Synthetic Organic Chemistry Group, Department of Chemistry, Graduate School of Engineering Science

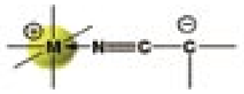
Professor: Takeshi Naota, Associate Professor: Yasushi Imada, Assistant Professors: Naruyoshi Komiya, Hikaru Takaya

URL: http:/cobalt.chem.es.osaka-u.ac.jp/orgsyn/index-e.html/
E-mail: naota@chem.es.osaka-u.ac.jp

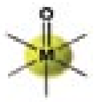
This research group aims to provide a new chemistry and synthetic methodologies for the synthesis of highly functionalized organic and organometallic molecules. Our areas of interest include the elucidation of selective organic transformations, studies on the chemical control of reactive intermediates, and the creation of innovative organic functional materials.

Construction of Reactive Intermediates Aiming at the Development of Useful Organic Transformations

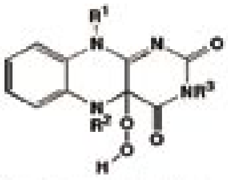
In order to ensure the sustainable development of human society, based on the high-degree utilization of materials, it is essential to provide forward-looking technologies for ecochemical organic transformations. Basic research on the construction of reactive intermediates and the elucidation of their dynamic behaviors is continuing with the aim of 1) exploiting new reactions, 2) improving the catalytic activity and selectivity of fundamental reactions, and 3) reducing environmental loading. For example, a new type of reactive intermediates such as transition metal cyanocarbanions, polymetallic Lewis acids, oxometal species and flavin compounds have been constructed for use as a key catalytic active species in carbon-carbon bond forming reactions and oxidation reactions. The correlation between the structure and reactivity of these catalytic intermediates has been extensively studied in order to fully understand the nature of the catalysis, aiming at the establishment of a [fundamental][leading] principle of environmentally friendly catalytic processes for organic transformations.



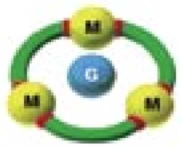
transition metal cyanocarbanions



oxometals



flavin hydroperoxide



multinuclear organometallics

Environmentally Friendly Catalytic Processes

One of our strategies for the development of novel catalytic reactions is based on the simulation of the functions of enzymes such as amine oxidases, flavoenzymes, and cytochrome P-450 using simple transition metal complex catalysts. Various biomimetic oxidations which include 1) dehydrogenative oxidation of amines with transition metal catalysts, 2) catalytic oxidative transformation of secondary amines to nitrones, 3) ruthenium-catalyzed oxidations of various substrates such as amines, amides, and hydrocarbons with peroxides, have been developed. These methods provide a range of versatile strategies for the synthesis of fine chemicals and biologically active compounds such as alkaloids, amino acids, and β-lactams. Important progress has been made so that the aerobic oxidation of organic compounds such as non-activated hydrocarbons can now be performed very efficiently under mild reaction conditions. Other successful examples are the development of redox Lewis acid and base catalysts enabling reactions to proceed under neutral conditions. Low valent ruthenium hydride complexes have proven to be excellent catalysts which can act as either redox Lewis acid or base catalysts. New types of catalytic transformations of nitriles, such as hydration of nitriles, amidation of amines, and esterification of alcohols with nitriles can be performed under neutral conditions. The same catalyst can be used for direct formation of carbon nucleophiles by C-H activation of pronucleophiles, such as nitriles and carbonyl compounds, and hence catalytic aldol-type reactions and Michael-type addition reactions can be performed under neutral and mild reaction conditions. Furthermore, palladium- and rhodium-catalyzed coupling reactions of allylic compounds with nucleophiles and carbonylation reactions have also been explored.

Creation of Functional Materials Utilizing the Dynamic Behaviors of Multinuclear Organometallics

The synthesis and function of multinuclear organometallic compounds that allow flexible conformational changes and possess self-assembling properties have been extensively studied in order to open up [new possibilities for][a new aspect of] materials conversions. A series of new types of multinuclear organometallic compounds has been prepared by the controlled assembly of transition metal salts with connection ligands bearing bis-bidentate moieties linked with flexible spacers. Dynamic behaviors such as specific rotation, host-guest complexation properties and self-assemblies have appeared as a result of weak non-bonding interactions in the well-designed cavity of these complexes. Based on these findings, we are currently studying the exploitation of conceptually novel functional organometallic materials such as stimuli-responsive instant gelators for organic fluids, molecular timer devices, and catalysts that activate specific organic transformations.

References（main papers in 2005-2007）

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