

Division of Synthetic Chemistry - Organoelement Chemistry -

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Visitor

Prof DRIESS, Matthias Technical University Berlin, Germany, 30 November - 1 December 2005

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 2005)

Presentations

Some Unique Reactions of Kinetically Stabilized Si-aromatic Compounds with Haloalkanes and Polyaromatic Hydrocarbons, Tokitoh N, Shinohara A, Takeda N, Sasamori T, 14th International Symposium on Organosilicon Chemistry (ISOS XIV), Würzburg, 31 July - 5 August 2005 (invited).

New Aspects in the Chemistry of Kinetically Stabilized Dipnictenes, Tokitoh N, Mieda E, Nagahora N, Sasamori T, Takeda N, Takagi N, Nagase S, 2005 International Chemical Congress of Pacific Basin Societies (Pacifichem 2005), Honolulu, 15 - 20 December 2005 (invited).

Grants

Tokitoh N, Takeda N, Sasamori T, 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.

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.

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.

Sasamori T, Synthesis of Novel Molecular Wire with π Electron Systems Containing Silicon and Phosphorus, Kinki Invention Center, 1 April 2005 - 31 March 2006.

Tajima T, Synthesis of Novel Chemical Species Containing a Heavier Group 14 Element by Taking Advantage of Dilithiometalanes Bearing a Bulky Substituent and Their Properties, Grant-in-Aid for JSPS Fellows, 1 April

Synthesis of the First Stable Stannaaromatic Compounds: 2-Stannanaphthalene

The chemistry of aromatic compounds containing a heavier group 14 element 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 of kinetically stabilized sila- and germaaromatic compounds by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), and revealed their considerable aromaticity based on their molecular structures, spectroscopic properties, and reactivities. Recently, we have succeeded in the synthesis of the first stable neutral stannaaromatic compound, 2-stannanaphthalene **1**. 2-Stannanaphthalene **1** was synthesized by the dehydrobromination of the corresponding bromostannane **2** with LDA in hexane at -40°C . The NMR chemical shifts indicate the ring current effect on the 2-stannanaphthalene ring of **1**. The X-ray crystallographic analysis of **1** revealed the planar geometry of the 2-stannanaphthalene ring. All experimental results supported the aromatic character of **1**. In addition, 2-stannanaphthalene **1** was found to behave as an η^6 -arene ligand in the ligand exchange reaction with $[\text{Cr}(\text{CH}_3\text{CN})_3(\text{CO})_3]$ giving the first stable η^6 -2-stannanaphthalene chromium complex **3**.

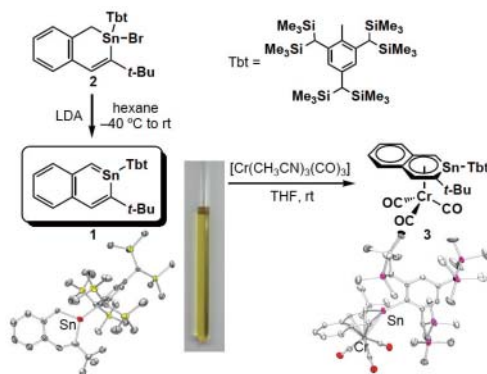


Figure 1. Syntheses of the first stable 2-stannanaphthalene **1** and its η^6 - $\text{Cr}(\text{CO})_3$ complex **3**.

2004 - 31 December 2005.

Mizuhata Y, Synthesis, Structure, and Properties of Kinetically Stabilized Tin-carbon Double-bond Compounds, Grant-in-Aid for JSPS Fellows, 1 April 2005 - 31 March 2007.

Awards

Sasamori T, Inoue Research Award for Young Scientists, Studies on the Synthesis of Low-coordinated Species of Heavier Group 15 Elements Utilizing Kinetic Stabilization, 4 February 2005.

Shinohara A, Takeda N, Sasamori T, Tokitoh N, BCSJ

Synthesis and Applications of New Polythioether Ligands Tethered with Bulky Substituents

The chemistry of cyclic polythioether ligands has been extensively studied, and it has been revealed that they can stabilize the metals with unusual valency, such as trivalent palladium. Acyclic polythioether ligands are also expected to show similar properties, however, the chemistry of acyclic polythioether ligands has been less explored.

New polythioether ligands **4** and **5** tethered with two Tbt groups were synthesized. Reactions of **4** with Na_2PdCl_4 gave a distorted octahedral palladium complex **6**. The X-ray structural analysis of **6** showed weak but distinct interactions between the terminal sulfur atoms and the central palladium atom ($\text{S}\cdots\text{Pd}$ distances: $3.1755(8)$ Å).

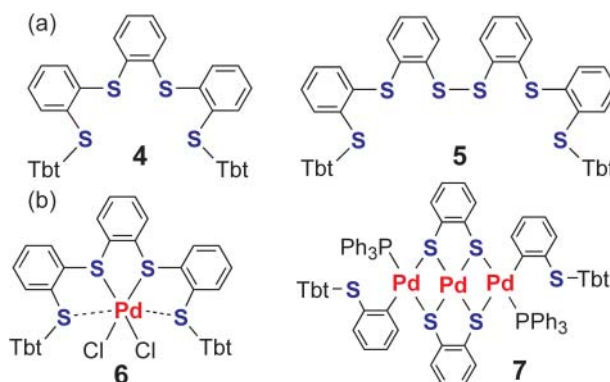


Figure 2. (a) Novel cyclic polythioether ligands **4** and **5**. (b) Structure of the PdCl_2 complex **6** and Pd trinuclear complex **7**.

Ligand **5** reacted with 3 molar amounts of $[\text{Pd}(\text{PPh}_3)_4]$ to give the trinuclear complex **7** in 58% yield. The formation of **7** can be explained in terms of the initial insertion of the $\text{Pd}(0)$ atom to the S–S bond of **5** and the successive insertion of the two $\text{Pd}(0)$ atoms to the C–S bonds.

Award (The Best Article of the Month), Synthesis of Kinetically Stabilized 1-Silanaphthalenes and Their Properties, 15 June 2005.

Mizuhata Y, The Best Poster Award, Synthesis of a Stable 2-Stannanaphthalene and Its Structure and Properties, 10th Symposium of the Society of Silicon Chemistry, Japan, 28 October 2005.

Takeda N, The ICR Award for Young Scientists, “Synthesis of Novel Organosilicon Species by Taking Advantage of a Silylene Bearing Bulky Substituents and the Elucidation of Their Properties”, 2 December 2005.