

# 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 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

Studies on Introduction of Functional Groups onto the [4Fe-4C] Cluster: Application for Construction of Functional Molecules Containing Transition-metal Clusters, Okazaki M, 21st Century COE on Kyoto University Alliance for Chemistry "The 3rd Organoelement Chemistry Seminar", 26 October, Kyoto, Japan.

Introduction of Functional Groups onto the Fe<sub>4</sub>C<sub>4</sub> Clusters, Okazaki M, 2006 Workshop on Organometallic Chemistry, 1–2 December, Kyoto, Japan.

Synthesis of Haloacetylene- and Dihaloacetylene-Coordinated Tetrairon Clusters and Their Reactivities toward Nucleophiles, Yoshimura K, Uehira K, Takano M, Okazaki M, Ozawa F, 53rd Symposium on Organometallic Chemistry, 8 September, Osaka, Japan.

$\pi$ -Conjugated Organometallic Complexes with Highly Efficient  $d\pi$ - $p\pi$  Interaction between Platinum and  $sp^2$ -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.

Diphosphinidene-cyclobutene-coordinated Complexes: Structures and Catalysis, Ozawa F, The 3rd RIKEN Symposium on the Frontiers of Organometallic Chemistry, 6

October, Wako, Japan (Invited).

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

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

### Grants

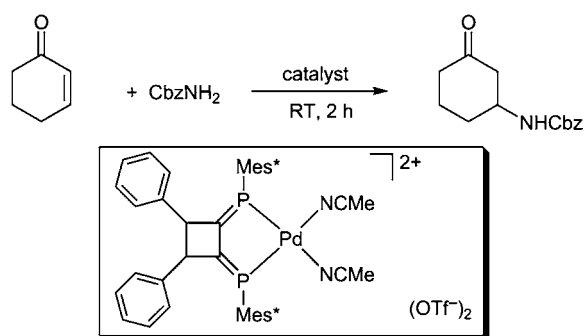
Okazaki M, Chemistry of "Ethyne Cation"-Coordinated Transition-Metal Clusters, Grant-in-Aid for Young Scientists (B), April 2005–March 2007.

Ozawa F, Okazaki M, Synergistic Effects of Transition Metals and Heavier Main Group Elements in Functional Organometallic Complexes, Grant-in-Aid for Priority Area "Synergy of Elements", September 2006–March 2010.

Ozawa F, Creation and Applications of Acidic Transition Metal Hydrides, Grant-in-Aid for Priority Area "Advanced Molecular Transformations", April 2006–March 2007.

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

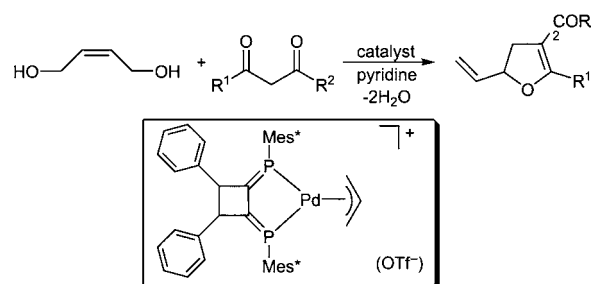
Cationic palladium(II) and rhodium(I) complexes bearing 1,2-diaryl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene ligands (DPCB-Y) were prepared and their structures and catalytic activity were examined (aryl = phenyl (DPCB), 4-methoxyphenyl (DPCB-OMe), 4-(trifluoromethyl)phenyl (DPCB-CF<sub>3</sub>)). The palladium complexes [Pd(MeCN)<sub>2</sub>(DPCB-Y)]X<sub>2</sub> (X = OTf, BF<sub>4</sub>, BAr<sub>4</sub> (Ar = 3,5-bis(trifluoromethyl)phenyl)) were prepared by the reactions of DPCB-Y with [Pd(MeCN)<sub>4</sub>]<sub>2</sub>X<sub>2</sub>, which were generated from Pd(OAc)<sub>2</sub> and HX in MeCN. On the other hand, the rhodium complexes [Rh(MeCN)<sub>2</sub>(DPCB-Y)]OTf were prepared by the treatment of [Rh(μ-Cl)(cyclooctene)<sub>2</sub>] with DPCB-Y in CH<sub>2</sub>Cl<sub>2</sub>, 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 CbzNH<sub>2</sub> 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

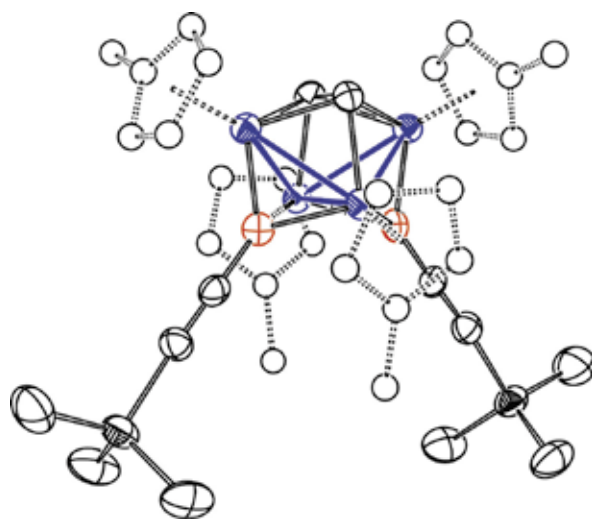
The palladium-catalyzed allylation is a useful synthetic means of constructing C-C, C-N, and C-O bonds. ( $\pi$ -Allyl)palladium triflate coordinated with 1,2-bis(4-methoxyphenyl)-3,4-bis(2,4,6-tri-*t*-butylphenylphosphinidene)cyclobutene (DPCB-OMe), [Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(DPCB-OMe)]OTf, efficiently catalyzes cyclodehydration of *cis*-2-butene-1,4-diol with active methylene compounds such as acetylacetone and ethyl acetoacetate 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 Fe<sub>4</sub> Framework

Metal clusters have recently attracted much attention due to their rich redox properties. We previously reported the syntheses of [Cp'<sub>4</sub>Fe<sub>4</sub>(HCCH)(HCCR)]<sup>+</sup> (Cp' = C<sub>3</sub>H<sub>4</sub>Me, R = alkyl, alkynyl, S<sup>*p*</sup>Tol, PPh<sub>2</sub>) via bromination of the HCCH moiety in [Cp'<sub>4</sub>Fe<sub>4</sub>(HCCH)<sub>2</sub>]<sup>+</sup>, followed by nucleophilic substitution. Similarly, [Cp'<sub>4</sub>Fe<sub>4</sub>(HCCR)<sub>2</sub>]<sup>+</sup> (R = -C≡CSiMe<sub>3</sub>, [1-anti]<sup>+</sup>) was obtained from the reaction of a dibromo-substituted cluster with HC≡CSiMe<sub>3</sub>/CuI/NHEt<sub>2</sub>. Interestingly, there is an equilibrium between [1-anti]<sup>+</sup> and its isomer [Cp'<sub>4</sub>Fe<sub>4</sub>(HCCH)(RCCR)]<sup>+</sup> ([1-syn]<sup>+</sup>). In contrast, transformation between their neutral forms was not observed. Oxidation of [1-anti]<sup>+</sup> led to the exclusive formation of [Cp'<sub>4</sub>Fe<sub>4</sub>(HCCH)(μ<sub>3</sub>-CR)<sub>2</sub>]<sup>2+</sup> ([2]<sup>2+</sup>) (Figure 1). Both structural changes should proceed through the intramolecular recombination of Fe-Fe and C-C bonds on the Fe<sub>4</sub>C<sub>4</sub> core.



**Figure 1.** Molecular structure of [Cp'<sub>4</sub>Fe<sub>4</sub>(HCCH)(μ<sub>3</sub>-C≡CSiMe<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> ([2]<sup>2+</sup>).