International Research Center for Elements Science – Organotransition Metal Chemistry –

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Prof
OZAWA, Fumiyuki
(D Eng)

Assist Prof
WAKIOKA, Masayuki
(D Eng)

Assist Prof
TAKEUCHI, Katsuhiko
(D Sc)

Researcher(pt)

ICHIHARA, Nobuko

Students

TAGUCHI, Hiro-omi (D1)
IIZUKA, Eisuke (M2)
TANIGAWA, Ippei (M2)
SASAKI, Daichi (M1)
TAKAHASHI, Rina (M1)
XU, Kai (RS)
TANAKA, Yuto (UG)
YAMASHITA, Natsumi (UG)

Scope of Research

This laboratory aims to establish 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 using direct arylation.

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

Selected Publications

Chang, Y.-H.; Tanigawa, I.; Taguchi, H.; Takeuchi, K.; Ozawa, F., Iridium(I) Complexes Bearing a Noninnocent PNP-Pincer Type Phosphaalkene Ligand: Catalytic Application to Base-Free N-Alkylation of Amines with Alcohols, *Eur. J. Inorg. Chem.* (in press).

Chang, Y.-H.; Takeuchi, K.; Wakioka, M.; Ozawa, F., C-H Bond Cleavage of Acetonitrile by Iridium Complexes Bearing PNP-Pincer Type Phosphaalkene Ligands, *Organometallics*, **34,** 1957-1962 (2015).

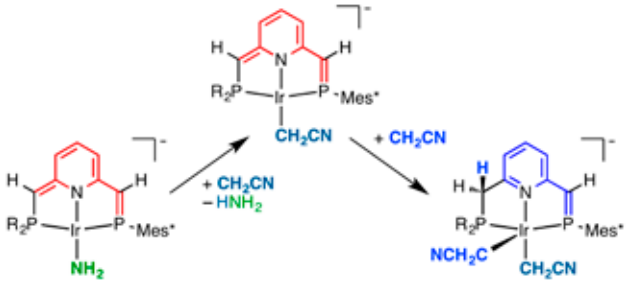
Iizuka, E.; Wakioka, M.; Ozawa, F., Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Synthesis of Donor-Acceptor Polymers with Dithienosilole (DTS) and Thienopyrroledione (TPD) Units, *Macromolecules*, **48,** 2989-2993 (2015).

Taguchi, H.; Chang, Y.-H.; Takeuchi, K.; Ozawa, F., Catalytic Synthesis of an Unsymmetrical PNP-Pincer Type Phosphaalkene Ligand, *Organometallics*, **34,** 1589-1596 (2015).

Wakioka, M.; Nakamura, Y.; Montgomery, M.; Ozawa, F., Remarkable Ligand Effect of $P(2\text{-}MeOC_6H_4)_3$ on Palladium-Catalyzed Direct Arylation, *Organometallics*, **34,** 198-205 (2015).

C–H Bond Cleavage of Acetonitrile by Iridium Complexes Bearing PNP-pincer Type Phosphaalkene Ligands

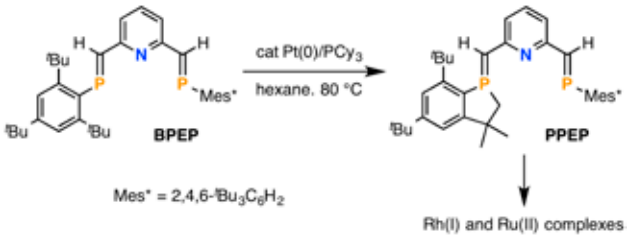
A novel parent amido complex of iridium(I), K[Ir(NH_2)(PPEP*)], coordinated with a dearomatized PNP-pincer-type phosphaalkene ligand (PPEP*) has been prepared by deprotonation with KHMDS from [Ir(NH_2)(PPEP)], with benzophospholanylmethyl and phosphaethenyl groups at the 2,6-positions of pyridine. K[Ir(NH_2)(PPEP*)] has two base points at PPEP* and NH_2 ligands and, thus, successively reacts with two molecules of CH_3CN via heterolytic cleavage of the C–H bond. X-ray structural analysis of the product complex K[Ir(CH_2CN)$_2$(PPEP)] reveals remarkable elongation of the P=C bond, indicative of the occurrence of strong π-back-donation from iridium to PPEP.



Scheme 1. Reaction of [Ir(NH_2)(PPEP)] with acetonitrile.

Catalytic Synthesis of an Unsymmetrical PNP-pincer Type Phosphaalkene Ligand

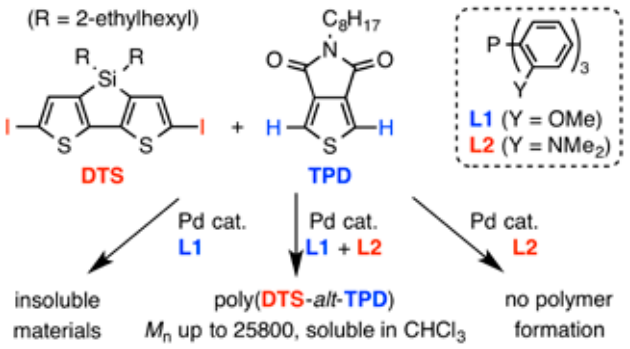
An unsymmetrical PNP-pincer-type phosphaalkene ligand, 2-(phospholanylmethyl)-6-(2-phosphaethenyl)-pyridine (PPEP), has been prepared from 2,6-bis(2-phosphaethenyl)pyridine (BPEP) by intramolecular C–H addition/cyclization of the 2-phosphaethenyl group with a 2,4,6-tri-tert-butylphenyl substituent (CH=PMes*). The reaction proceeds in hexane in the presence of a catalytic amount of [Pt(PCy_3)$_2$] (20 mol %) at 80 °C in a sealed tube, giving PPEP in 32% isolated yield, along with a byproduct of 2,6-bis(phospholanylmethyl)pyridine (BPMP) and a Pt(II) phosphanido complex. The PPEP ligand reacts with [Rh(μ-Cl)(C_2H_4)$_2$]$_2$ and [RuCl_2(PPh_3)$_3$] to afford [RhCl(PPEP)] (**1**) and [RuCl_2(PPh_3)(PPEP)] (**2**), respectively. Complex **1** easily undergoes C–H addition/cyclization at the other CH=PMes* group to afford the 2,6-bis(phospholanylmethyl)pyridine complex [RhCl(BPMP)] (**3**), whereas **2** is stable against C–H addition/cyclization. Treatment of **2** with ^{t}BuOK forms [RuCl(PPh_3)(PPEP*)] (**4**), coordinated with an unsymmetrical PNP-pincer-type phosphaalkene ligand containing a dearomatized pyridine unit (PPEP*).



Scheme 2. Pt(0)/PCy_3 catalyzed C–H addition/cyclization of BPEP to give PPEP.

A Mixed-ligand Approach to Palladium-catalyzed Direct Arylation Polymerization: Synthesis of Donor–Acceptor Polymers with Dithienosilole (DTS) and Thienopyrroledione (TPD) Units

We examined the synthesis of an alternating copolymer with dithienosilole (DTS) and thienopyrroledione (TPD) units via palladium-catalyzed direct arylation polymerization (DArP). Although DArP is attractive as an easy preparation method of π-conjugated polymers without the need for pre-preparation of organometallic monomers, a major problem is that the resulting polymers are occasionally insolubilized in catalytic systems. We have found that the combined use of P(2-$MeOC_6H_4$)$_3$ (**L1**) and P(2-$Me_2NC_6H_4$)$_3$ (**L2**) ligands enables the synthesis of poly(DTS-*alt*-TPD) with good solubility and high molecular weight (M_n up to 25800), and high yield. NMR investigation into the early stage of polymerization revealed two types of side reactions affording structural defects, oxidative coupling (homocoupling) of TPD-H groups and reduction of DTS-I to DTS-H. The combined use of **L1** and **L2** was also effective in preventing these side reactions.



Scheme 3. Synthesis of donor–acceptor polymers with DTS and TPD units via DArP.