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

Chang, Y.-H.; Nakajima, Y.; Tanaka, H.; Yoshizawa, K.; Ozawa, F., Facile N-H Bond Cleavage of Ammonia by an Iridium Complex Bearing a Non-innocent PNP-Pincer Type Phosphaalkene Ligand, *J. Am. Chem. Soc.*, **135,** 11791-11794 (2013).

Wakioka, M.; Nakamura, Y.; Hihara, Y.; Ozawa, F.; Sakaki, S., Factors Controlling the Reactivity of Heteroarenes in Direct Arylation with Arylpalladium Acetate Complexes, *Organometallics*, **32,** 4423-4430 (2013).

Nakajima, Y.; Okamoto, Y.; Chang, Y.-H.; Ozawa, F., Synthesis, Structures, and Reactivity of Ruthenium Complexes with PNP-pincer Type Phosphaalkene Ligands, *Organometallics*, **32,** 2918-2925 (2013).

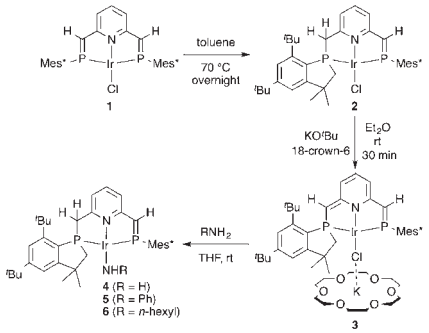
Chang, Y.-H.; Nakajima, Y.; Ozawa, F., A Bis(phosphaethenyl)pyridine Complex of Iridium(I): Synthesis and Catalytic Application to N-Alkylation of Amines with Alcohols, *Organometallics*, **32,** 2210-2215 (2013).

Wakioka, M.; Kitano, Y.; Ozawa, F., A Highly Efficient Catalytic System for Polycondensation of 2,7-Dibromo-9,9-dioctylfluorene and 1,2,4,5-Tetrafluorobenzene via Direct Arylation, *Macromolecules*, **46,** 370-374 (2013).

N–H Bond Cleavage of Ammonia by an Iridium Complex Bearing a Non-innocent PNP-Pincer Type Phosphaalkene Ligand

Late transition metal complexes with a pyridine-based PNP-pincer ligand have attracted a great deal of attention owing to their facile cleavage of non-activated bonds via non-innocent behavior of the ligand. Herein, we describe the synthesis and reactions of novel iridium complex **3** with an unsymmetrical PNP-pincer ligand composed of a dearomatized pyridine core and benzophospholanylmethyl and phosphaethenyl arms at the 2,6-positions, which was prepared in two steps from [IrCl(BPEP)] (**1**, BPEP = 2,6-bis[2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]-pyridine) (Scheme 1).

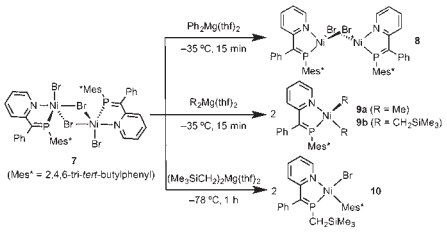
Phosphaalkenes with a P=C bond possess an extremely low-lying π* orbital around the phosphorus atom, and thus exhibit strong π-accepting ability toward transition metals. Reflecting this particular ligand property of phosphaalkene, complex **3** undergoes extended π-conjugation over the molecule, and exhibits extremely high reactivity toward N–H bond cleavage of ammonia and amines to afford the corresponding amido complexes **4-6** in quantitative yields (Scheme 1).



Scheme 1. Synthesis of **3** and its reactivity toward ammonia and amines.

Synthesis of Phosphaethenylpyridine-Ni Complex and Its Reactivity toward Organomagnesium Reagents

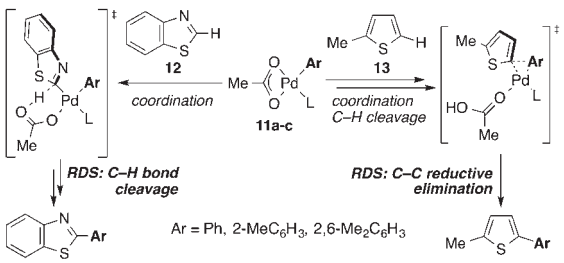
Recently, we have demonstrated that phosphaalkene ligand successfully stabilizes low oxidation state complexes like a Fe(I) aryl mesityl complex. In this study, we report the synthesis of novel phosphaalkene–Ni complex $[NiBr_2(pep)]_2$ (**7**) (PEP = 2-(1-phenyl-2-phosphaethenyl)pyridine) and its unique reactivity toward organomagnesium reagents. Complex **7** was synthesized by the reaction of PEP with $[NiBr_2(dme)]$ (dme = 1,2-dimethoxyethane) in benzene at 60°C. The reaction of **7** with $Ph_2Mg(thf)_2$ affords an one-electron reduction product, bromine-bridged Ni(I) dimer **8**. Additionally, dialkylmagnesiums ($R_2Mg(thf)_2$; R = Me, CH_2SiMe_3) also reacted with **7** at –35°C to give dialkyl Ni(II) complexes **8** and **9**. However, the reaction of dialkylmagnesiums at –78°C did not give monoalkyl complexes but gave monoaryl complexes **10** with exchange of the alkyl and Mes* groups. These results indicate that the exchange of the alkyl and Mes* groups would occur on a high-valent Ni complex intermediate.



Scheme 2. Reactivity of **7** toward organomagnesium reagents.

Factors Controlling the Reactivity of Heteroarenes in Direct Arylation with Arylpalladium Acetate Complexes

The palladium-catalyzed direct arylation of heteroarenes with aryl halides has emerged as a viable alternative to conventional cross-coupling reactions. We report a detailed mechanistic study on factors controlling the reactivity of heteroarenes in direct arylation with well-defined models of the presumed intermediate [PdAr(O_2CMe-κ^2*O*) L] (**11a-c**, Ar = Ph, 2-MeC_6H_3, 2,6-$Me_2C_6H_3$). The reactivity order of heteroarenes was evaluated by competitive reactions, showing that benzothiazole (**12**, pK_a = 27) is significantly less reactive than 2-methylthiophene (**13**, pK_a = 42). The reaction of **13** obeyed simple second-order kinetics, and the deuterium-labeling experiments and DFT calculations indicated the occurrence of rate-determining reductive elimination. On the other hand, the reaction of **12** displayed saturation kinetics due to the occurrence of relatively stable coordination of **12** prior to C–H bond cleavage. This coordination stability enhances the activation barrier for C–H bond cleavage, thereby causing the modest reactivity of **12**.



Scheme 3. Reaction of **11a-c** with heteroarenes **12** and **13**.