

Development of Novel Catalytic Organic Transformations

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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, Photocatalysis

Our research interests lie in the development of catalytic reaction systems toward ideal (highly efficient, selective, green, safe, simple, etc.) organic transformations. In particular, development of a wide variety of the heterogeneous aqua-catalytic systems, continuous flow catalytic systems, and super active catalysts working at ppm-ppb loading levels, have been achieved. Furthermore, we have recently been developing a novel photocatalysis where, for example, the electrophilic substitution of carbonyl groups took place under visible-light irradiation (Figure 1).

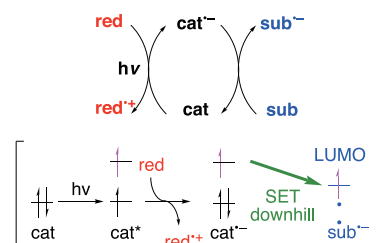


Figure 1. The outlined concept of photocatalytic reductive activation of substrate (e.g. carbonyls).

Selected Publications

- G. Hamasaka, D. Roy, A. Tazawa and Y. Uozumi, "Arylation of Terminal Alkynes by Aryl Iodides Catalyzed by a Parts-per-Million Loading of Palladium Acetate," *ACS Catal.* **9**, 11640–11646 (2019).
- 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).

1. Photocatalytic Carbinol Cation/Anion Umpolung: Direct Addition of Aromatic Aldehydes and Ketones to Carbon Dioxide¹⁾

We have developed a new photocatalytic umpolung reaction of carbonyl compounds to generate anionic carbinol synthons. Aromatic aldehydes or ketones reacted with carbon dioxide in the presence of an iridium photocatalyst and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzimidazole (DMBI) as a reductant under visible-light irradiation to furnish the corresponding α -hydroxycarboxylic acids through nucleophilic addition of the resulting carbinol anions to electrophilic carbon dioxide.

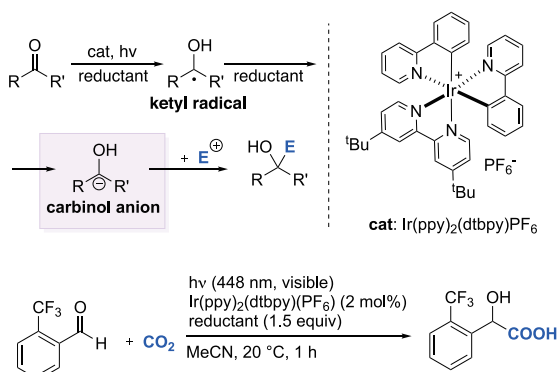


Figure 2. Photocatalytic Eelectrophilic Substitution of Carbonyls with Carbon Dioxide via Carbinol Anion Species.

2. Palladium-Catalyzed Aminocarbonylation of Aryl Halides with *N,N*-Dialkylformamide Acetals²⁾

We developed a protocol for the palladium-catalyzed aminocarbonylation of aryl halides using less-toxic formamide acetals as bench-stable aminocarbonyl sources under neutral conditions. Various aryl (including heteroaryl) halides reacted with *N,N*-dialkylformamide acetals in the presence of a catalytic amount of Pd₂(dba)₃ and xantphos to give the corresponding aromatic carboxamides at 90–140 °C without any activating agents or bases in up to quantitative chemical yield. This protocol was applied to aryl bromides, aryl iodides, and trifluoromethanesulfonic acid, as well as to relatively less-reactive aryl chlorides. A wide range of functionalities on the aromatic ring of the substrates were tolerated under the amino-

carbonylation conditions. The catalytic aminocarbonylation was used to prepare the insect repellent *N,N*-diethyl-3-methylbenzamide as well as a synthetic intermediate of the dihydrofolate reductase inhibitor triazinate.



Figure 3. Palladium-Catalyzed Aminocarbonylation with *N,N*-Dialkylformamide Diacetals.

3. Cyanide-Free Cyanation of Aryl Iodides with Nitromethane by Using an Amphiphilic Polymer-Supported Palladium Catalyst³⁾

A cyanide-free aromatic cyanation was developed using nitromethane as a cyanide source in water with an amphiphilic polystyrene–poly(ethylene glycol) (PS–PEG) resin-supported palladium catalyst and an alkyl halide (*i.e.*, 1-iodobutane). The cyanation proceeded through the palladium-catalyzed cross-coupling of aryl halides and nitromethane, followed by transformation of the resultant nitromethylarene intermediates into nitriles by 1-iodobutane.

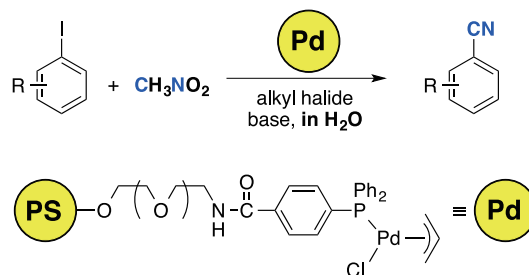


Figure 4. Cyanation of Aryl Iodides with Nitromethane by Using an Amphiphilic PS-PEG resin-Supported Palladium Catalyst in Water.

References

- 1) S. Okumura and Y. Uozumi, *Org. Lett.* **23**, 7194–7198 (2021). DOI: 10.1021/acs.orglett.1c02592
- 2) S. Hirata, T. Osako and Y. Uozumi, *Helv. Chim. Acta* **104**, e2100162 (2021). DOI: 10.1002/hlca.202100162
- 3) T. Suzuka, R. Niimi and Y. Uozumi, *Synlett* **33**, 40–44 (2022). DOI: 10.1055/a-1675-0018

Award

OKUMURA, Shintaro; The Society of Synthetic Organic Chemistry, Fujifilm Research Proposal Award (2021).