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Cooperative Catalyses of Transition Metal Anion and Typical Metal Cation

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The anionic transition metal complexes, so-called ate complexes and their potent catalytic activities remained undeveloped in sharp contrast with neutral and cationic transition metal complexes. Since the ate complexes are synthesized in situ by reacting transition metal complexes with organometallic reagents such as organolithium and -magnesium reagents, the ate complexes consist with transition metal anion and Lewis acidic typical metal cation. We hypothesized that the anionic charge on transition metal center activates metal center itself and own ligands as nucleophile, and the counter cation coordinates to leaving group in substrates. In addition, these metal centers are closely coexisted by electrostatic interaction leading to kinetic activation of substrates (Figure 1). These thermodynamic and kinetic activations indeed enable carbon-carbon bond formations via the cleavage of strong chemical bonds such as C–F and C–O bonds.

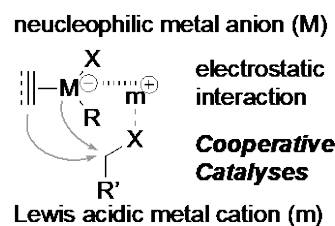


Figure 1. Cooperative catalyses of ate complexes

When alkyl fluorides were used as carbon electrophiles, cross-coupling reaction with sterically congested tertiary alkyl Grignard reagents,¹ regioselective hydroalkylation of 1,3-dienes,² and dimerizative alkylarylation of 1,3-butadiene³ were achieved. In these reactions, alkyl fluorides gave the best results among alkyl (pseudo)halides. Mechanistic studies indicated that Lewis acidic counter cation of the ate complexes efficiently activates C(sp³)–F bond, one of the strongest single bonds in organic compounds.⁴

Another representative reactivity of the ate complexes is the bond cleavage of etheral C–O bond at the vinylic position realizing cross-coupling reaction of alkenyl ethers with aryl Grignard reagents.^{5,6} Interestingly, more reactive C(sp²)–Br bond in aromatic ring survived under the reaction conditions.

Some of these ate complexes were successfully isolated and determined their molecular structures and chemical behavior.^{3–5,7,8}

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PROFILE

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He finished his BSc in 2004 and MSc in 2006 at Graduate School of Engineering Science, Osaka University and received his Ph.D. in 2009 from Osaka University under the supervision of Profs K. Mashima and T. Ohshima. During his Ph.D. course, he worked with Prof K. Kirchner, Vienna University of Technology, Austria in 2004. He became an Assistant Professor at Graduate School of Engineering, Osaka University in 2009, working with Prof N. Kambe. He was promoted to Associate Professor at Osaka University in 2017 and was appointed as Associate Professor at Graduate School of Engineering, The University of Tokyo in 2018. His research interests include the development of multi-metallic catalytic systems for the cooperative activation of substrates toward challenging transformations. He received a number of distinguished young investigator's awards including Chemistry Award BCA 2018, Incentive Award in Synthetic Organic Chemistry, Japan in 2018, Thieme Chemistry Journals Award 2019, The Japan Petroleum Institute Award for Encouragement of Research and Development in 2019, The SPACC Young Investigator Award in 2019, The Commendation for Science and Technology by MEXT, The Young Scientists' Award in 2020, The 2020 Mitsui Chemicals Catalysis Science Award for Creative Work, and Research Incentive Award of Japan Society of Coordination Chemistry in 2020. E-mail: iwasaki@chembio.t.u-tokyo.ac.jp