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<th>International Research Center for Elements Science</th>
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Kyoto University
Scope of Research

This laboratory aims at establishment of new synthetic methodologies and new functional materials by designing well-defined catalysts based on transition metal chemistry. New concepts and ideas of molecular-based catalysts are accumulated by mechanistic investigations using kinetic techniques on the reaction intermediates and elementary processes. The research subjects include: (1) development of novel ligand systems for catalysis, (2) functionalization of organic substrates on transition-metal clusters, and (3) development of highly efficient ways of constructing functional organic molecules.

Research Activities (Year 2004)

Presentations


Bromination of Four Acetylenic Protons on Cp‘dFe(η6CCH2). Reactivity of the Resulting Bromoacetylene Fragments toward Nucleophiles, Okazaki M, Takano M (Tohoku Univ.), Ohtani T., (Tohoku Univ.) Tobita H (Tohoku Univ.), Ogino H (The Univ. of the Air), The 12th Japan-Korea Joint Symposium on Organometallic and Coordination Chemistry, 3-6 August, Sendai, Japan.


Grants
Catalytic C-O Bond Cleavage of Allylic Alcohols and Ethers Using Diphosphinidenecyclobutene-Coordinated Palladium Complexes

We recently found that (π-allyl)palladium complex 1 bearing 1,2-bis(4-methoxyphenyl)-3,4-bis(2,4,6-tri-tert-butylphenylphosphinidenecyclobutene (DPCB-OMe) efficiently catalyzes direct conversion of allylic alcohols into N- and C-allylation products under mild conditions. In this study, we have elucidated a novel catalytic mechanism given in Scheme 1 [1]. Thus, unlike common allylation reactions involving oxidative addition of a C-O bond to a Pd(0) species, the C-O bond of allylic alcohols is cleaved by the action of hydridopalladium complex A. Proton-transfer from the Pd to the OH group in B, followed by elimination of water from C, forms π-allyl complex 1. We reasoned that strong π-accepting ability of DPCB-OMe ligand as an sp²-hybridized phosphorus compound efficiently stabilizes C as a Pd(0) species by π-back-donation to facilitate the proton-transfer in B.

This novel catalysis is applied to deallylation of a variety of allyl ethers in aniline to give corresponding alcohols in high yields under mild conditions (Scheme 2) [2]. The reactions can be performed in air without loss of a variety of functionalities including vinyl, alkynyl, hydroxy, acetoxy, silyloxy, and acetal groups.

Reversible Cleavage and Recombination of Acetylenic Carbon-Carbon Bond on a Tetrairon Cluster Coupled with Two-Electron Redox Reaction

Two-electron reduction of 2 resulted in the coupling of two methyldiene ligands to afford 3 (Scheme 3) [3]. The point we wish to stress is that formation and cleavage of the carbon-carbon bond can be controlled on the Fe₄ core by two-electron reduction and oxidation. Two-electron oxidation of 3 led to the cleavage of the carbon-carbon bond to reproduce 2. To our knowledge, our present study is the first example, in which the reversible carbon-carbon bond cleavage and formation occurs between acetylene and two methyldiene fragments via two-electron oxidation and reduction.

Scheme 3. Reversible carbon-carbon bond formation induced by two-electron redox reaction.


(Z)-Selective Cross-Dimerization of Arylacetylenes with Silylacetylenes Catalyzed by Vinylideneruthenium Complexes

Vinylideneruthenium complex 4 serves as good catalyst precursors for (Z)-selective cross-dimerization between acetylenes and silylacetylenes in the presence of N-methylpyrrolidine (Scheme 4). The reactions proceed at room temperature to afford (Z)-1-aryl-4-silyl-1-buten-3-yne in over 90% regio- and stereo-selectivities. The resulting enynes are efficiently desilylated by treatment with K₂CO₃ in MeOH to give terminal alkenylacetylenes (ArCH=CH-C≡CH) with (Z)-configurations.

Scheme 4. Ruthenium-catalyzed cross-dimerization between arylacetylenes and silylacetylenes.


Award