

International Research Center for Elements Science – Organic Main Group Chemistry –

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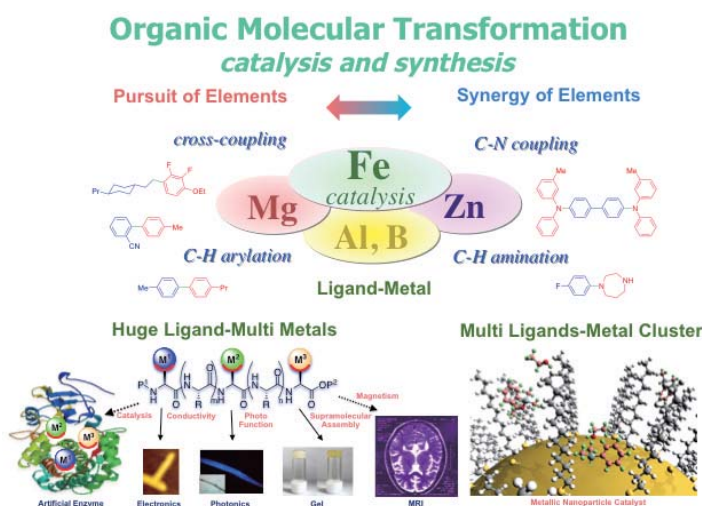
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Scope of Research

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 synergistic effects of multi-element center interactions for the catalysis with the help of quantum chemical methods and synchrotron X-ray absorption spectroscopy.



KEYWORDS

Selective Organic Reaction
Iron Catalyst
Metalated Peptide Catalyst
Metallic Nanoparticle Catalyst
Organic Synthesis

Selected Publications

- Hashimoto, S.; Ikuta, T.; Shiren, K.; Nakatsuka, S.; Nakamura, M.; Hatakeyama, T., Triplet-Energy Control of Polycyclic Aromatic Hydrocarbons by BN Replacement: Development of Ambipolar Host Materials for Phosphorescent OLEDs, *Chem. Mater.*, (in press).
- Hashimoto, S.; Nakatsuka, S.; Nakamura, M.; Hatakeyama, T., Construction of a Highly Distorted Benzene Ring in a Double Helicene, *Angew. Chem. Int. Ed.*, **53**, 14074-14076 (2014).
- Aoki, Y.; Imayoshi, R.; Hatakeyama, T.; Takaya, H.; Nakamura, M., Synthesis of 2,7-Disubstituted 5,10-Diaryl-5,10-dihydrophenazines via Iron-catalyzed Intramolecular Ring-Closing C-H Amination, *Heterocycles*, **90**, 893-900 (2014).
- Takaya, H.; Isozaki, K.; Haga, Y.; Ogata, K.; Naota, T., Synthesis and Self-Assembling Properties of Pt-Complex-Bound Oligoglutamic Acids, *Chem. Lett.*, **43**, 1167-1169 (2014).

Iron-Catalyzed Intermolecular and Intramolecular C-H Amination of Diarylamines

Transition-metal-catalyzed aromatic amination is of great importance in the field of organic synthesis, pharmaceuticals, and materials science. Recently we developed an iron-catalyzed aromatic amination giving various triarylamines. Further investigation for novel reactivities of iron-catalyst in amination reactions has led us to discover the unprecedented intermolecular C-H amination of diarylamines that provides various *o*-phenylene diamines. In addition, subsequent intramolecular C-H amination of the diamine products under iron catalysis was found to furnish 5,10-diaryl-5,10-dihydrophenazine derivatives, which are highly attractive compounds in material science.

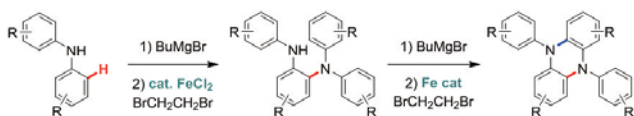


Figure 1. Iron-catalyzed intermolecular and intramolecular C-H amination of diarylamines.

Characterization of Solution-phase Organoiron Catalyst by Synchrotron X-ray Absorption Spectroscopy

In the past a few decades, iron-catalysts have regained much attention in cross-coupling chemistry due to their unprecedented reactivity and the practical advantages. However the mechanistic understanding remains limited because characterization of organoiron intermediates in solution has been hampered by their paramagnetic nature and instability toward air and moisture. We have succeeded in determining

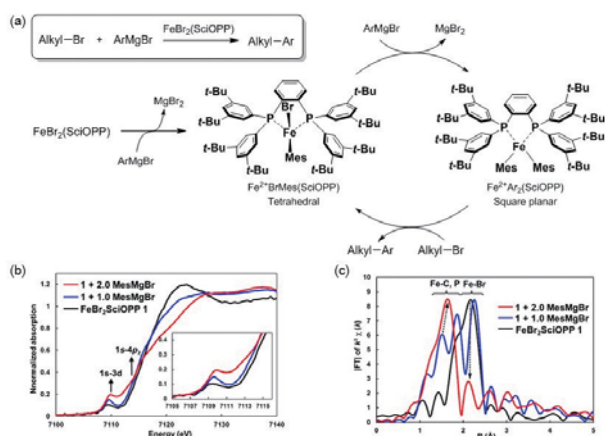


Figure 2. (a) $\text{FeBr}_2(\text{SciOPP})$ -catalyzed KTC-coupling of an arylmagnesium halide with an alkylhalide and the reaction mechanism. (b) The Fe K-edge XANES spectra and (c) the Fe K-edge EXAFS spectra: THF solutions of $\text{FeBr}_2(\text{SciOPP})$ and reaction mixtures of $\text{FeBr}_2(\text{SciOPP})$ with 1.0 and 2.0 equivalents of MesMgBr .

the solution-phase structure of organoiron species in $\text{FeBr}_2(\text{SciOPP})$ -catalyzed coupling reaction between ArMgBr and alkyl halides by using synchrotron X-ray absorption spectroscopies. XANES and EXAFS spectra demonstrated the reactions of $\text{FeBr}_2(\text{SciOPP})$ with 1.0 or 2.0 equivalents of MesMgBr in THF afforded tetrahedral $\text{FeBrMes}(\text{SciOPP})$ and square-planer $\text{FeMes}_2(\text{SciOPP})$, respectively. By consideration of these results with examination of their reactivities, i.e., $\text{FeMes}_2(\text{SciOPP})$ was found to react with an alkyl halide to give the corresponding coupling product and $\text{FeBrMes}(\text{SciOPP})$, the intermediacy of the mesityliron complexes in the $\text{FeBr}_2(\text{SciOPP})$ -catalyzed cross-coupling reaction.

Supramolecular Approach for Creating Enhanced Catalysis of Metallic Nanoparticles

This project focuses on the development of highly active and selective metallic nanoparticle catalysts based on supramolecular approaches. To achieve this purpose, four key methodologies act considerably important roles: 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 4) plasmonic resonance with light. We aim to create a new class of catalyst system using a range of transition metallic nanoparticles.

