

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 spectroscopy and 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 using direct arylation.

KEYWORDS

Transition Metal Complex
Homogeneous Catalyst
Reaction Mechanism
Low-coordinate Phosphorus Ligand
 π -Conjugated Polymer



Selected Publications

Takita, R.; Fujita, D.; Ozawa, F., Direct Arylation of Heteroarenes Catalyzed by a Pd/1,10-Phenanthroline Complex, *Synlett (Special Issue Dedicated to Professors Lixin Dai and Xiyun Lu)*, 959-963 (2011).

Nakajima, Y.; Shiraishi, Y.; Tsuchimoto, T.; Ozawa, F., Synthesis and Coordination Behavior of Cu^I Bis(phosphaethenyl)pyridine Complexes, *Chem. Commun.*, **47**, 6332-6334 (2011).

Okazaki, M.; Tsuchimoto, T.; Nakazawa, Y.; Takano, M.; Ozawa, F., Reaction of Bromoacetylene with Primary Amine on a Butterfly-Type Tetrairon Core to Give Isonitrile and Methyne through Oxidation and Deprotonation, *Organometallics*, **30**, 3487-3489 (2011).

Synthesis and Coordination Behavior of Cu(I) Bis(phosphaethenyl)pyridine Complexes

Phosphaalkenes with P=C bond(s) are low-coordinate phosphorus compounds, which possess extremely low-lying π^* orbitals around the phosphorus atom(s) and thus exhibit strong π -acceptor properties towards transition metals. In this study, we found that Cu(I) complexes bearing BPEP as a PNP-pincer type phosphaalkene ligand undergo effective bonding interactions with SbF_6^- and PF_6^- as non-coordinating anions to give $[\text{Cu}(\text{SbF}_6)(\text{BPEP})]$ and $[\text{Cu}_2(\text{BPEP})_2(\mu\text{-PF}_6)]^+$, respectively [BPEP = 2,6-bis(1-phenyl-2-phosphaethenyl)pyridine]. NMR and theoretical studies indicated a reduced anionic charge of the $\mu\text{-PF}_6$ ligand, which is induced by the strong π -accepting ability of BPEP.

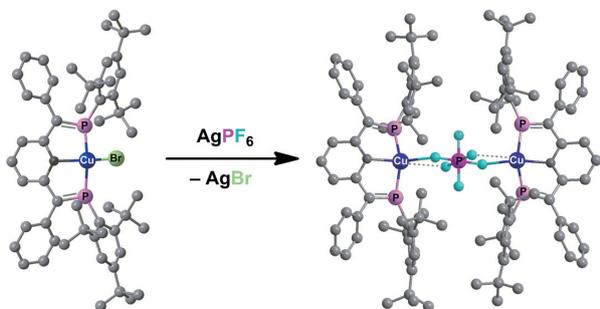


Figure 1. Formation of $[\text{Cu}_2(\text{BPEP})_2(\mu\text{-PF}_6)]^+[\text{PF}_6]^-$.

Redox Chemistry of Bis(phosphaethenyl)pyridine Iron Complexes

Redox chemistry of iron complexes has drawn increasing attention in connection with activation of small molecules in enzymatic systems. In this study, we investigated the redox properties of iron dibromide $[\text{FeBr}_2(\text{BPEP})]$ and iron monobromide $[\text{FeBr}(\text{BPEP})]$ coordinated with BPEP as a tridentate PNP-pincer type phosphaalkene ligand. Treatment of $[\text{FeBr}_2(\text{BPEP})]$ with $\text{Mes}_2\text{Mg}(\text{THF})_2$ (Mes = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$) led to one-electron reduction to afford $[\text{FeBr}(\text{BPEP})]$, followed by transmetalation giving $[\text{FeMes}(\text{BPEP})]$ with a four-coordinate Fe(I) center (Figure 2). It is likely that the π -conjugation effect, which is derived from the $d\pi\text{-}p\pi$ interaction between the Fe(I) and BPEP ligand, is responsible for the easy reduction of $[\text{FeBr}_2(\text{BPEP})]$ to Fe(I) complexes.

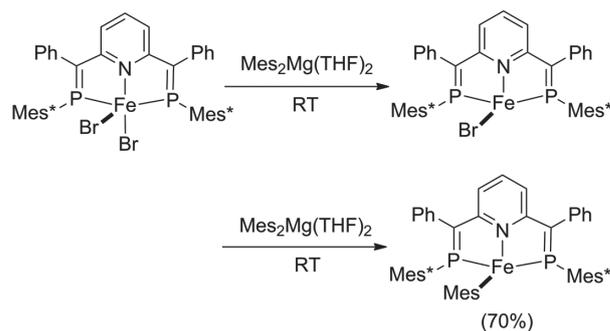


Figure 2. Reaction of $[\text{FeBr}_2(\text{BPEP})]$ with $\text{Mes}_2\text{Mg}(\text{THF})_2$.

Synthesis of End-capped Head-to-tail Regioregular Poly(3-hexylthiophene)s via Direct Arylation

While the catalytic dehydrohalogenative coupling of heteroarenes with aryl halides (so-called direct arylation) has received much attention in synthetic organic chemistry as an advanced means of C–C bond formation, its application to polycondensation has been poorly implemented until very recently. In this study, we have succeeded in the synthesis of head-to-tail regioregular poly(3-hexylthiophene)s end-capped with aryl groups (Ar-HT-P3HTs) using palladium-catalyzed polycondensation via direct arylation. As a typical example, heating a THF solution of 2-bromo-3-hexylthiophene (**1**), bromobenzene (1 equiv), $\text{Pd}\{o\text{-tolyl}\}_3$ (**2**, 2 mol%), **L** (2 mol%), Cs_2CO_3 (1 equiv), and KOAc (1 equiv) at 125°C for 36 h resulted in the formation of Ph-HT-P3HT with 99% regioregularity and M_n of 7100 in 99% yield, where 95% of the initiated end of polymer is capped with phenyl group as confirmed by ^1H NMR spectroscopy (Figure 3).

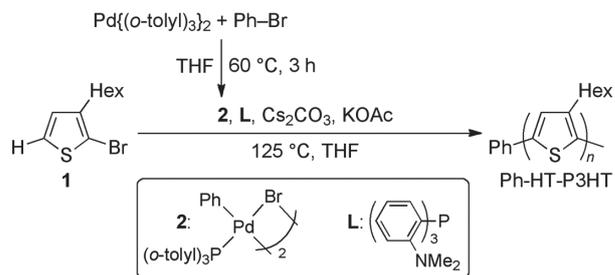


Figure 3. Synthesis of phenyl-capped HT-P3HT via direct arylation.