

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, and (2) preparation of π -conjugated polymers by the use of well defined cross-coupling reactions.

KEYWORDS

Transition Metal Complex
Homogeneous Catalyst
Reaction Mechanism
Synergistic Effect



Selected Publications

Wakioka M, Ikegami M, Ozawa F: Stereocontrolled Synthesis and Photoisomerization Behavior of All-cis and All-trans Poly(m-phenylenevinylene)s, *Macromolecules*, **43**, 6980-6985 (2010).

Wang Q, Takita R, Kikuzaki Y, Ozawa F: Palladium-Catalyzed Dehydrohalogenative Polycondensation of 2-Bromo-3-hexylthiophene: An Efficient Approach to Head-to-Tail Poly(3-hexylthiophene), *J. Am. Chem. Soc.*, **132**, 11420-11421 (2010).

Nakajima Y, Nakao Y, Sakaki S, Tamada Y, Ono T, Ozawa F: Electronic Structure of Four-coordinate Iron(I) Complex Supported by a Bis(phosphaethenyl)pyridine Ligand, *J. Am. Chem. Soc.*, **132**, 9934-9936 (2010).

Wakioka M, Ozawa F: Substituent Effects on P-C Reductive Elimination from Styrylpalladium(II) Phosphine Complexes, *Organometallics*, **29**, 5570-5578 (2010).

Nakajima Y, Nakatani M, Hayashi K, Shiraishi Y, Takita R, Okazaki M, Ozawa F: Synthesis and Structures of Platinum Diphenylacetylene and Dithiolate Complexes Bearing Diphosphinidene-cyclobutene Ligands (DPCB-Y), *New. J. Chem.*, **34**, 1713-1722 (2010).

Substituent Effects on P–C Reductive Elimination from Styrylpalladium(II) Phosphine Complexes

While the P–C reductive elimination of hydrocarbyl and phosphine ligands is frequently observed, its mechanistic information has been limited. In this work, we prepared a series of styryl palladium complexes **1**, having a series of para substituents with different electronic properties on Ar and Ar' groups, and examined their reductive elimination in the presence of added PMeAr'_2 by kinetic experiments. The kinetic data are consistent with the reaction process involving prior association of **1** with PMeAr'_2 to form a five-coordinate intermediate (A), which subsequently undergoes P–C reductive elimination to give **2**. The rate constant for P–C reductive elimination (k) increases to a great extent as the electron-donating ability of para substituents increases, and showed a good Hammett correlation with the σ_p values of substituents [$\rho = -2.43$ and -4.8 (for Ar and Ar', respectively)].

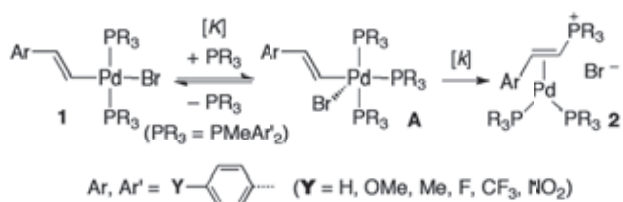


Figure 1. P–C reductive elimination from **1** in the presence of added PMeAr'_2 .

Palladium-Catalyzed Dehydrohalogenative Polycondensation of 2-Bromo-3-hexylthiophene: An Efficient Approach to Head-to-Tail Poly(3-hexylthiophene)

Poly(3-alkylthiophene)s are among the most promising π -conjugated polymers for the development of flexible electronic devices. It has been documented that their physical properties are strongly affected by the regioregularity of the thiophene units, and head-to-tail polymers are superior to regiorandom isomers. In this work, we examined the synthesis of head-to-tail poly(3-hexylthiophene) (HT-P3HT) using palladium-catalyzed dehydrogenative polycondensation of 2-bromo-3-hexylthiophene (**3**). The reaction of **3** with **4** and **5** as catalyst precursors gave HT-P3HT with high molecular weight ($M_n = 30600$, $M_w/M_n = 1.60$) and high regioregularity (98%) in almost quantitative yield (99%). This process, which does not require prepreparation of organometallic reagents, should be of benefit with respect to reduced waste generation and fewer reaction steps.

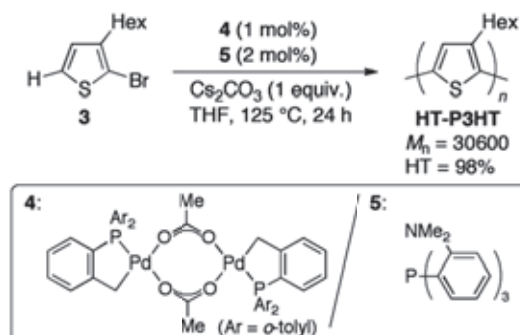


Figure 2. Palladium-catalyzed dehydrohalogenative polycondensation of 2-bromo-3-hexylthiophene (**3**).

Electronic Structure of Four-coordinate Iron(I) Complex Supported by a Bis(phosphoethenyl)pyridine Ligand

A 15-electron iron complex with a formal Fe(I) center, $[\text{FeBr}(\text{BPEP})]$ (BPEP = 2,6-bis(1-phenyl-2-phosphaethenyl)pyridine), was prepared by one-electron reduction of the dibromide precursor $[\text{FeBr}_2(\text{BPEP})]$. The single-crystal diffraction analysis revealed a distorted trigonal monopyramidal arrangement around the iron center. DFT calculations for a model complex revealed two highly delocalized molecular orbitals formed by bonding and antibonding interactions between the d_{2z} (Fe) and π^* (BPEP) orbitals. Orbital occupancy analysis demonstrated the electronic structure with a high-spin Fe(I) center. The effective interaction between iron and BPEP was concluded to be responsible for the highly distorted structure of $[\text{FeBr}(\text{BPEP})]$, with its rather uncommon trigonal monopyramidal configuration.

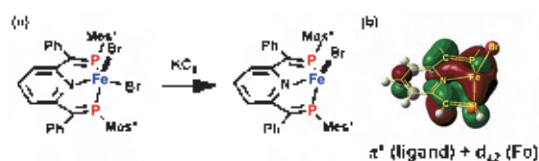


Figure 3. (a) Formation of $[\text{FeBr}(\text{BPEP})]$, (b) delocalized molecular orbital of $[\text{FeBr}(\text{BPEP})]$.