Department of Chemistry
香港城市大學
City University of Hong Kong

Special Departmental Seminar

By

Prof. Kazushi Mashima

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Osaka University, Japan

Base-metal Cluster Catalysts: Reactions and Mechanism

Date: **24 September 2026 (Thursday)**

Time: **11:00 am – 12:00 noon**

Venue: **B5-211 (Blue Zone, 5th Floor)**
Yeung Kin Man Academic Building
City University of Hong Kong

For abstract, please refer to the attached sheet.

Contact: Prof. Michael CHAN (3442-9678, mcwchan@cityu.edu.hk)

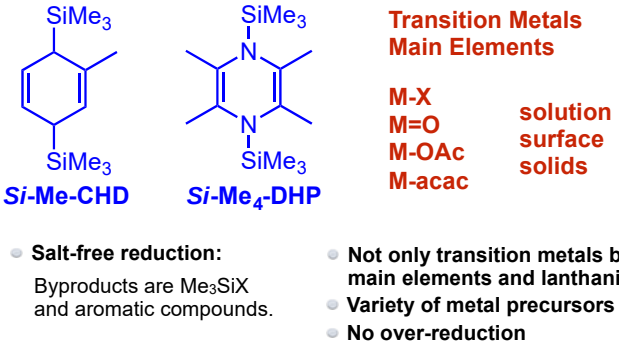
~ All Are Welcome ~

Abstract

Prof. Mashima has focused his interest in development of metal-catalyzed reactions based on his deep understanding of reaction mechanisms by an aid of comprehensive organometallic chemical approaches including isolation and determination of intermediate species as well as kinetics. His achievements are thus highlighted by the following lecture titles.

Title 1: Organosilicon Compounds as Unique Salt-Free Reducing Reagents of Metal Compounds, Generating Catalytically Active Species

Low-valent transition metal complexes have been utilized as reagents and catalysts for various bond formation reactions. Various reagents have been developed for reducing higher oxidation metal precursors such as metal halides; however, the interaction of the resulting salts with the in situ generated low-valent or zero-valent metal species disturbed their intrinsic reactivity and catalytic performance. We recently developed a conceptionally new methodology for generating low-valent catalytically active metal species in a salt-free manner upon treating metal sources with versatile reducing reagents such as 3,6-bis(trimethylsilyl)-1,4-cyclohexadienes and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazines. It is highlighted to apply the salt-free reduction method for reducing vanadium, tungsten, nickel compounds and so on for generating catalytically active species. In this presentation, we will also deliver that diboron compounds potentially serve as another reducing reagents.



(1) Synthesis of Multisubstituted Cyclopentadiene Derivatives from 3,3-Disubstituted Cyclopropenes and Internal Alkynes Catalyzed by Low-Valent Niobium Complexes
T. Akiyama, T. Kusamoto, K. Mashima, and H. Tsurugi, *J. Am. Chem. Soc.*, **2024**, *149*, 33338-33348.

(2) Evaluation of Tungsten Catalysis among Early Transition Metals for N-Aryl-2,3,4,5-tetraarylpyrrole Synthesis: Modular Access to N-Doped π-Conjugated Material Precursors
Hayato Tsurugi, Takuya Akiyama, Connor W. Frye, Yuya Kakiuchi, Kazushi Mashima, and Ian A. Tonks, *Inorg. Chem.*, **2024**, *63*, 3037-3046.

(3) Bis(neopentylglycolato)diboron (B_2nep_2) as a bidentate ligand and a reducing agent for early transition metal chlorides giving $MCl_4(B_2nep_2)$ complexes
Hiromu Hosoya, Takuya Akiyama, Kazushi Mashima, and Hayato Tsurugi, *Dalton Trans.*, **2023**, *52*, 13154-13160.

(4) Pyridine-mediated B-B Bond Activation of $(RO)_2B\text{-}B(OR)_2$ for Generating Borylpyridine Anions and Pyridine-stabilized Boryl Radicals as Useful Boryl Reagents in Organic Synthesis
Luis Carlos Misal Castro, Ibrahim Sultan, Hayato Tsurugi, Kazushi Mashima, *Synthesis*, **2021**, *53* (18), 3211-3226.

(5) Direct Synthesis of Indoles from Azoarenes and Ketones with Bis(neopentylglycolato)diboron Using 4,4'-Bipyridyl as an Organocatalyst
Luis Calros Misal Castro, Ibrahim Sultan, Kohei Nishi, Hayato Tsurugi, Kazushi Mashima, *J. Org. Chem.* **2021**, *86* (4), 3287-3299.

(6) Salt-free Reduction of Transition Metal Complexes by Bis(trimethylsilyl)cyclohexadiene, -dihydropyrazine, and -4,4'-bipyridinylidene Derivatives.
Hayato Tsurugi and Kazushi Mashima, *Acc. Chem. Res.*, **52**, 769-779 (2019).

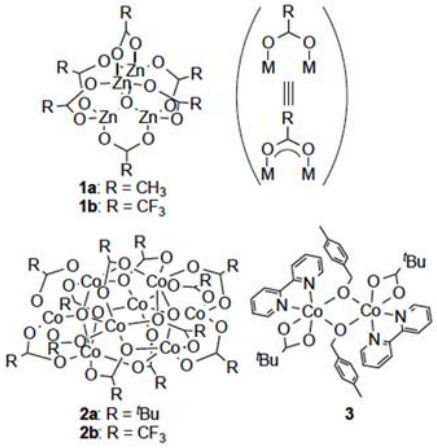
(7) Synthesis of Pyridylimido Complexes of Tantalum and Niobium by Reductive Cleavage of the N═N Bond of 2,2′-Azopyridine: Precursors for Early–Late Heterobimetallic Complexes
Kento Kawakita, Yuya Kakiuchi, Evan P. Beaumier, Ian A. Tonks, Hayato Tsurugi, Kazushi Mashima, *Inorg. Chem.* **2019**, *58* (22), 15155-15165.

(8) A New Protocol to Generate Catalytically Active Species of Group 4—6 Metals by Organosilicon-based Salt-free Reductants.
Hayato Tsurugi and Kazushi Mashima, *Chem. Eur. J.*, **25**, 913-919 (2019).

(9) Bis(imido)vanadium(V)-Catalyzed [2+2+1] Coupling of Alkynes and Azobenzenes Giving Multisubstituted Pyrroles. Kento Kawakita, Evan P. Beaumier, Yuya Kakiuchi, Hayato Tsurugi, Ian A. Tonks and Kazushi Mashima *J. Am. Chem. Soc.* **2019**, *141* (10), 4194-4198.
(10) Nickel-catalyzed cyanation of aryl halides and triflates using acetonitrile via C–CN bond cleavage assisted by 1,4-bis(trimethylsilyl)-2,3,5,6-tetramethyl-1,4-dihydropyrazine.
Yohei Ueda, Nagataka Tsujimoto, Taiga Yurino, Hayato Tsurugi, Kazushi Mashima, *Chem. Sci.*, **10**, 994-999 (2019).
(11) Low Temperature Activation of Supported Metathesis Catalysts by Organosilicon Reducing Agents. Victor Mougel, Ka-Wing Chan, Georges Siddiqi, Kento Kawakita, Haruki Nagae, Hayato Tsurugi, Kazushi Mashima, Olga Safonova, and Christophe Coperet, *ACS Cent. Sci.*, **2**, 569-576 (2016).

Title 2: Enzymatic Catalytic Performance of Cluster Catalysts of Zinc, Cobalt and Manganese for Chemoselective Transesterification and Amide Alcoholysis

The catalytic transformation of ester moiety provides both key intermediate and protecting group in organic chemistry. KM originally found that μ-oxo-tetranuclear zinc cluster $Zn_4(OCOCF_3)_6O$ served as an unique and efficient catalyst for chemoselective acylation of hydroxy group in the presence of amino group. KM recently found that such the chemoselective acylation was achieved using not only zinc carboxylates but also various carboxylates of first-row late transition metals such as Mn, Fe, Co, and Cu. He demonstrated that octanuclear cobalt carboxylate clusters $[Co_4(OCOR)_6O]_2$ supported by nitrogen-containing ligands such as 2,2'-bipyridine were an efficient catalyst system for the chemoselective transesterification, and confirmed that an alkoxide-bridged dinuclear cobalt(II) complex, $Co_2(OCO^tBu)_2(bpy)_2(OCH_2\text{-}C_6H_4\text{-}4\text{-}CH_3)_2$, was a key intermediate through an ordered ternary complex mechanism, similar to dinuclear metallo-enzymes, providing a chemical insight into the reason why various esterase, peptidase and so on favourably contain Mn, Co, and Zn as their dinuclear active sites. Recently, KM also found that manganese clusters mediate not only the same chemoselectivity for transesterification but also esterification of amide bond through the amide C-N bond cleavage.



(1) Esterification of Tertiary Amides: Remarkable Additive Effects of Potassium Alkoxides for Generating Hetero Manganese-Potassium Dinuclear Active Species
Takahiro Hirai, Daiki Kato, Binh Khanh Mai, Shoichiro Katayama, Shoko Akiyama, Haruki Nagae, Fahmi Himo, Kazushi Mashima, *Chem. Eur. J.*, **2020**, *26* (47), 10735-10742.
(2) Catalytic Cleavage of Amide C−N Bond: Scandium, Manganese, and Zinc Catalysts for Esterification of Amides Kazushi Mashima, Yuji Nishii, Haruki Nagae, *Chem. Rec.* **2020**, *20* (4), 332-343.
(3) Dinuclear manganese alkoxide complexes as catalysts for C–N bond cleavage of simple tertiary N,N-dialkylamides to give esters.
Haruki Nagae, Takahiro Hirai, Daiki Kato, Shusei Soma, Shin-ya Akebi, and Kazushi Mashima *Chem. Sci.*, **10**, 2860-2868 (2019).
(4) Zinc-catalyzed Esterification of N-β-Hydroxyethylamides; Removal of Directing Groups under Mild Conditions.
Yuji Nishii, Takahiro Hirai, Sarah Fernandez, Paul Knochel, and Kazushi Mashima, *Eur. J. Org. Chem.*, (34), 5010-5014 (2017).
(5) Enzyme-like Catalysis via Ternary-Complex Mechanism: Alkoxy-bridged Dinuclear Cobalt Complex Mediates Chemoselective *O*-Esterification over *N*-Amidation.
Yukiko Hayashi, Stefano Santoro, Yuki Azuma, Fahmi Himo, Takashi Ohshima, and Kazushi Mashima, *J. Am. Chem. Soc.*, **135**, 6192-6199 (2013).
(6) Zinc-Catalysed Amide Cleaved Esterification of β-Hydroxyethylamides.
Yusuke Kita, Yuji Nishii, Takafumi Higuchi, and Kazushi Mashima, *Angew. Chem. Int. Ed.*, **51**, 5723-5726 (2012).
(7) Additive Effect of N-Heteroaromatics on Transesterification Catalyzed by Tetranuclear Zinc Cluster.
Y. Maegawa, Y. Hayashi, T. Iwasaki, T. Ohshima, and K. Mashima, *ACS Catalysis*, **1**, 1178-1182 (2011).
(8) Enzyme-Like Chemoselective Acylation of Alcohols in the Presence of Amines Catalyzed by a Tetranuclear Zinc Cluster.
T. Ohshima, T. Iwasaki, Y. Maegawa, A. Yoshiyama, and K. Mashima, *J. Am. Chem. Soc.*, **130**, 2944-2945 (2008); Highlighted in Nature, 452, 415-416 (2008); Science, 319, 1163 (2008).

Biography

Prof. Kazushi Mashima received his PhD degree (1986) from Osaka University, supervised by Professor emeritus Akira Nakamura. Before receiving his PhD degree from Osaka University, in 1983 he was appointed Assistant Professor at the Institute for Molecular Science, Okazaki National Institutes, working with the late Professor Hidemasa Takaya. He moved to the Faculty of Engineering, Kyoto University, as Assistant Professor in 1989, continuing to work with Professor Hidemasa Takaya, and then moved to the Faculty of Science, Osaka University, as Assistant Professor in 1991, working with Professor emeritus Akira Nakamura. He was promoted to Associate Professor at the Faculty (now Graduate School) of Engineering Science, Osaka University in 1994, and then to full Professor at the Graduate School of Engineering Science, Osaka University in 2003. Since April, 2022, he is a Specially Appointed Professor, Graduate School of Pharmaceutical Sciences, Osaka University.

In addition, in 1992 he performed a post-doctoral fellowship with Professor M. A. Bennett at the Australian National University, and then in 1993 he was an Alexander von Humboldt fellow with Professor W. A. Herrmann, Technische Universität München.

He received ‘Progress Award in Synthetic Organic Chemistry, Japan in 1994’, ‘BCSJ Award (the best paper award of Bull. Chem. Soc. Jpn.) in 2000’, ‘The Chemical Society of Japan Award for Creative Work for 2008’, ‘The 9th Green and Sustainable Chemistry Award, Awarded by the Ministry of Education, Culture, Sports, Science and Technology in 2010’, and ‘The Award of the Society of Polymer Science, Japan in 2010’. In 2018, he received ‘The Chemical Society Japan Awards in 2017’ and ‘Prize for Science and Technology (Research Category), The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology in 2018’. In 2019, he received Humboldt Research Award from Alexander von Humboldt Foundation, Germany, and Schlenk Lecture Award (University Tuebingen, Germany) sponsored by BASF. In 2025, he received the ‘Polymer Science Achievement Award’ (Society of Polymer Science, Japan).