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Kyoto University
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 kinetic techniques on the reaction intermediates and elementary processes. The research subjects include: (1) development of novel ligand systems for catalysis, (2) creation of functional metal complexes based on synergistic effects, (3) construction of \( \pi \)-conjugation system including transition-metals, and (4) development of functional molecules including transition-metal clusters.

### Research Activities (Year 2006)

**Presentations**


Introduction of Functional Groups onto the \(\text{Fe}_2\text{C}_4\) Clusters, Okazaki M, 2006 Workshop on Organometallic Chemistry, 1–2 December, Kyoto, Japan.


\( \pi \)-Conjugated Organometallic Complexes with Highly Efficient \( d\pi–p\pi \) Interaction between Platinum and sp²-Hybridized Phosphorus Ligand, Ozawa F, Hayashi K, Nakatani M, Okazaki M, Toyota K, Yoshifuji M, XXII International Conference on Organometallic Chemistry (ICOMC 2006), 23–28 July, Zaragoza, Spain.


Stereocontrolled Synthesis and Optical Properties of All-cis Poly(arylene vinylene)s, Ozawa F, Lectureship of the Chemistry Research Promoton Center, National Science Council, Republic of China, 8 November, Institute of Chemistry, Academia Sinica, Taipei, Taiwan (Invited).

Highly Active Catalysts Bearing Diphosphinidencyclobutene Ligands (DPCB), Ozawa F, Lectureship of the Chemistry Research Promoton Center, National Science Council, Republic of China, 9–10 November, National Tsing Hua University, Hsinchu, and National Taiwan University, Taipei, Taiwan (Invited).

**Grants**

Okazaki M, Chemistry of “Ethynyl Cation”-Coordinated Transition-Metal Clusters, Grant-in-Aid for Young Scientists (B), April 2005–March 2007.


Synthesis and Catalytic Properties of Cationic Palladium(II) and Rhodium(I) Complexes Bearing Diphosphinidene Cyclobutene Ligands

Cationic palladium(II) and rhodium(I) complexes bearing 1,2-diaryl-3,4-bis[(2,4,6-tri-t-butyl)phenyl]phosphinidene cyclobutene ligands (DPCB–Y) were prepared and their structures and catalytic activity were examined (aryl = phenyl (DPCB), 4-methoxyphenyl (DPCB–OMe), 4-(trifluoromethyl)phenyl (DPCB–CF₃)). The palladium complexes [Pd(MeCN)₂(DPCB–Y)]X₂ (X = OTf, BF₄, BAr₄) were prepared by the reactions of DPCB–Y with [Pd(MeCN)₄]X₂, which were generated from Pd(OAc)₂ and HX in MeCN. On the other hand, the rhodium complexes [Rh(MeCN)₂(DPCB–Y)]OTf were prepared by the treatment of [Rh(µ-Cl)(cyclooctene)₂]₂ with DPCB–Y in CH₂Cl₂, followed by treatment with AgOTf in the presence of MeCN. The cationic complexes catalyzed conjugate addition of benzyl carbamate to α,β-unsaturated ketones.

Scheme 1. Hydroamidation of enones with CbzNH₂ catalyzed by DPCB-Pd complex.

Cyclodehydration of cis–2-Butene-1,4-diol with Active Methylene Compounds Catalyzed by a Diphosphinidene Cyclobutene-coordinated Palladium Complex

The palladium-catalyzed allylation is a useful synthetic means of constructing C–C, C–N, and C–O bonds. (π-Allen)palladium triflate coordinated with 1,2-bis(4-methoxyphenyl)-3,4-bis(2,4,6-tri-t-butyl)phenylphosphinidene cyclobutene (DPCB–OMe), [Pd(η₅-C₅H₅)(DPCB–OMe)]OTf, efficiently catalyzes cyclodehydration of cis–2-butene-1,4-diol with active methylene compounds such as acetylacetone and ethyl acetooacetate in toluene in the presence of pyridine. The reactions can be performed in air, giving 2-vinyl-2,3-dihydrofurans in good to high yields.

Scheme 2. Cyclodehydration of cis–2-butene-1,4-diol with acetylacetone catalyzed by DPCB-Pd complex and pyridine.

Redox-Induced Recombination of C–C Bonds on Fe₄ Framework

Metal clusters have recently attracted much attention due to their rich redox properties. We previously reported the syntheses of [Cp’₄Fe₄(HCH)(HCCR)]⁺ (Cp’ = C₅H₄Me, R = alkyl, alkynyl, S’ Tol, PPh₂) via bromination of the HCH moiety in [Cp’₄Fe₄(HCH)]⁺, followed by nucleophilic substitution. Similarly, [Cp’₄Fe₄(HCCR)]⁺ (R = –C≡CSiMe₃, [1-anti]) was obtained from the reaction of a dibromo-substituted cluster with HCC≡CSiMe₃/CuI/NHEt₂. Interestingly, there is an equilibrium between [1-anti]⁺ and its isomer [Cp’₄Fe₄(HCH)(RCCR)]⁺ ([1-syn]). In contrast, transformation between their neutral forms was not observed. Oxidation of [1-anti]⁺ led to the exclusive formation of [Cp’₄Fe₄(HCH)(µ₃-C≡CR)]²⁺ ([2]²⁺) (Figure 1). Both structural changes should proceed through the intramolecular recombination of Fe–Fe and C–C bonds on the Fe₄C₄ core.

Figure 1. Molecular structure of [Cp’₄Fe₄(HCH)(µ₃-C≡CSiMe₃)]²⁺ ([2]²⁺).