

# ORGANOHETEROATOM CHEMISTRY

## Annual Research Review

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

In the course of our study on heterocyclobutanes containing a highly coordinate main group element, we have synthesized the first tricoordinate 1,2-iodoxetane **1** and tetracoordinate 1,2-selenazetidene **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-azaphosphetene **3** by the reaction of an iminophosphorane bearing the Martin ligand with the corresponding alkyne.

A-1) *J. Am. Chem. Soc.*, **123**, 1507-1508 (2001).

A-3) *Org. Lett.*, **3**, 691-694 (2001).

A-12) *Chem. Commun.*, 2096-2097 (2001).

### (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.

A-17) *Chem. Lett.*, 1204-1205 (2001).

### (3) "Synthesis of 5-Carbaphosphatranes"

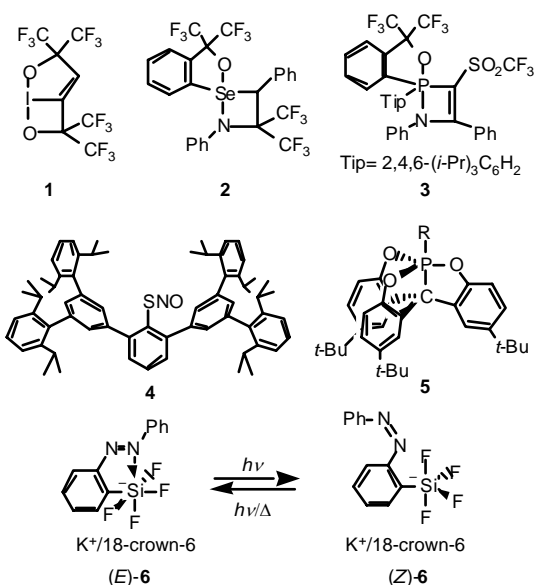
The characteristics of silatranes and phosphatranes, which are known as bioactive species and basic catalysts, respectively, are strongly attributable to the transannular dative bond of nitrogen to the central atom. Replacement of the dative bond by a covalent bond would supply different reactivity and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

A-5) *J. Am. Chem. Soc.*, **123**, 3387-3388 (2001).

### (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-13) *J. Am. Chem. Soc.*, **123**, 10778-10779 (2001).



## A. Original Papers

- 1) T. Kawashima, K. Hoshiba and N. Kano: "Synthesis, Structure, and Reactions of a Tricoordinate 1,2-Iodoxetane" *J. Am. Chem. Soc.*, **123**, 1507-1508 (2001).
- 2) F. Ohno, T. Kawashima and R. Okazaki: "Synthesis and Thermolysis of Novel Spiroselenuranes Bearing Two Oxaselenetane Rings: Double Oxirane Formation Reactions from 1,5-Dioxa-4 $\lambda^4$ -selenaspiro[3.3]heptanes" *Chem. Commun.*, 463-464 (2001).
- 3) N. Kano, Y. Daicho, N. Nakanishi and T. Kawashima: "Synthesis, Crystal Structure, and Thermolysis of the First Tetracoordinate 1 $\lambda^4$ ,2-Selenazetidines: Aziridine Formation Reaction from a Four-Membered Heterocycle Bearing Highly Coordinate Selenium" *Org. Lett.*, **3**, 691-694 (2001).
- 4) N. Kano, F. Komatsu and T. Kawashima: "Synthesis and Structures of Azobenzenes Bearing Silyl, Germyl, and Stannyl Groups at 2-Position" *Chem. Lett.*, 338-339 (2001).
- 5) J. Kobayashi, K. Goto and T. Kawashima: "5-Carbaphosphatranes: The First Main Group Atrane Bearing a 1-5 Covalent Bond" *J. Am. Chem. Soc.*, **123**, 3387-3388 (2001).
- 6) K. Goto, T. Saiki, S. Akine, T. Kawashima and R. Okazaki: "Synthesis and Reactions of Conformational Isomers of a Stable Selenenic Acid Bearing a Bridged Calix[6]arene Framework" *Heteroatom Chem.*, **12**, 195-197 (2001).
- 7) N. Kano, J.-H. Xing, A. Kikuchi and T. Kawashima: "Formation and X-ray Crystallographic Analysis of a 1,2 $\lambda^5$ -Oxaphosphol-5(2H)-one" *Heteroatom Chem.*, **12**, 282-286 (2001).
- 8) Y. Uchiyama, N. Kano and T. Kawashima: "Synthesis and Structure of a Novel Ladder-type Organobismuth Compound with Bismuth-Oxygen Interactions" *Organometallics*, **20**, 2440-2442 (2001).
- 9) N. Kano, N. Nakanishi, Y. Daicho and T. Kawashima: "Novel Ring System with an Se-O-N Linkage: Synthesis and Crystal Structure of the First 1,2 $\lambda^4$ ,5-Oxaselenazolidine" *Chem. Lett.*, 610-611 (2001).
- 10) T. Kawashima, N. Yamashita, T. Kannabe and R. Okazaki: "Unusual Products in Reactions Using Ethyldimesitylborane, Mesityllithium, and Carbonyl Compounds" *Heteroatom Chem.*, **12**, 354-357 (2001).
- 11) N. Kano, N. Nakagawa and T. Kawashima: "A Disilane Containing Two Heptacoordinate Silicon Atoms and Dithiocarboxylate Ligands" *Angew. Chem., Int. Ed.*, **40**, 3450-3452 (2001).
- 12) N. Kano, A. Kikuchi and T. Kawashima: "The First Isolable Pentacoordinate 1,2 $\lambda^5$ -Azaphosphetene: Synthesis, X-ray Crystallographic Analysis, and Dynamic Behaviour" *Chem. Commun.*, 2096-2097 (2001).
- 13) N. Kano, F. Komatsu and T. Kawashima: "Reversible Photocontrol of the Coordination Number of Silicon in a Tetrafluorosilicate Bearing a 2-(Phenylazo)phenyl Group" *J. Am. Chem. Soc.*, **123**, 10778-10779 (2001).
- 14) K. Goto, M. Nagahama, T. Mizushima, K. Shimada, T. Kawashima and R. Okazaki: "The First Direct Oxidative Conversion of a Selenol to a Stable Selenenic Acid: Experimental Demonstration of Three Processes Included in the Catalytic Cycle of Glutathione Peroxidase" *Org. Lett.*, **3**, 3569-3572 (2001).
- 15) S. Akine, K. Goto and T. Kawashima: "Conformational Mobility of the Bridged Calix[6]arenes with Allyl and Ethyl Groups at the Lower Rim" *Bull. Chem. Soc. Jpn.*, **74**, 2167-2174 (2001).
- 16) K. Saruhashi, K. Goto and T. Kawashima: "Structural Characterization of a Pentacoordinate Monohydrosilane with the Apical Si-H Bond" *Chem. Heterocycl. Compd.*, 1524-1525 (2001).
- 17) K. Goto, (Y. Hino), Y. Takahashi, T. Kawashima, (G. Yamamoto), (N. Takagi) and (S. Nagase): "Synthesis,

Structure, and Reactions of the First Stable Aromatic *S*-Nitrosothiol Bearing a Novel Dendrimer-Type Steric Protection Group" *Chem. Lett.*, 1204-1205 (2001).

- 18) K. Goto, T. Okumura and T. Kawashima: "Synthesis, Structure, and Reactions of a Novel Triarylsilanol with a Bowl-Type Framework: A Silanol Extremely Resistant to Self-Condensation" *Chem. Lett.*, 1258-1259 (2001).
- 19) K. Goto, (G. Yamamoto), B. Tan and R. Okazaki: "A Novel Dendrimer-Type *m*-Terphenyl Substituent for the Kinetic Stabilization of Highly Reactive Species" *Tetrahedron Lett.*, **42**, 4875-4877 (2001).

### C. Proceedings

- 1) T. Kawashima, K. Hoshiba and N. Kano: "Synthesis and Structure of a Tricoordinate 1,2-Iodoxetane", *Proceedings of the Ninth International Conference on Inorganic Ring Systems (IRIS-IX)*, Saarbrücken, Germany, July 2000, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **168-169**, 141-144 (2001).
- 2) N. Kano, Y. Daicho, N. Nakanishi and T. Kawashima: "Synthesis and Thermolysis of the Novel Ring Systems Containing Nitrogen and Tetracoordinate Selenium", *Proceedings of the Ninth International Conference on Inorganic Ring Systems (IRIS-IX)*, Saarbrücken, Germany, July 2000, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **168-169**, 259-262 (2001).
- 3) J. Kobayashi, K. Goto and T. Kawashima: "Synthesis and Structure of 5-Carbaphosphatrane", *Proceedings of the Ninth International Conference on Inorganic Ring Systems (IRIS-IX)*, Saarbrücken, Germany, July 2000, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **168-169**, 597-600 (2001).

### D. Books

- 1) T. Kawashima and R. Okazaki: "Four-membered Rings with 1 Phosphorus Atom" in "Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain", ed by F. Mathey, Pergamon, Amsterdam (2001), Chapter 3.2, pp. 106-165.