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Kyoto University
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.

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.


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

Grants


sp²-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 alkylation of aniline and active methylene compounds with allylic alcohols [1]. These reactions proceed via a novel alkylation mechanism including a hydridopalladium intermediate, which is significantly acidic due to the unique coordination property of DPCB ligand.

![Figure 1. X-ray structure of 1.](image)


### Alkyne Insertion into cis-Silyl(stannyl)platinum(II) Complexes

Addition of inter-element linkages to alkynes catalyzed by group 10 metal complexes has attracted a great deal of recent interest. We have elucidated the mechanism of alkyne insertion into cis-silyl(stannyl)platinum complexes (2), which are models of key intermediates for palladium-catalyzed silylstannylation of unsaturated hydrocarbons [2]. Complexes 2 undergo competitive insertion of alkynes into the Pt–Sn and Pt–Si bonds. The ratio of the resulting insertion complexes 3 to 4 is significantly affected by the types of silyl and phosphine ligands and alkynes employed. The variations thus observed have been reason-ably interpreted on the basis of the insertion mechanism involving associative displacement of one of the phosphine ligands in 2 with alkynes, followed by competitive migration of the stannyl and silyl ligands on the alkyne ligand in the resulting 5 and 6 (Scheme 2).

![Scheme 2. Mechanism of alkyne insertion into cis-silyl(stannyl)platinum(II) complexes 2.](image)


### Polyaddition of 2,7-Diethynyl-9,9-dioctyl fluorene Using Regio- and Stereoselective Alkyne-Dimerization Catalysts

We have succeeded in regio- and stereoselective synthesis of poly(fluorene ethynylene vinylene)s 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].

![Scheme 3. Regio- and stereoselective synthesis of PFEVs.](image)