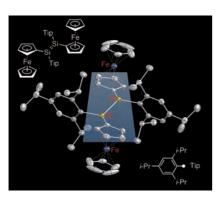
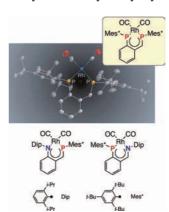


Figure 1. Structure of 1,2-Bis(ferrocenyl)disi

Syntheses of Phosphorus Analogues of Schiff Base and Their Coordination Chemistry

Schiff-base type N,P- or P,P-chelating ligands, phosphorus analogues of imino–anilido ligands, were designed and synthesized as a new type of ligands toward transition metals, and the rhodium–carbonyl complexes bearing the novel imino–phosphido, phosphaalkenyl–anilido, and phosphaalkenyl–phosphido ligands were synthesized as stable crystalline compounds. Their structures were definitively revealed by X-ray crystallographic analysis, showing



the unique electronic features of the ligands. In addition, the effective transinfluence of the phosphorus atom was suggested on the basis of the structural parameters and spectroscopic features of the isolated complexes.

Figure 2. Rhodium Complexes Bearing Phosphorus Analogues of Schiff Base

tion of 9-Anthryldiphosphene with Electron-Deficient Olefins: Transformation of a Diaryldiphosphene to Alkylaryldiphosphenes, *Organometallics*, **28**, 3604-3607 (2009).

Presentations

New Progress in the Chemistry of Silaaromatic Compounds, Tokitoh N, 14th Japan-Korea Joint Symposium on Organometallic and Coordination Chemistry, Nagoya, Japan, 9 October 2009 (invited).

Synthesis and Properties of Novel Functionalized Disilenes and a Stable Diaryldisilyne, Tokitoh N, 5th European Silicon Days, Vienna, Austria, 21 September 2009 (plenary).

Synthesis and Structures of Novel Rhodium Complexes Bearing a Schiff-base Type N,P-Chelating Ligands, Sasamori T, Matsumoto T, Tokitoh N, 12th International Symposium on Inorganic Ring Systems, Goa, India, 19 August 2009 (invited).

Some New Reactions of a Kinetically Stabilized Silabenzene and Isolation of a Stable 1,1'-Disila-4,4'-biphenyl, Tokitoh N, Tanabe Y, Mizuhata Y, 13th International Symposium on Novel Aromatic Compounds, Luxembourg, 22 July 2009 (invited).

Grants

Tokitoh N, Sasamori T, 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 2010.

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 "Synergy of Elements", 1 April 2007–31 March 2010.

Mizuhata Y, Construction of Novel Silicon–Silicon Double-Bond Compounds Bearing Alkynyl Substituents, Grant-in-Aid for Young Scientists (B), 1 April 2009–31 March 2012.

Awards

Sasamori T, Progress Award in Silicon Chemistry, Japan, The Society of Silicon Chemistry, Japan, 31 October 2009.

Mieda E, The Best Poster Award, The 13th Symposium of the Society of Silicon Chemistry, Japan, 31 October 2009.

Yuasa A, Sasamori T, Tokitoh N, BCSJ Award, The Chemical Society of Japan, July 15, 2009.

Yuasa A, CSJ Student Presentation Award 2009, The 89th Annual Meeting of the Chemical Society of Japan, 13 April 2009.