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Scope of Research

This is a new research laboratory launched in the 2003 academic year, aiming 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) synthesis and catalytic properties of transition metal-heavy element complexes, and (3) development of highly efficient ways of constructing functional organic molecules.

Research Activities (Year 2003)

Presentations
Convenient Route to Thio- and Selenocarbene Ruthenium Complexes Serving as Highly Selective Catalysts for Ring-Opening/Cross Metathesis, Katayama H, Nagao M, Ozawa F, The 15th International Symposium on Olefin Metathesis and Related Chemistry (ISOM XV), 28 July - 1 August, Kyoto, Japan.

Synthesis, Structure, and Alkyn Insertion Reactions of Platinum-Group 14 Element Complexes, Sagawa T, Ozawa F, 92nd CATSJ Meeting, 18 - 21 September, Tokushima, Japan.


Highly Reactive Organometallic Complexes Bearing Diphosphinidenecyclobutene Ligands: Synthesis and Catalysis, CSJ Hiroshima Seminar, 6 December, Higashihiroshima, Japan.

Grants


(π-Allyl)palladium Complexes Bearing Diphenphosinidene Cyclobutene Ligands (DPCB): Highly Active Catalysts for Direct Conversion of Allylic Alcohols

sp3-Hybridized phosphorus compounds have a marked tendency to engage in metal-to-phosphorus π-backbonding and have a strong π-acceptor property comparable to that of the carbonyl ligand. Therefore, unlike common phosphine and cyclopentadienyl ligands, DPCB may effectively enhance the electrophilicity of metal centers. We have found in this study that (π-allyl)palladium complex (1) bearing DPCB ligands effectively catalyze the direct allylation of aniline and active methylene compounds with allylic alcohols [1]. These reactions proceed via a novel allylation mechanism including a hydridopalladium intermediate, which is significantly acidic due to the unique coordination property of DPCB ligand.

![Image](image_url)

Scheme 1. Direct conversion of allylic alcohols catalyzed by (DPCB)-Pd(π-allyl) complex 1.

Polyaddition of 2,7-Diethynyl-9,9-dioctylfluorene Using Regio- and Stereoselective Alkyne-Dimerization Catalysts

We have succeeded in regio- and stereoselective synthesis of polyfluorene ethynylene vinylenes using catalytic polyaddition process (Scheme 3). The structure of vinylene units clearly reflects the nature of catalysts observed in the prototype dimerization reactions of arylacetylenes. These polymers show marked differences in optical properties dependent on the structure of the main chain [3].

![Image](image_url)

Scheme 3. Regio- and stereoselective synthesis of PFEVs.