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 $\pi$-conjugated polymers by using direct arylation.

**KEYWORDS**

Transition Metal Complex  
Homogeneous Catalyst  
Reaction Mechanism  
Low-coordinate Phosphorus Ligand  
$\pi$-Conjugated Polymer

**Selected Publications**


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-YC₆H₄NH₂ (Y = H, MeO, Me, Cl, Br, NO₂) by [K(18-crown-6)][Ir(Cl)(PPEP*)] (1a) bearing a dearomatized PNP-pincer type phosphaalkene ligand (PPEP*) to afford [Ir(NHC₆H₄Y)(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)(NH₃)(PPEP*)]. The difference between the N–H bond cleavage processes of aniline and ammonia is examined by DFT calculations.

Effects of PAr₃ Ligands on Direct Arylation of Heteroarenes with Isolated [Pd(2,6-Me₂C₆H₃)(μ-O₂CMe)(PAr₃)]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-Me₂C₆H₃)(O₂CMe-κ₂O)(PAr₃)] (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 PAr₃ (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 PAr₃ 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.