

# International Research Center for Elements Science - Organotransition Metal Chemistry -

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## 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) creation of functional metal complexes based on synergistic effects, (3) construction of  $\pi$ -conjugation system including transition-metals, and (4) development of functional molecules including redox-active transition-metal clusters.

## Research Activities (Year 2007)

### Publications

Jensen R S, Umeda K, Okazaki M, Ozawa F, Yoshifuji M: Synthesis and Catalytic Properties of Cationic Palladium(II) and Rhodium(I) Complexes Bearing Diposphinidene-cyclobutene Ligand, *J. Organomet. Chem.*, **692**, 286-294 (2007).

Hayashi A, Ishiyama T, Okazaki M, Ozawa F: Cationic Iridium(III) Complexes Bearing Phosphaalkene and 2-Pyridylphenyl Ligands, *Organometallics*, **26**, 3708-3712 (2007).

Hayashi A, Okazaki M, Ozawa F, Tanaka R: Synthesis, Structures, and Catalytic Properties of Late-Transition-Metal 2,6-Bis(2-phosphaethenyl)pyridine Complexes, *Organometallics*, **26**, 5246-5249 (2007).

### Presentations

Construction of Novel Reaction Sites on Transition-Metal Complexes Enhanced by Low-Coordinated Phosphorus Compounds, Ozawa F, The 87th Annual Meeting of the Chemical Society of Japan, 25–28 March 2007, Osaka, Japan (Invited).

Electron-Induced Structural Changes in [4Fe–4C] Cluster Core, Okazaki M, Takano M, Ohtani T, Yoshimura K, Ozawa F, Ogino H, The 1st Asian Conference on Coordination Chemistry, 30 July 2007, Okazaki, Japan.

Construction of Functional Molecules Possessing [4Fe–4C] Core, Okazaki M, The 56th Symposium on Coordination Chemistry of Japan, 16 September 2007, Nagoya, Japan (Invited).

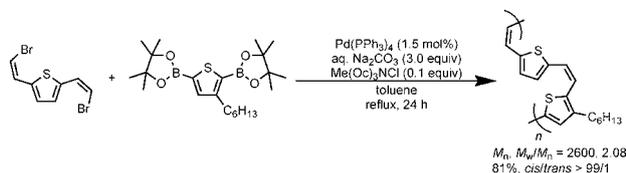
Stereocontrolled Synthesis of All-cis Poly(arylene vinylene)s: Effects of Primary Structures on Photo-Induced Insolubilization in Thin Films, Yamamoto Y, Wakioka M, Mutoh Y, Takita R, Katayama H, Ozawa F, The 10th Pacific Polymer Conference, 4–7 December 2007, Kobe, Japan.

### Grants

Ozawa F, Okazaki M, Takita R, Synergistic Effects of Transition Metals and Heavier Main Group Elements in Functional Organometallic Complexes, Grant-in-Aid for Priority Area “Synergy of Elements”, 1 September 2006–31 March 2010.

## Syntheses and Characteristics of All-cis Poly(arylene vinylene)s Containing Thienylene Groups in Main Chains

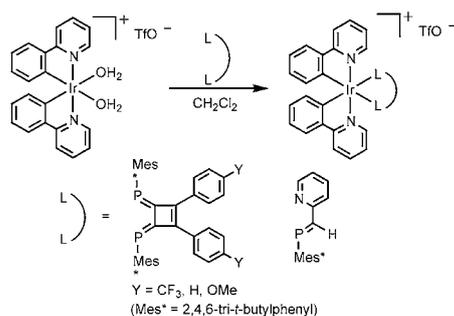
All-cis poly(arylene vinylene)s (PAV) containing thiophene derivatives have been prepared in a highly stereocontrolled manner based on Suzuki-Miyaura coupling according to a procedure we previously developed. It has been found that thin films of all-cis PAVs are insolubilized and well immobilized under UV-irradiation, along with cis-to-trans one-way photoisomerization. This phenomenon has been successfully applied to construction of novel carrier transfer materials showing great enhancement of carrier mobility upon photo-induced insolubilization.



**Scheme 1.** Synthesis of all-cis PAV containing thiophene in main chain.

## Cationic Iridium(III) Complexes Bearing Phosphaalkenes and 2-Pyridylphenyl Ligands

We have synthesized a new series of cationic iridium(III) complexes bearing phosphaalkene and 2-pyridylphenyl ligands and examined their electrochemical and

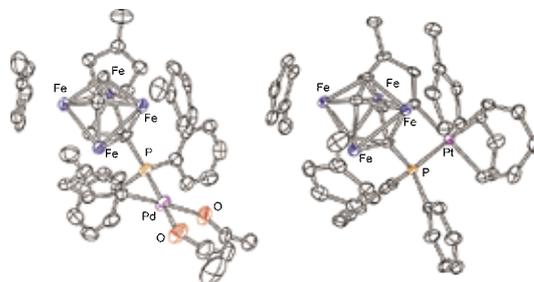


**Scheme 2.** Synthesis of Ir(III) complexes bearing phosphaalkene and 2-pyridylphenyl ligands.

photophysical properties. It has been confirmed that the metal  $t_{2g}$  levels can be tuned by chemical modification of the phosphaalkene ligands. The DPCB-CF<sub>3</sub> ligand in **1** serves as a particularly effective  $\pi$ -acceptor to cause bluish-green luminescence at 492 nm.

## Synthesis and Property of Phosphine Ligands Possessing Redox-Active [4Fe-4C] Core Substituents

Treatment of [Cp\*<sub>4</sub>Fe<sub>4</sub>(HCCCH)<sub>2</sub>] (**1**, Cp\* =  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me) with 2 equiv. NBS resulted in the exclusive formation of [Cp\*<sub>4</sub>Fe<sub>4</sub>(HCCCH)(HCC-Br)]<sup>+</sup> (**[2]**<sup>+</sup>). The generated bromoacetylene part on the tetrairon core is highly electrophilic and reacted with HPPH<sub>2</sub> in the presence of NEt<sub>3</sub> to give [Cp\*<sub>4</sub>Fe<sub>4</sub>(HCCCH)(HCC-PPh<sub>2</sub>)]<sup>+</sup> (**[3]**<sup>+</sup>). Reaction of **[3]**<sup>+</sup> with [Cp<sub>2</sub>Co] afforded the neutral form **3**. To estimate the *s* character of the lone pair of **3**, the NMR coupling constant <sup>1</sup>J(P-Se) of the phosphine selenide **4** was measured. The <sup>1</sup>J(P-Se) value of **4** (693 Hz) is significantly smaller than those in Se=PR<sub>3</sub> [R = Ph (755 Hz), <sup>t</sup>Bu (708 Hz), Cy (706 Hz)], indicating the exceptionally electron-releasing character of **3**. Complexation of **3** with Pd(II) and Pt(II) metals have been achieved under the mild conditions.



**Figure 1.** Molecular structure of Pd(II) and Pt(II) complexes having cluster ligands.

Okazaki M, Mihara H, Construction of Novel Functional Molecules by Hybridization of Biomolecules with Transition Metal Clusters, Grant-in-Aid for Exploratory Research, 1 April 2007–31 March 2009.

Okazaki M, Mihara H, Construction of Novel Catalysts Based on Flexible Structural Changes of Multimetallic Cores, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2007–31 March 2008.

Okazaki M, Chemistry of Nonplanar Carbocations Bridged over Transition Metals, Mitsubishi Chemical Corporation Fund, 1 April 2007–31 March 2008.

Takita R, Development of Catalytic Reactions Using Low Coordinate Phosphine Ligands, Grant-in-Aid for Young Scientists (Start-up), 1 August 2007–31 March 2009.