Research Activities (Year 2002)

Presentations

Chalcogenation reaction of kinetically stabilized doubly bonded systems between heavier group 15 elements, Sasamori T, Takeda N, Tokitoh N, 20th International Symposium on the Organic Chemistry of Sulfur, 14 - 19 July, Flagstaff, USA.


Grants

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


Takeda N, Synthesis of novel multiple-bond species of silicon by taking advantage of silylene–isocyanide complexes and
Synthesis and properties of the first stable germabenzene

In recent decades, much attention has been focused on the chemistry of \([4n+2]\)\(\pi\)-electron ring systems containing heavier group 14 elements. However, no synthesis and isolation of these compounds as stable molecules had been reported until quite recently due to their extremely high reactivity. We have recently succeeded in the synthesis and characterization of the first stable silabenzene, 2-silanaphthalene, 9-silaanthracene, and 2-germanaphthalene by taking advantage of an efficient steric protection group, Tbt group (vide infra). These successful results naturally prompted us to extend this method to the synthesis of a germabenzene, the most fundamental germaaromatic compound having a simple 6 \(\pi\)-electron ring system.

The first stable germabenzene 1 was successfully synthesized by the reaction of the corresponding chlorogermane 2 with LiN(\(i\)-Pr)\(_2\) in THF. Although the structural and spectroscopic data and theoretical calculations showed that 1 had aromaticity, in the reactions with MeOH, MesCNO, styrene, phenylacetylene, and 2,3-dimethyl-1,3-butadiene, 1 underwent 1,2- and/or 1,4-addition to the 1-germabuta-1,3-diene moiety reflecting the extremely high reactivity of the Ge–C double bond.

The reactions of 1 with M(CH\(_3\)CN)\(_3\)(CO)\(_3\) \([M = Cr, Mo]\) gave the corresponding \(\eta^5\)-germabenzene complexes of group 6 metals 3. These results are very interesting because 3 is the first \(\eta^5\)-germabenzene complexes and these reactions are the first examples showing the aromatic character of germabenzene from the viewpoint of reactivity.

Synthesis, structures, and properties of novel doubly bonded systems between heavier group 15 elements

Recently, there has been much interest in compounds with a double bond between heavier group 15 elements.

The first stable distibenes and dibismuthenes were successfully synthesized by taking advantage of efficient steric protection groups, Tbt and Bbt groups. The crystallographic analysis, and spectroscopic studies of these stable dipnictenes and theoretical calculations of model compounds led to the systematic comparison of structural parameters and physical properties for all homonuclear doubly bonded systems between heavier group 15 elements.

In addition, condensation of Mes*PH\(_2\) (Mes = 2,4,6-tri-\(t\)-tert-butylphenyl) with BbtBiBr\(_2\) using 1,8-diazabicyclo[5.4.0]undec-7-ene as a base afforded the first stable phosphabismuthene Mes*P=BiBbt, which is also the first stable double-bond compound between the third and sixth row main group elements.