

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 experimental methods such as kinetic techniques as well as theoretical methods. The research subjects include: (1) development of novel organotransition metal systems for catalysis based on precise ligand design, (2) preparation of π -conjugated polymers by the use of well defined cross-coupling reactions, and (3) development of functional molecules including redox-active transition-metal clusters.

Research Activities (Year 2009)

Publications

Wakioka M, Nakajima Y, Ozawa F: Mechanism of C-P Reductive Elimination from *trans*-[Pd(CH=CHPh)Br(PMePh₂)₂], *Organometallics*, **28**, 2527-2534 (2009).

Wakioka M, Mutoh Y, Takita R, Ozawa F: A highly Selective Catalytic System for the Cross-Coupling of (*E*)-Styryl Bromide with Benzeneboronic Acid: Application to the Synthesis of All-Trans Poly(arylenevinylene)s, *Bull. Chem. Soc. Jpn.*, **82**, 1292-1298 (2009).

Okazaki M, Takano M, Ozawa F: Redox-responsive Recombination of Carbon-Carbon Bonds on Flexible Tetrairon Cores, *J. Am. Chem. Soc.*, **131**, 1684-1685 (2009).

Presentations

Synthesis and Properties of Bis(phosphaethenyl)pyridine Iron Complexes, Ozawa F, Nakajima Y, The 14th Japan-Korea Joint Symposium on Organometallic and Coordination Chemistry, 9 October 2009, Nagoya, Japan (Invited).

Synthesis and Properties of All-cis Poly(arylene vinylene)₂, Ozawa F, Takita R, NSYU-KU Bilateral Symposium on Materials Chemistry, 23 September 2009, Kaohsiung, Taiwan.

Grants

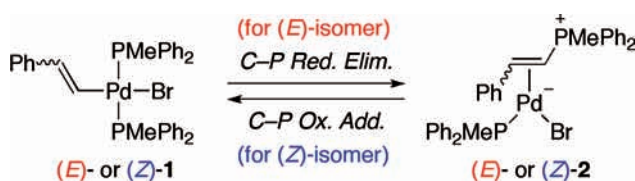
Ozawa F, Okazaki M, Takita R, Nakajima Y, Synergistic Effects of Transition Metals and Heavier Main Group Elements in Functional Organometallic Complexes, Grant-in-Aid for Priority Area "Synergy of Elements", 1 September 2006–31 March 2010.

Ozawa F, Takita R, Nakajima Y, Studies of Cross-coupling Reactions for Precise Synthesis of π -Conjugated Polymers, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2008–31 March 2010.

Okazaki M, Construction of Functional Molecules Based on Characteristics of Polymetallic Cores, Grant-in-Aid for Scientific Research(B), 1 April 2008–31 March 2012.

Mechanism of C-P Reductive Elimination from *trans*-[Pd(CH=CHPh)Br(PMePh₂)₂]

While the C-P reductive elimination of hydrocarbyl and phosphine ligands are frequently observed in catalytic processes promoted by palladium phosphine complexes, its mechanistic information has been limited. In this work, we prepared the (*E*)- and (*Z*)-styryl isomers of *trans*-[Pd(CH=CHPh)Br(PMePh₂)₂] (**1**) and [Pd(η^2 -PhCH=CHPMePh₂)Br(PMePh₂)] (**2**), and examined their C-P reductive elimination (**1** \rightarrow **2**) and C-P oxidative addition (**2** \rightarrow **1**) behaviors. Kinetics and thermodynamics of the reactions are strongly affected by *E/Z* configurations of the styryl group and solvent polarity. The (*E*)-isomer of **1** undergoes C-P reductive elimination easily in polar CD₂Cl₂ to afford (*E*)-**2** in high selectivity, whereas C-P oxidative addition of (*Z*)-**2** giving (*Z*)-**1** takes place favorably in non-polar C₆D₆. X-Ray diffraction analysis and DFT calculations for **1** and **2** provided reasonable accounts for these reaction features. Kinetic examinations revealed two types of C-P reductive elimination processes, which involve pre-dissociation and association of PMePh₂ ligand, respectively.

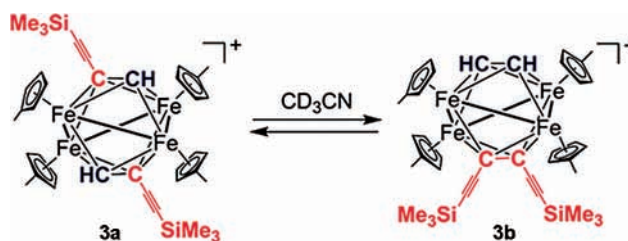


Scheme 1. C-P reductive elimination and oxidative addition behaviors of complexes **1** and **2**.

Redox-Responsive Recombination of Carbon-Carbon Bonds on Flexible Tetrairon Cores

Although there have been many studies on tetranuclear transition metal clusters, the interconversion between each cluster core structure remains poorly understood. Based on these facts, we investigated the geometry interconversion of the tetrairon core using [(η^5 -C₅H₄Me)₄Fe₄(Me₃SiCCH)₂] (PF₆) (**3a**) as a probe. When a brown powder of **3a** was dissolved in acetonitrile, **3a** was converted to **3b**. Equilibrium was reached at a 74:26 molar ratio within 1 week at 303

K. The isomerization proceeds through a cubane-like transition state, in which recombination of a carbon-carbon bond occurs.



Scheme 2. Recombination of carbon-carbon bonds on tetrairon cores.

The Effects of Primary Structures on Photo-induced Insolubilization of All-cis Poly(*p*-phenylenevinylene)s in Thin Films

All-cis PPVs prepared by Suzuki-Miyaura-type polycondensation undergo photo-induced insolubilization in thin films, along with cis-to-trans isomerization of vinylene linkages to give all-trans PPVs. This phenomenon has been investigated in detail, using all-cis and all-trans PPVs with a range of molecular weights and terminal structures. It has been found that the all-cis configuration serves as a particularly important factor.

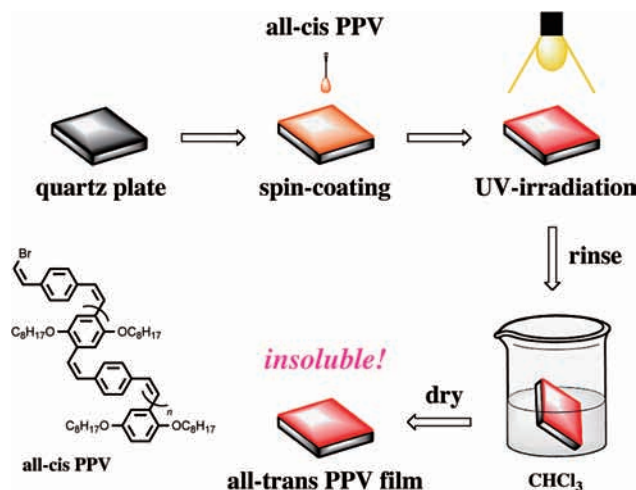


Figure 1. Photo-induced insolubilization of all-cis poly(*p*-phenylenevinylene)s in thin films.

Takita R, Development of Efficient Synthetic Methodologies Based on Direct Functionalization Reactions, Grant-in-Aid for Young Scientists (B), 1 April 2009–31 March 2011.

Nakajima Y, Efficient Photoreduction of Carbon Dioxide Catalyzed by an Iron Complex Bearing a Phosphaalkene Ligand, PRESTO Program, Japan Science and Technology Agency, 1 October 2009–31 March 2012.