ORGANOHETERATOM CHEMISTRY

Annual Research Review

(1) "Synthesis and Thermolysis of Heteracyclobutanes Containing Highly Coordinate Main Group Elements"

In the course of our study on heteracyclobutanes containing a highly coordinate main group element, we have synthesized the first tricoordinate 1,2-iodoxetane 1 and tetracoordinate 1,2-selenazetidine 2. A novel ligand was designed for the synthesis of 1. It was found that 1 has a dimeric structure based on intermolecular interaction between iodine and oxygen of the four-membered ring in the solid state. We revealed the thermal reactivity of 1. On the other hand, it was found by X-ray analysis that 2 has a pseudo-trigonal bipyramidal structure with oxygen and nitrogen atoms at the apical positions. Thermolysis of 2 afforded the corresponding aziridine, indicating that 2 has the reactivity similar to that of the oxaselenetane. Furthermore, we have succeeded in the synthesis and isolation of pentacoordinate 1,2-azaphosphatranes 3 by the reaction of an iminophosphorane bearing the Martin ligand with the corresponding alkyne.


(2) "Development and Applications of Novel Bowl-shaped Molecules"

S-nitrosothiols (R-SNO) have been attracting attention in view of their role as potential biocatalysts and reagents for the storage and transport of nitric oxide (NO). By taking advantage of a newly-designed bowl-type steric protection group, we have succeeded in the synthesis of the first stable aromatic S-nitrosothiol 4. X-ray crystallographic analysis revealed that the C-S-N-O linkage of 4 adopts the syn conformation, which is in agreement with the results of theoretical calculation. High thermal stability of 4 indicated that the bowl-type substituent efficiently suppresses its bimolecular decomposition.


(3) “Synthesis of 5-Carbaphosphatranes”

The characteristics of silatranes and phosphatranes, which are known as bioactive species and basic catalysts, respectively, are strongly attributable to the transannular dative bond of nitrogen to the central atom. Replacement of the dative bond by a covalent bond would supply different reactivity and structure to the compound. From such a viewpoint, we have synthesized 5-carbaphosphatranes 5 as the first main group arane derivatives bearing a 1-5 covalent bond, which has the perfectly “anti-apicophilic” arrangement.


(4) "Reversible Photocontrol of the Coordination Number of Silicon in Highly Coordinate Organosilicon Compounds"

Chemical properties of silicon compounds are strongly affected by the coordination number of the central silicon atom. We have synthesized silicon compounds 6 with an azo group as both chromophore and coordination site and demonstrated reversible photocontrol of the coordination number between 5 and 6 by photo-isomerization of the azo group.


A. Original Papers


17) K. Goto, (Y. Hino), Y. Takahashi, T. Kawashima, (G. Yamamoto), (N. Takagi) and (S. Nagase): "Synthesis,


C. Proceedings


D. Books