

Chemistry of Cyclic Compounds Containing a Highly Coordinated Phosphorus Atom

Takayuki Kawashima

Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan

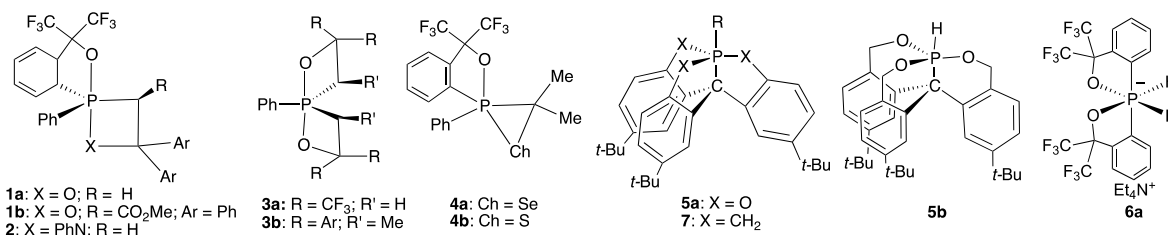
Present address: Graduate School of Science and Technology, Gunma University, Kiryu, Gunma-ken, Japan

e-mail: kawashima.t@gunma-u.ac.jp

Since our first report on stable 1,2-oxaphosphphetanes **1a** bearing the Martin ligand, we have investigated the syntheses and reactivities of the titled compounds.[1] In this presentation, I wish to summarize mainly synthetic methods for these compounds.

For four-membered compounds, we succeeded in synthesizing a 3-methoxycarbonyl-1,2-oxaphosphetane **1b**, an intermediate of the Wittig reaction of a stabilized phosphorus ylide with a carbonyl compound, which has never been observed even spectroscopically.[2] We also synthesized 1,2-azaphosphetidine **2** as a mixture of *N*- and *C*-apical pseudorotamers.[3] Furthermore, we could obtain 1,3,2λ⁵-oxazaphosphetidines, intermediates of aza-Wittig reactions and spirobis[1,2-oxaphosphetidines] **3a,b** having two oxaphosphetane rings.[4] Then, we tried to synthesize two three-membered ring compounds **4a,b** containing a pentacoordinated phosphorus and a chalcogen atoms.[5]

As one of anti-apicophilic phosphorus compounds, we reported 5- and 6-carbaphosphatranes **5a,b** with three oxygen atoms at the equatorial positions and a carbon and hydrogen (carbon) atoms at the apical positions.[6,7] For compounds containing a hexacoordinated phosphorus atom, we synthesized dihydrophosphate **6a** and its isomer with two Martin ligands and applied them to umpolung of a hydrogen atom of water.[8] The details of the conversion from 1-hydro-6-carbaphosphatranes **5b** to tetraalkylhydro- and pentaalkylphosphoranones **7** will also be presented.



References

- [1] T. Kawashima, K. Kato, R. Okazaki, *J. Am. Chem. Soc.*, **1992**, *114*, 4008-4010.
- [2] T. Kawashima, K. Kato, R. Okazaki, *Angew. Chem., Int. Ed. Engl.*, **1993**, *32*, 869-870.
- [3] T. Kawashima, T. Soda, R. Okazaki, *Angew. Chem., Int. Ed. Engl.*, **1996**, *35*, 1096-1098.
- [4] For **3a**: T. Kawashima, H. Takami, R. Okazaki, *J. Am. Chem. Soc.*, **1994**, *116*, 4509-4510.
- [5] For **4a**: S. Sase, N. Kano, T. Kawashima, *J. Am. Chem. Soc.*, **2002**, *124*, 9706-9707.
- [6] J. Kobayashi, K. Goto, T. Kawashima, M. W. Schmidt, S. Nagase, *J. Am. Chem. Soc.*, **2002**, *124*, 3703-3712.
- [7] S. Nakafuji, J. Kobayashi, T. Kawashima, M. W. Schmidt, *Inorg. Chem.*, **2005**, *44*, 6500-6502.
- [8] For **6a**: H. Miyake, N. Kano, T. Kawashima, *J. Am. Chem. Soc.*, **2009**, *131*, 16622-16623.