

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

<http://om.kuicr.kyoto-u.ac.jp>



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  $\pi$ -conjugated polymers using direct arylation.

### KEYWORDS

Transition Metal Complex  
Homogeneous Catalyst  
Reaction Mechanism  
Low-coordinate Phosphorus Ligand  
 $\pi$ -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).

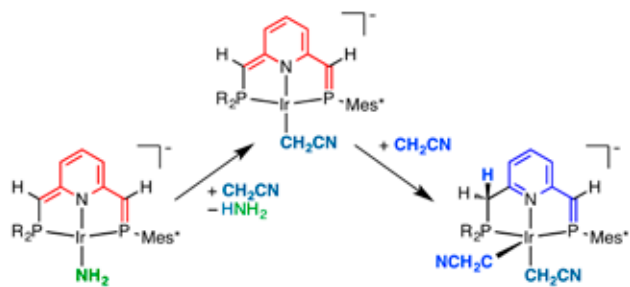
Iizuka, E.; Wakioka, M.; Ozawa, F., Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Synthesis of Donor-Acceptor Polymers with Dithienosilole (DTS) and Thienopyrroledione (TPD) Units, *Macromolecules*, **48**, 2989-2993 (2015).

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  $P(2\text{-MeOC}_6\text{H}_4)_3$  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

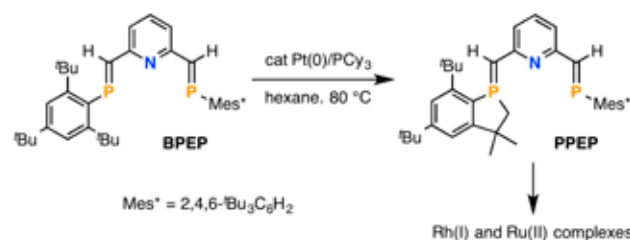
A novel parent amido complex of iridium(I),  $K[\text{Ir}(\text{NH}_2)(\text{PPEP}^*)]$ , coordinated with a dearomatized PNP-pincer-type phosphaalkene ligand (PPEP\*) has been prepared by deprotonation with KHMDS from  $[\text{Ir}(\text{NH}_2)(\text{PPEP})]$ , with benzophospholanymethyl and phosphoethenyl groups at the 2,6-positions of pyridine.  $K[\text{Ir}(\text{NH}_2)(\text{PPEP}^*)]$  has two base points at PPEP\* and  $\text{NH}_2$  ligands and, thus, successively reacts with two molecules of  $\text{CH}_3\text{CN}$  via heterolytic cleavage of the C–H bond. X-ray structural analysis of the product complex  $K[\text{Ir}(\text{CH}_2\text{CN})_2(\text{PPEP}^*)]$  reveals remarkable elongation of the P=C bond, indicative of the occurrence of strong  $\pi$ -back-donation from iridium to PPEP.



Scheme 1. Reaction of  $[\text{Ir}(\text{NH}_2)(\text{PPEP})]$  with acetonitrile.

## Catalytic Synthesis of an Unsymmetrical PNP-pincer Type Phosphaalkene Ligand

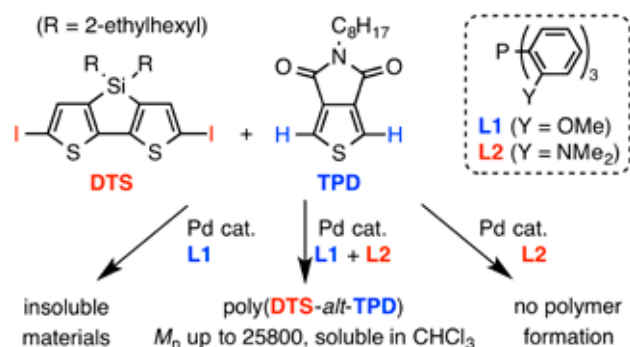
An unsymmetrical PNP-pincer-type phosphaalkene ligand, 2-(phospholanymethyl)-6-(2-phosphaethenyl)-pyridine (PPEP), has been prepared from 2,6-bis(2-phosphaethenyl)pyridine (BPEP) by intramolecular C–H addition/cyclization of the 2-phosphaethenyl group with a 2,4,6-tri-tert-butylphenyl substituent ( $\text{CH}=\text{PMes}^*$ ). The reaction proceeds in hexane in the presence of a catalytic amount of  $[\text{Pt}(\text{PCy}_3)_2]$  (20 mol %) at 80 °C in a sealed tube, giving PPEP in 32% isolated yield, along with a byproduct of 2,6-bis(phospholanymethyl)pyridine (BPMP) and a Pt(II) phosphanido complex. The PPEP ligand reacts with  $[\text{Rh}(\mu\text{-Cl})(\text{C}_2\text{H}_4)_2]$  and  $[\text{RuCl}_2(\text{PPh}_3)_3]$  to afford  $[\text{RhCl}(\text{PPEP})]$  (**1**) and  $[\text{RuCl}_2(\text{PPh}_3)(\text{PPEP})]$  (**2**), respectively. Complex **1** easily undergoes C–H addition/cyclization at the other  $\text{CH}=\text{PMes}^*$  group to afford the 2,6-bis(phospholanymethyl)pyridine complex  $[\text{RhCl}(\text{BPMP})]$  (**3**), whereas **2** is stable against C–H addition/cyclization. Treatment of **2** with  $t\text{BuOK}$  forms  $[\text{RuCl}(\text{PPh}_3)(\text{PPEP}^*)]$  (**4**), coordinated with an unsymmetrical PNP-pincer-type phosphaalkene ligand containing a dearomatized pyridine unit (PPEP\*).



Scheme 2.  $\text{Pt}(0)/\text{PCy}_3$  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  $\pi$ -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  $\text{P}(2\text{-MeOC}_6\text{H}_4)_3$  (**L1**) and  $\text{P}(2\text{-Me}_2\text{NC}_6\text{H}_4)_3$  (**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.