

International Research Center for Elements Science – Synthetic Organotransformation –

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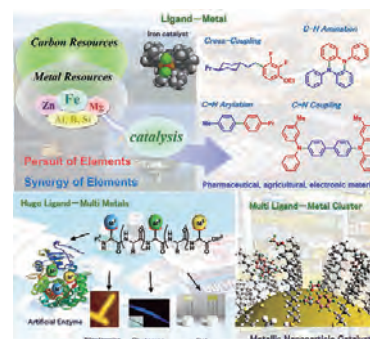
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Scope of Research

Our research activity focuses on the development of new molecular transformations, which can contribute to better or ideal synthesis of functional molecules as well as to exploitation of new chemical (metal and carbon) resources. The present research subjects are (1) metal-catalyzed carbon-carbon and carbon-heteroatom bond forming reactions by using universal metals such as iron (2) development of smart materials based on synergistic effect of various metals on artificial peptides (3) development of smart metallic nanoparticle catalysts based on supramolecular approaches (4) understanding of reaction mechanism of these catalytic reactions with the help of quantum chemical methods and synchrotron X-ray absorption spectroscopy.



KEYWORDS

Selective Organic Reaction Iron Catalyst Metalated Peptide Metallic Nanoparticle Catalyst Solution-Phase XAS Analysis

Selected Publications

Aoki, Y.; Toyoda, T.; Kawasaki, H.; Takaya, H.; Sharma, A. K.; Morokuma, K.; Nakamura, M., Iron-Catalyzed Chemoselective C-N Coupling Reaction: A Protecting-Group-Free Amination of Aryl Halides Bearing Amino or Hydroxy Groups, *Asian J. Org. Chem.*, **9**, 372-376 (2020).
Agata, R.; Lu, S.; Matsuda, H.; Isozaki, K.; Nakamura, M., Regio- and Stereoselective Synthesis of 1,4-enynes by Iron-catalyzed Suzuki-Miyaura Coupling of Propargyl Electrophiles under Ligand-free Condition, *Org. Biomol. Chem.*, **18**, 3022-3026 (2020).
Iwamoto, T.; Mizuhata, Y.; Tokitoh, N.; Nakamura, M., Development of P- and N-chirogenic Ligands Based on Chiral Induction from a Phosphorous Donor to a Nitrogen Donor in Palladium Complexes, *Organometallics*, **39**, 1672-1677 (2020).
Kanazawa, Y.; Mitsudome, T.; Takaya, H.; Hirano, M., Pd/Cu-Catalyzed Dehydrogenative Coupling of Dimethyl Phthalate: Synchrotron Radiation Sheds Light on the Cu Cycle Mechanism, *ACS Catal.*, **10**, 5909-5919 (2020).
Isozaki, K.; Taguchi, T.; Ishibashi, K.; Shimoaka, T.; Kurashige, W.; Negishi, Y.; Hasegawa, T.; Nakamura, M.; Miki, K., Mechanistic Study of Silane Alcoholysis Reactions with Self-Assembled Monolayer-Functionalized Gold Nanoparticle Catalysts, *Catalysts*, **10**, 908 (2020).

Iron-Catalyzed Cross-Coupling Reactions

Transition-metal-catalyzed carbon–carbon and carbon–heteroatom bond forming reactions are powerful tools for the synthesis of functional molecules. Our group focuses on use of iron as a catalyst, and so far developed a variety of iron-catalyzed cross-coupling reactions, some of which can't be achieved by conventional transition-metal catalysts such as palladium. As recent representative examples, we developed the chemoselective iron-catalyzed C–N coupling reaction of diarylamines with protecting group-free haloanilines/halophenols (Figure 1a), which is of significant interest due to the applicability for the straightforward synthesis of protecting group-free intermediates for organic luminescent materials. By using DFT calculation, we proposed a catalytic cycle of dimeric-Fe-amide complex involving oxidative addition, 1,3-shift of halide anion, reductive elimination, and transmetalation steps (Figure 1b).

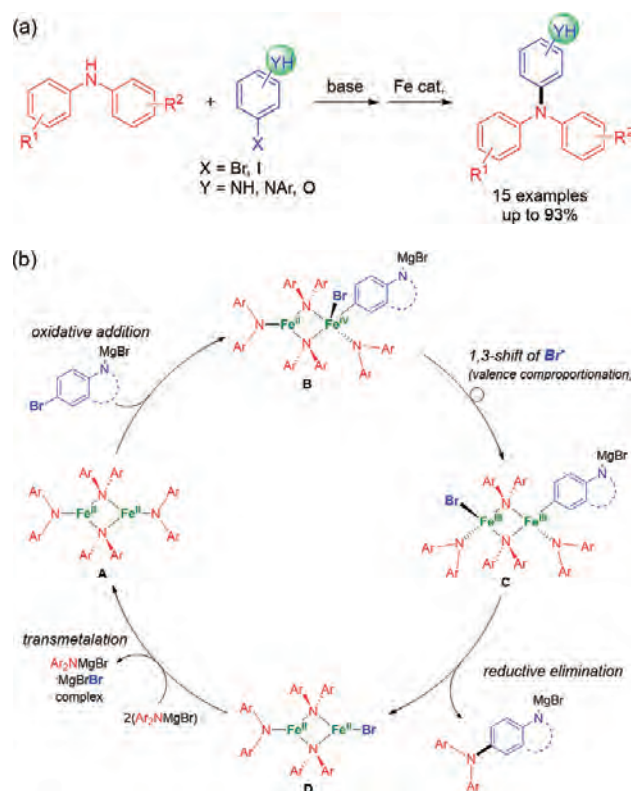


Figure 1. Iron-catalyzed chemoselective C–N coupling reaction with protecting group-free haloanilines and halophenols. (a) General reaction scheme and (b) a simplified plausible catalytic cycle.

Moreover, we developed ligand-free iron-catalyzed Suzuki–Miyaura coupling of lithium (*E*)- or (*Z*)-alkenylborates with propargyl electrophiles in stereospecific manner (Figure 2). The highly stereospecific nature of iron catalysis was demonstrated by the synthesis of tetrasubstituted 1,4-enyne, which has not been achieved by conventional catalytic methods.

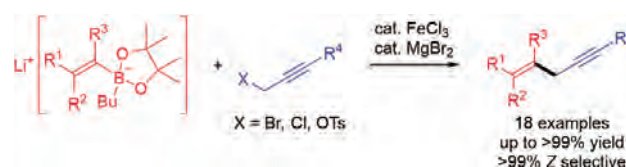


Figure 2. Iron-catalyzed Suzuki–Miyaura coupling of alkenylborates with propargyl electrophiles under ligand-free condition.

Novel Transition-Metal Catalyst Bound with Functional Amino Acid or Peptide

This project focuses on development of smart materials based on synergistic effect of various metals on artificial peptides. Based on this concept, we have developed novel ruthenium complex bound with norvaline, which catalyze efficient and selective oxidation of several methoxy-benzene analogues to quinones. Now we are trying further modification of the catalysts toward investigation of future chemical resources.

Supramolecular Approach for Creating Enhanced Catalysis of Metallic Nanoparticles

This project focuses on the development of highly active and selective metallic nanoparticle and cluster catalysts. To achieve this purpose, four key methodologies have been developed: 1) creation of reaction field with advanced self-assembly, 2) design of selective molecular transformation with multi-points intermolecular interaction, 3) size selective synthesis of metallic nanoparticles and clusters, and 4) utilization of plasmonic resonance with light.

