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

Lin, Y.-F.; Ichihara, N.; Nakajima, Y.; Ozawa, F., Disproportionation of Bis(phosphaethenyl)pyridine Iron(I) Bromide Induced by tBuNC, *Organometallics*, (in press).

Wakioka, M.; Nakamura, Y.; Hihara, Y.; Ozawa, F.; Sakaki, S., Effects of PAr3 Ligands on Direct Arylation of Heteroarenes with Isolated $[Pd(2,6\text{-}Me_2C_6H_3)(\mu\text{-}O_2CMe)(PAr_3)]_4$ Complexes, *Organometallics*, **33,** 6247-6252 (2014).

Takeuchi, K.; Minami, A.; Nakajima, Y.; Ozawa, F., Synthesis and Structures of Nickel Complexes with a PN-Chelate Phosphaalkene Ligand, *Organometallics*, **33,** 5365-5370 (2014).

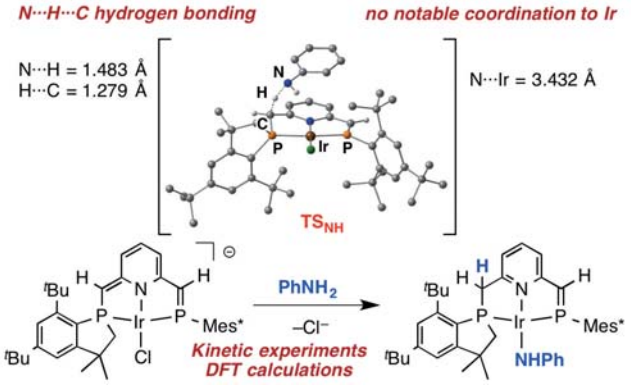
Lin, Y.-F.; Nakajima, Y.; Ozawa, F., Reduction of an Fe(I) Mesityl Complex Induced by π-Acid Ligands, *Dalton Trans*., **43,** 9032-9037 (2014).

Chang, Y.-H.; Nakajima, Y.; Tanaka, H.; Yoshizawa, K.; Ozawa, F., Mechanism of N–H Bond Cleavage of Aniline by a Dearomatized PNP-Pincer Type Phosphaalkene Complex of Iridium(I), *Organometallics*, **33,** 715-721 (2014).

Wakioka, M.; Ichihara, N.; Kitano, Y.; Ozawa, F., A Highly Efficient Catalyst for the Synthesis of Alternating Copolymers with Thieno[3,4-c] pyrrole-4,6-dione Units via Direct Arylation Polymerization, *Macromolecules*, **47,** 626-631 (2014).

Mechanism of N–H Bond Cleavage of Aniline by a Dearomatized PNP-Pincer Type Phosphaalkene Complex of Iridium(I)

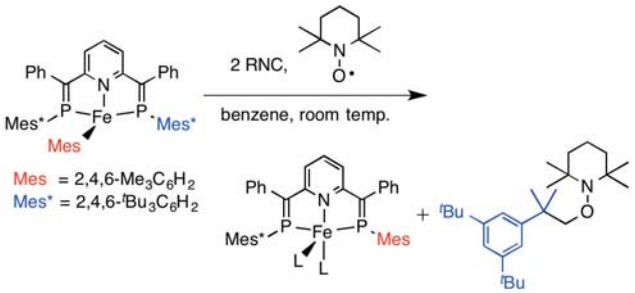
Detailed mechanistic investigations using kinetic and theoretical methods have been conducted for deprotonative N–H bond cleavage of *p*-$YC_6H_4NH_2$ (Y = H, MeO, Me, Cl, Br, NO_2) by [K(18-crown-6)][Ir(Cl)(PPEP*)] (**1a**) bearing a dearomatized PNP-pincer type phosphaalkene ligand (PPEP*) to afford [Ir(NHC_6H_4Y)(PPEP)] (**2**) with an aromatized ligand (PPEP). While 1a is in equilibrium with [K(18-crown-6)]Cl (**3**) and [Ir(PPEP*)] (**4**) in solution, the N–H bond cleavage proceeds via association of **1a** with aniline, where the coordination of aniline to iridium is insignificant; instead, aniline is associated with PPEP* by hydrogen bonding. In contrast, the N–H bond cleavage of ammonia proceeds via the pentacoordinate intermediate [Ir(Cl)(NH_3)(PPEP*)]. The difference between the N–H bond cleavage processes of aniline and ammonia is examined by DFT calculations.



Scheme 1. Mechanism of N–H bond cleavage of aniline by [Ir(Cl)(PPEP*)]–.

Reduction of an Fe(I) Mesityl Complex Induced by π-Acid Ligands

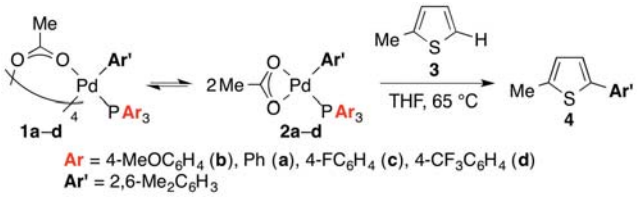
Treatment of the Fe(I) mesityl complex [Fe(Mes)(BPEP-Ph)] (BPEP-Ph = 2,6-bis[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine) with π-acid ligands (L = CO, RNC) leads to one-electron reduction via Mes group migration from Fe to P, followed by homolytic elimination of the 2,4,6-$tBu_3C_6H_2$ group, to afford Fe(0) complexes of the formula [Fe$(L)_2$(BPEP-Ph*)] (BPEP-Ph* =2-[1-phenyl-2-mesityl-2-phosphaethenyl]-6-[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine). This reduction process is supported by radical trapping experiments and theoretical studies. The 2,4,6-*t*Bu3C_6H_2• radical is captured by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in high yield. DFT calculations reveal the mechanism of Mes group migration with a reasonable energy profile.



Scheme 2. One-election reduction process of [Fe(Mes)(BPEP-Ph)] induced by isocyanides.

Effects of PAr_3 Ligands on Direct Arylation of Heteroarenes with Isolated [Pd(2,6-$Me_2C_6H_3$)(μ-O_2CMe)(PAr_3)]$_4$ Complexes

The palladium-catalyzed direct arylation of heteroarenes with aryl halides has attracted considerable attention as a simple cross-coupling process. It is generally accepted that this catalysis proceeds via an arylpalladium carboxylate intermediate. In this study, we investigated the ligand effects on reactivity of arylpalladium acetates (**1a–d**) (Scheme 3). While **1a–d** have a tetrameric form in the solid state, they are in rapid equilibrium with the monomeric species [Pd(2,6-$Me_2C_6H_3$)(O_2CMe-κ^2O)(PAr_3)] (**2a–d**) in solution. Complexes **1a–d** react with thiophene **3** in THF at 65 °C to give the direct arylation product (4) in high yields. The reaction is accelerated by electron-deficient PAr_3 (**1b < 1a < 1c < 1d**). The ligand effects are also examined by DFT calculations. Unlike the general assumption, the C–H bond cleavage process is relatively insensitive to electronic properties of PAr_3 ligands. Instead, the reaction of **2** invokes the C–C reductive elimination process as the rate-determining step, and the activation energy is significantly reduced by electron-deficient ligands.



Scheme 3. Ligand effects on direct arylation of 2-methylthiophene with arylpalladium acetate complexes.