TITLE:
<International Research Center for Elements Science>Organotransition Metal Chemistry

AUTHOR(S):

CITATION:
<International Research Center for Elements Science>Organotransition Metal Chemistry. ICR Annual Report 2013, 20: 56-57

ISSUE DATE:
2013

URL:
http://hdl.handle.net/2433/185240

RIGHT:
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**
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).

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 [NiBr₂(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 [NiBr₂(dme)] (dme = 1,2-dimethoxyethane) in benzene at 60°C. The reaction of 7 with Ph₂Mg(thf)₂ affords an one-electron reduction product, bromine-bridged Ni(I) dimer 8. Additionally, dialkylmagnesiums (R₂Mg(thf); R = Me, CH₂SiMe₃) 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.

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 [PdAr₂(O₂CMe-κ₂O) L] (11a-c, Ar = Ph, 2-MeC₆H₅, 2,6-Me₂C₆H₃). The reactivity order of heteroarenes was evaluated by competitive reactions, showing that benzothiazole (12, pKₐ = 27) is significantly less reactive than 2-methylthiophene (13, pKₐ = 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.