

Development of Heterogeneous Catalysis toward Ideal Chemical Processes

Department of Life and Coordination-Complex Molecular Science
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Education

1984 B.S. Hokkaido University
1990 Ph.D. Hokkaido University

Professional Employment

1988 JSPS Research Fellow
1988 Research Associate, Hokkaido University
1990 Assistant Professor, Hokkaido University
1994 Research Associate, Columbia University
1995 Lecturer, Kyoto University
1997 Professor, Nagoya City University
2000 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies
2007 Research team leader, RIKEN
2014 Distinguished Professor, Three George University
2003 Research Project Leader, JST CREST Project (–2008)
2008 Research Project Leader, NEDO Project (–2012)
2011 Deputy Research Project Leader, JST CREST (–2016)
2014 Research Project Leader, JST ACCEL Project (–2019)

Awards

1991 Eisai Award, Synthetic Organic Chemistry
1998 The Pharmaceutical Society of Japan Award for Young Scientist
2007 The Chemical Society of Japan (CSJ) Award for Creative Work
2007 MEXT Ministerial Award for Green Sustainable Chemistry
2010 Inoue Prize for Science
2014 The Commendation for Science and Technology by the Minister of MEXT (Research Category)

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Keywords

Transition Metal Catalysis, Green Chemistry, Organic Synthesis

Our research interests lie in the development of transition metal-catalyzed reaction systems toward ideal (highly efficient, selective, green, safe, simple, etc.) organic transformations. In particular, we have recently been developing the heterogeneous aquacatalytic systems, continuous flow catalytic systems, and super active catalysts working at ppm-ppb loading levels. Thus, for example, a variety of palladium catalysts were designed and prepared promoting carbon–carbon bond forming reactions at ppm-ppb loading levels (Figure 1).

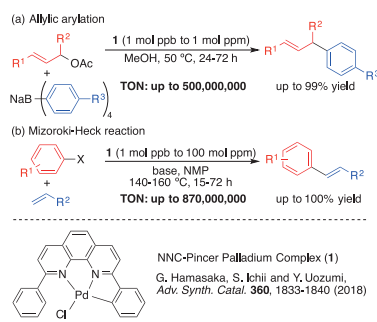


Figure 1. Typical Examples of Pd-Catalyzed Carbon–Carbon Bond Forming Reactions with ppm-ppb Loading Levels of an NNC-Pincer Pd Complexes.

Selected Publications

- R. David and Y. Uozumi, “Recent Advances in Palladium-Catalyzed Cross-Coupling Reactions at ppm-ppb Molecular Catalyst Loadings (review),” *Adv. Synth. Catal.* **360**, 602–625 (2018).
- T. Osako, K. Torii, S. Hirata and Y. Uozumi, “Chemoselective Continuous-Flow Hydrogenation of Aldehydes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Resin,” *ACS Catal.* **7**, 7371–7377 (2017).
- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, “Self-Assembled Poly(imidazole-palladium): Highly Active, Reusable Catalyst at Parts per Million to Parts per Billion Levels,” *J. Am. Chem. Soc.* **134**, 3190–3198 (2012).
- G. Hamasaka, T. Muto and Y. Uozumi, “Molecular-Architecture-Based Administration of Catalysis in Water: Self-Assembly of an Amphiphilic Palladium Pincer Complex,” *Angew. Chem., Int. Ed.* **50**, 4876–4878 (2011).
- Y. Uozumi, Y. Matsuura, T. Arakawa and Y. M. A. Yamada, “Asymmetric Suzuki-Miyaura Coupling in Water with a Chiral Palladium Catalyst Supported on Amphiphilic Resin,” *Angew. Chem., Int. Ed.* **48**, 2708–2710 (2009).
- Y. M. A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, “A Nanoplatinum Catalyst for Aerobic Oxidation of Alcohols in Water,” *Angew. Chem., Int. Ed.* **46**, 704–706 (2007).
- Y. Uozumi, Y. M. A. Yamada, T. Beppu, N. Fukuyama, M. Ueno and T. Kitamori, “Instantaneous Carbon–Carbon Bond Formation Using a Microchannel Reactor with a Catalytic Membrane,” *J. Am. Chem. Soc.* **128**, 15994–15995 (2006).

1. C–H Arylation of Thiophenes with Aryl Bromides by a Parts-per-Million Loading of a Palladium NNC-Pincer Complex¹⁾

A palladium NNC-pincer complex efficiently catalyzed the direct arylation of thiophene derivatives with extremely low palladium loadings of the order of parts per million. Thus, the reaction of various thiophenes with aryl bromides in the presence of 25–100 mol ppm of chlorido[(2-phenyl- κ -C²)-9-phenyl-1,10-phenanthroline- κ ²-N,N']palladium(II) NNC-pincer complex, K₂CO₃, and pivalic acid in *N,N*-dimethylacetamide afforded the corresponding 2- or 5-arylated thiophenes in good to excellent yields. A combination of the present C–H arylation and Hiyama coupling with the same NNC-pincer complex provides an efficient synthesis of unsymmetrical 2,5-thiophenes with catalyst loadings at mol ppm levels.

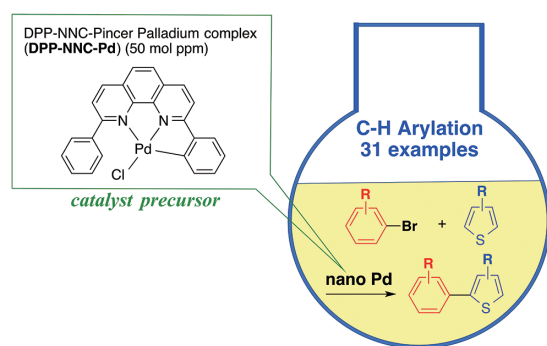


Figure 2. C–H Arylation of Thiophenes with Aryl Bromides by a Parts-per-Million Loading of a Palladium NNC-Pincer Complex.

2. A Convolutated Polyvinylpyridine-Palladium Catalyst for Suzuki-Miyaura Coupling and C–H Arylation²⁾

The development of highly active and reusable supported catalysts for Suzuki-Miyaura coupling and catalytic C–H arylation is important for fundamental and applied chemistry, with these reactions being used to produce medical compounds and functional materials. We found that a mesoporous composite made of a linear poly(4-vinylpyridine) and tetrachloropalladate acted as a dual-mode catalyst for a variety of cross-coupling reactions, with both Pd nanoparticles and a Pd complex catalyst being observed under different conditions. The polyvinylpyridine-palladium composite was readily prepared via the molecular convolution of poly(4-vinylpyridine) and sodium tetrachloropalladate to provide a hardly soluble polymer-metal composite. The Suzuki-Miyaura coupling and the C–H arylation of aryl chlorides and bromides with arylboronic acids, thiophenes, furans, benzene, and anisole proceeded in the presence of 0.004 mol% (40 mol ppm) to 1 mol% Pd to afford the corresponding coupling products in high yields. Furthermore, the catalyst was reused without an

appreciable loss of activity. Pharmaceutical compounds and functional materials were synthesized via the coupling reactions. N₂ gas adsorption/desorption analysis indicated that the catalyst had a mesoporous nature, which played a crucial role in the catalysis. In the Suzuki-Miyaura couplings, in situ generated palladium nanoparticles in the polymer matrix were catalytically active, while a polymeric Pd(II) complex was crucial in the C–H arylations. These catalytic species were investigated via XAFS, XPS, far-infrared absorption, and Raman spectroscopies, as well as DFT calculations.

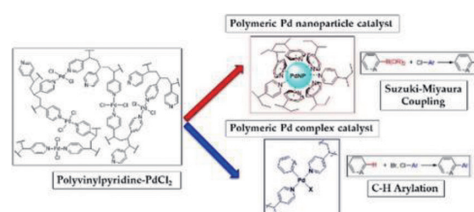


Figure 3. Polyvinylpyridine-Palladium Catalyst for Suzuki-Miyaura Coupling and C–H Arylation.

3. Synthesis of α -Tertiary Amines by the Ruthenium-Catalyzed Regioselective Allylic Amination of Tertiary Allylic Esters³⁾

We demonstrated a ruthenium-catalyzed regioselective allylic amination of tertiary allylic esters with various amines using [Cp*Ru(CH₃CN)₃][PF₆]/5,5'-dimethyl-2,2'-bipyridine (5,5'-diMe-2,2'-bpy) and related ruthenium catalytic systems, and successfully obtained a diverse range of α -tertiary amines as single regioisomers. The present ruthenium catalytic system was effective for reactions with various types of amines.

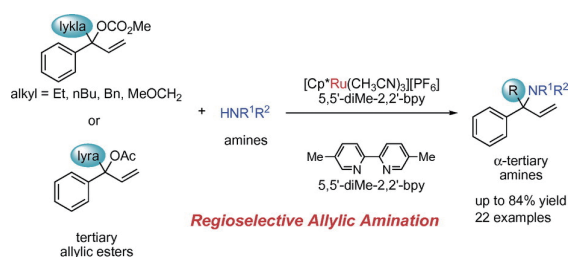


Figure 4. Ruthenium-catalyzed Regioselective Allylic Amination of Tertiary Allylic Esters.

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- 2) A. Ohno, T. Sato, T. Mase, Y. Uozumi and Y. M. A. Yamada, *Adv. Synth. Catal.* **362**, 4687–4698 (2020).
- 3) S. Ichii, G. Hamasaka and Y. Uozumi, *Chem. Lett.* **49**, 645–647 (2020).