

International Research Center for Elements Science - Organotransition Metal Chemistry -

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

Synthesis of Unsymmetrically End-Functionalized Poly(norbornene)s by Ring-Opening Metathesis Polymerization/Chain-Transfer System, Katayama H, Ozawa F, *et al.*, SPSJ 52nd Symposium on Macromolecules, 24 - 26 September, Yamaguchi, Japan.

Synthesis and Reactions of Hydridoplatinum(II) Complexes Bearing Diphosphinidene-cyclobutene Ligands (DPCB), Ishiyama T, Ozawa F, *et al.*, 50th Symposium on Organometallic Chemistry, Japan, 28 - 30 September, Osaka, Japan.

Development of Highly Selective Catalysis for the Synthesis of Tailored Polymers, Ozawa F, Katayama H, *et al.*,

JPI Symposium 2003 in Osaka, 17 - 19 November, Osaka, Japan.

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

Grants

Ozawa F, Reaction Control of Catalytic Intermediates, Grant-in-Aid for Scientific Research on Priority Areas, Oct. 2002 - Mar. 2006.

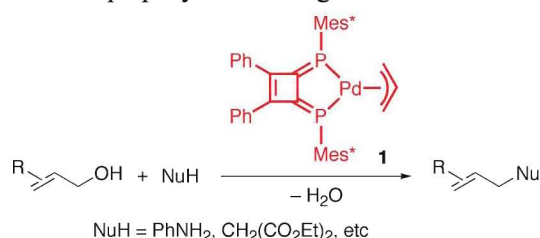
Ozawa F, Development of Novel Catalysis using 5-Membered Chelate Complexes with sp^2 -Hybridized Phosphorus Atoms, Grant-in-Aid for Scientific Research on Priority Areas, Apr. 2002 - Mar. 2004.

Ozawa F, Novel Organometallic Complexes with Phosphaalkene Ligands: Synthesis and Catalysis, Grand-in-Aid for Scientific Research (B) (2), Apr. 2003 - Mar. 2006.

Katayama H, Stereocontrolled Synthesis of π -Conjugated Polymers Using Transition Metal Catalysts, The Ogasawara Foundation for the Promotion of Science & Engineering, Apr. 2003 - Mar. 2004.

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

sp^2 -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.



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

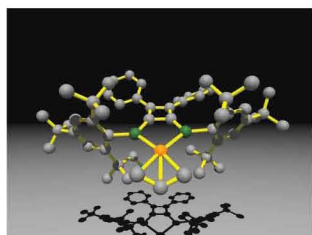


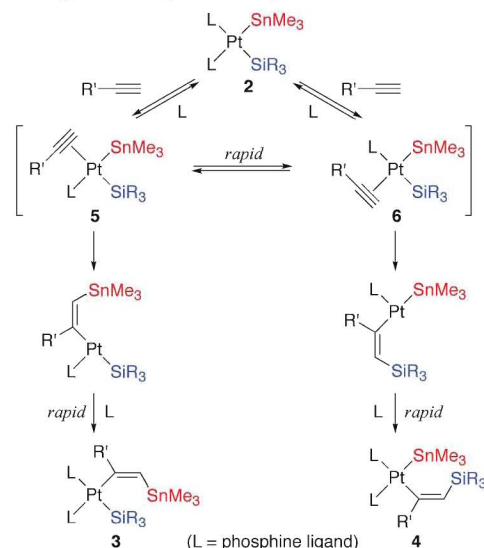
Figure 1. X-ray structure of **1**.

1. Ozawa F, Okamoto H, Kawagishi S, Yamamoto S, Minami T, Yoshifuji M, *J. Am. Chem. Soc.*, **2002**, *124*, 10968.

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).

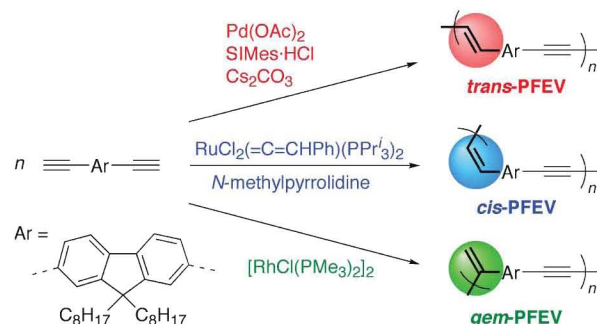


Scheme 2. Mechanism of alkyne insertion into *cis*-silyl(stannyl)platinum(II) complexes **2**.

2. Sagawa T, Sakamoto Y, Tanaka R, Katayama H, Ozawa F, *Organometallics*, **2003**, *22*, 4433.

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

We have succeeded in regio- and stereocontrolled 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 stereocontrolled synthesis of PFEVs.

3. Katayama H, Nakayama M, Nakano T, Wada C, Akamatsu K, Ozawa F, *Macromolecules*, in press.