Non-nucleophilic Chiral Borate Ions for Catalytic Control of Cationic Reactive Intermediates

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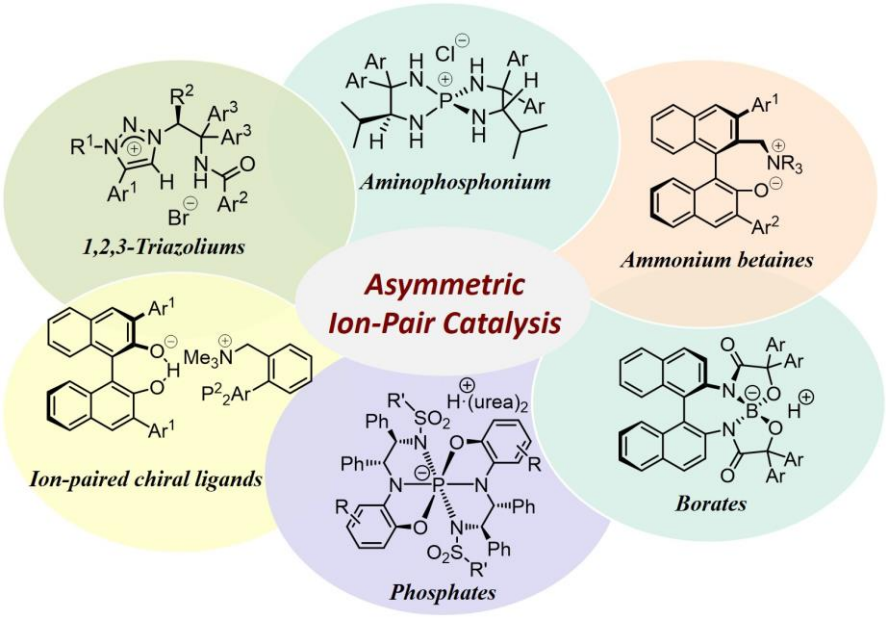
Abstract:
Anions and cations are among the most fundamental reactive species and are widely used to form new bonds for synthesizing desired organic molecules. Therefore, "organic ion-pair catalysis" that allows the direct control of a reactive ionic intermediate by the pairing organic ion through electrostatic interaction becomes important. However, the chemistry of exploiting organic ion pairs as molecular catalysts has been very limited. To address this intrinsic problem, we have designed and synthesized structurally well-defined and readily modifiable organic cations and anions for use as molecular catalysts capable of directly and precisely controlling counterions and ion radicals, leading to the development of synthetically relevant stereoselective carbon-carbon and carbon-heteroatom bond-forming reactions. In this lecture, I would like to present the details of this research stream with particular focus on the molecular design of non-nucleophilic chiral anions and their applications to asymmetric catalysis. Specifically, the development of a structurally robust chiral borate with tetradentate backbone, which exhibits a distinct ability to control prochiral cations and distonic radical cations in achieving otherwise difficult asymmetric carbon-carbon bond formations, will be discussed.[1,2]



References:
1. A Structurally Robust Chiral Borate Ion: Molecular Design, Synthesis, and Asymmetric Catalysis, D. Uraguchi, F. Ueoka, N. Tanaka, T. Kizu, W. Takahashi, and T. Ooi, *Angew. Chem. Int. Ed.*, **2020**, *59*, 11456-11461.
2. Urea as a Redox-Active Directing Group under Asymmetric Photocatalysis of Iridium-Chiral Borate Ion Pairs, D. Uraguchi, Y. Kimura, F. Ueoka, and T. Ooi, *J. Am. Chem. Soc.*, **2020**, *142*, 19462-19467.

Bio-Sketch of Speaker

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Takashi Ooi was born in 1965 in Nagoya, Japan. He received his Ph.D. (1994) from Nagoya University under the direction of Professor Hisashi Yamamoto. He has been granted a Fellowship of the Japan Society for the Promotion of Sciences (JSPS) for Japanese Junior Scientists (1992-1995), during which he joined the group of Professor Julius Rebek, Jr. at MIT as a postdoctoral fellow (1994-1995). He was appointed as an assistant professor at Hokkaido University in 1995 and promoted to a lecturer (1998). He moved to Kyoto University as an associate professor (2001), and became a full professor of Nagoya University in 2006. Since 2013, he has been a professor of Institute of Transformative Bio-Molecules (ITbM), Nagoya University. His current research interests are focused on the molecular design and precise structural control of chiral organic molecular catalysts, particularly ion-pair catalysts, for selective organic synthesis. As a principal investigator at ITbM, he has been deeply involved in the collaborative research with plant and animal biologists, aiming at providing molecular-level solutions to the problems of fundamental significance in the fields of parasitic plant eradication and circadian rhythm. He was awarded the Chugai Award in Synthetic Organic Chemistry, Japan (1997), Chemical Society of Japan Award for Young Chemist (1999), Thieme Journal Award (2006), JSPS Prize (2010), IBM Japan Science Prize (2011), Inoue Prize for Science (2013), Daiichi-Sankyo Award for Medicinal Organic Chemistry (2017), Swiss Chemical Society Lectureship Award (2019), Chemical Society of Japan Award (2020), and he was named a Fellow of the Royal Society of Chemistry (2014).

Recent Publications:

1. Catalytic Asymmetric Cyanoalkylation of Electron-Deficient Olefins with Potassium Cyanide and Alkyl Halides, K. Ohmatsu, Y. Morita, M. Kiyokawa, and T. Ooi, *J. Am. Chem. Soc.*, **2021**, *143*, 11218-11224.
2. Urea as a Redox-Active Directing Group under Asymmetric Photocatalysis of Iridium-Chiral Borate Ion Pairs, D. Uraguchi, Y. Kimura, F. Ueoka, and T. Ooi, *J. Am. Chem. Soc.*, **2020**, *142*, 19462-19467.
3. A Structurally Robust Chiral Borate Ion: Molecular Design, Synthesis, and Asymmetric Catalysis, D. Uraguchi, F. Ueoka, N. Tanaka, T. Kizu, W. Takahashi, and T. Ooi, *Angew. Chem. Int. Ed.*, **2020**, *59*, 11456-11461.