

# ORGANOHETEROATOM CHEMISTRY

## Annual Research Review

### (1) "Syntheses and Thermolyses of Heterocyclobutanes Containing a Highly Coordinate Main Group Element"

In the course of our study on heterocyclobutanes containing a highly coordinate main group element, we have synthesized 1,3,2λ<sup>5</sup>-oxazaphosphetidine **1** and 1,3,2λ<sup>5</sup>-diazaphosphetidine-4-thione **2** by cycloaddition reactions of the corresponding iminophosphorane with a ketone and an isothiocyanate, respectively. Formation of an imine and a cyclic phosphinate upon thermolysis of **1** shows that **1** is an intermediate of the aza-Wittig reaction. Compound **2** exhibited two reaction pathways upon thermolysis giving the iminophosphorane with the isothiocyanate, and a cyclic thiophosphinate with a carbodiimide, respectively. The formation of the latter two compounds suggests the bond recombination around the phosphorus atom of **2**.

Tetracoordinate 1,5-dioxo-4λ<sup>4</sup>-tellurapiro[3.3]heptane **3** bearing two 1,2-oxatelluretane rings was synthesized and crystallographically characterized. Thermolysis of **3** gave a mixture of the corresponding oxirane, olefin, and alcohol in contrast to those of other heterocyclobutanes containing a highly coordinate main group element. The reaction was found to proceed mainly via a radical pathway.

A-6) *Tetrahedron Lett.*, **43**, 6775-6778 (2002).

A-7) *Polyhedron*, **21**, 657-665 (2002).

### (2) "Synthesis, Structure, and Reactions of Heterocyclopropanes Containing a Highly Coordinate Main Group Element"

Three-membered ring compounds containing a highly coordinate heteroatom are interesting in view of their strained structures and the bonding properties of a polar hypervalent bond fixed in the ring system. We have succeeded in the synthesis of the first stable selenaphosphirane **4** and thiasiliranide **5** by taking advantage of the Martin ligand. Their strained molecular structures were characterized by X-ray crystallographic analysis. The characteristic solvent

effect in <sup>31</sup>P and <sup>77</sup>Se NMR spectra of **4** revealed the existence of the polar P–Se bond. The equilibrium of **4** with the phosphorus ylide and elemental selenium has also been revealed.

The hydrolysis of **5** afforded 3,3-dimethylbutanethiol indicating the potential relationship of the thiasiliranide with an intermediate of the Brook rearrangement, while reaction with aqueous HCl gave the α-mercaptoalkylsilane.

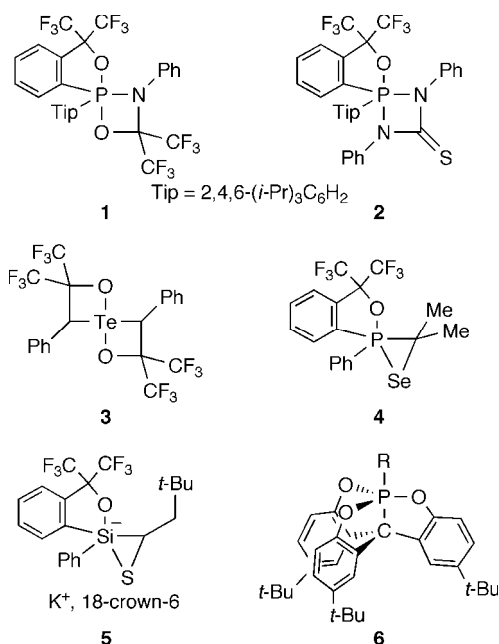
A-2) *J. Am. Chem. Soc.*, **124**, 9706-9707 (2002).

A-3) *J. Organomet. Chem.*, **643-644**, 504-507 (2002).

### (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. We have synthesized 5-carbaphosphatranes **6**, in which a P→N dative bond was replaced by the P–C covalent bond, and elucidated their structures and spectroscopic properties. The theoretical calculations indicated that the transannular bond in **6** is twice as strong as that of phosphatrane and more than 3 times stronger than that of silatrane, reflecting the difference between a covalent bond and the more ionic dative bonds.

A-1) *J. Am. Chem. Soc.*, **124**, 3703-3712 (2002).



## A. Original Papers

- 1) J. Kobayashi, K. Goto, T. Kawashima, (M. W. Schmidt) and (S. Nagase): "Synthesis, Structure, and Bonding Properties of 5-Carbaphosphatranes: A New Class of Main Group Atrane", *J. Am. Chem. Soc.*, **124**, 3703-3712 (2002).
- 2) S. Sase, N. Kano and T. Kawashima: "Synthesis and Structure of the First 1,2 $\sigma^5$ -Selenaphosphirane", *J. Am. Chem. Soc.*, **124**, 9706-9707 (2002).
- 3) K. Naganuma and T. Kawashima: "Synthesis and Structure of the First Pentacoordinate Thiasiliranides", *J. Organomet. Chem.*, **643-644**, 504-507 (2002).
- 4) R. Okazaki and K. Goto "Synthesis of Highly Reactive Organosulfur Compounds", *Heteroatom Chem.*, **13**, 414-418 (2002).
- 5) (Y. Naruse), (S. Inagaki), N. Kano, N. Nakagawa and T. Kawashima: "Hypercoordination to a Saturated Carbon Atom", *Tetrahedron Lett.*, **43**, 5759-5762 (2002).
- 6) N. Kano, T. Takahashi and T. Kawashima: "Synthesis, Structure, and Thermolysis of a Novel Spirotellurane Bearing Two 1,2-Oxatellurethane Rings, 1,5-Dioxa-4 $\lambda^4$ -tellurasp[3.3]heptane: Oxirane and Olefin Formation Reactions", *Tetrahedron Lett.*, **43**, 6775-6778 (2002).
- 7) S. Sase, N. Kano and T. Kawashima: "Fluoride Ion Abstraction of Phosphonium Cations from Their Counter Anion: a Novel Synthetic Method of Fluorophosphoranes", *Chem. Lett.*, 268-269 (2002).
- 8) N. Kano, J.-H. Xing, S. Kawa and T. Kawashima: "Cycloaddition Reactions of an Iminophosphorane Bearing the Martin Ligand with Some Double-bond Compounds: Syntheses, Structures and Thermolyses of a 1,3,2 $\lambda^5$ -Oxazaphosphetidine and a 1,3,2 $\lambda^5$ -Diazaphosphetidine-4-thione", *Polyhedron*, **21**, 657-665 (2002).

## C. Proceedings

- 1) (M. Yoshifuji) and T. Kawashima: "Preface", *Proceedings of the XVth International Conference on Phosphorus Chemistry (ICPC15)*, Sendai, Japan, July 2001, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **177**, No pp. given (2002).
- 2) J. Kobayashi, K. Goto and T. Kawashima: "Reactions of 1-Hydro-5-carbaphosphatrane: Tautomerization between Five-coordinate and Three-coordinate Species", *Proceedings of the XVth International Conference on Phosphorus Chemistry (ICPC15)*, Sendai, Japan, July 2001, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **177**, 1405-1407 (2002).
- 3) N. Kano, J.-H. Xing, A. Kikuchi, S. Kawa and T. Kawashima: "Synthesis of Four- and Five-membered Heterocycles Derived from an Iminophosphorane", *Proceedings of the XVth International Conference on Phosphorus Chemistry (ICPC15)*, Sendai, Japan, July 2001, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **177**, 1685-1687 (2002).
- 4) K. Goto, J. Kobayashi, T. Kawashima, (M. W. Schmidt) and (S. Nagase): "Bonding Properties of 5-Carbaphosphatranes", *Proceedings of the XVth International Conference on Phosphorus Chemistry (ICPC15)*, Sendai, Japan, July 2001, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **177**, 2037-2038 (2002).

- 5) S. Sase, N. Kano and T. Kawashima: "Synthesis of the First Stable Pentacoordinate Selenaphosphirane", *Proceedings of the XVth International Conference on Phosphorus Chemistry (ICPC15)*, Sendai, Japan, July 2001, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **177**, 2039-2040 (2002).
- 6) S. Sase, N. Kano and T. Kawashima: "Novel Synthetic Method of Fluorophosphoranes by Fluoride Ion Abstraction from Tetrafluoroborate", *Proceedings of the XVth International Conference on Phosphorus Chemistry (ICPC15)*, Sendai, Japan, July 2001, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **177**, 2041 (2002).
- 7) K. Goto, Y. Ohzu, H. Sato and T. Kawashima: "Synthesis of Novel Triarylphosphines Bearing a *m*-Terphenyl-based Dendrimer-type Framework", *Proceedings of the XVth International Conference on Phosphorus Chemistry (ICPC15)*, Sendai, Japan, July 2001, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **177**, 2179 (2002).

#### **D. Books**

- 1) (M. Yoshifuji) and T. Kawashima, Eds.: "Proceedings of the XVth International Conference on Phosphorus Chemistry (ICPC 15), Part I, Sendai, Japan, July 2001", *Phosphorus, Sulfur, Silicon Relat. Elem.*, **177 (6/7)**, 540 pp (2002).
- 2) (M. Yoshifuji) and T. Kawashima, Eds.: "Proceedings of the XVth International Conference on Phosphorus Chemistry (ICPC 15), Part II, Sendai, Japan, July 2001", *Phosphorus, Sulfur, Silicon Relat. Elem.*, **177 (8/9)**, 356 pp (2002).