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.

Scope of Research

Research Activities (Year 2007)

Publications


Presentations


Grants


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.

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 stanna-aromatic 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. Cp₂Fe/Cp₂Fe⁺) 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.


Awards
Mizuhata Y, Inoue Research Award for Young Scientists, 5 February 2007.
Nagahora N, Sasamori T, Tokito N, BCSJ Award (The Best Article of the Month), 15 October 2007.