Heterogeneous Catalytic Systems for Organic Chemical Transformations in Water

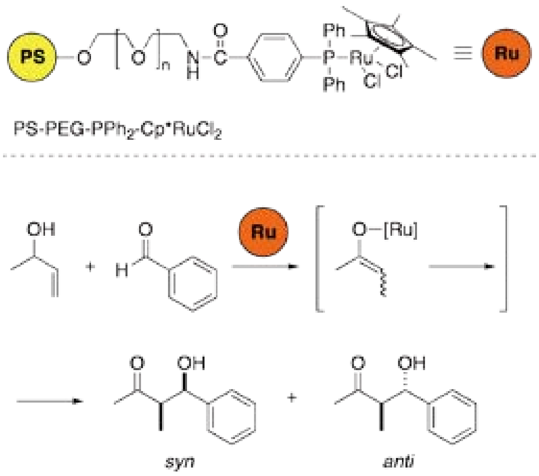
Department of Life and Coordination-Complex Molecular Science
Division of Complex Catalysis

UOZUMI, Yasuhiro	Professor
OSAKO, Takao	Assistant Professor
HAMASAKA, Go	Post-Doctoral Fellow
ZHOU, Haifeng	Post-Doctoral Fellow
KOBAYASHI, Noboru	Graduate Student
MUTO, Tsubasa	Graduate Student
SAKURAI, Fumie	Graduate Student
TORII, Kaoru	Technical Fellow
TAZAWA, Aya	Technical Fellow
SASAKI, Tokiyo	Secretary
FUKUSHIMA, Tomoko	Secretary

Various transition metal-catalyzed organic molecular transformations in water were achieved under heterogeneous conditions by use of an amphiphilic resin-supported ruthenium complexes, a boron-iridium heterobimetallic polymeric catalyst, or an architecture-based system of transition metal catalysis using an amphiphilic pincer palladium complex bearing hydrophilic and hydrophobic chains which were designed and prepared by this research group. In particular, tandem olefin migration-aldol condensation and dehydrative alkylation, which were performed in water under heterogeneous conditions, and development of an amphiphilic pincer palladium complex bearing hydrophilic and hydrophobic chains for an architecture-based system of transition metal catalysis are highlights among the achievements of the 2010–2011 period to approach what may be considered ideal chemical processes of next generation. Representative results are summarized hereunder.

1. Tandem Olefin Migration-Aldol Condensation in Water with an Amphiphilic Resin-Supported Ruthenium Complex[1,2]

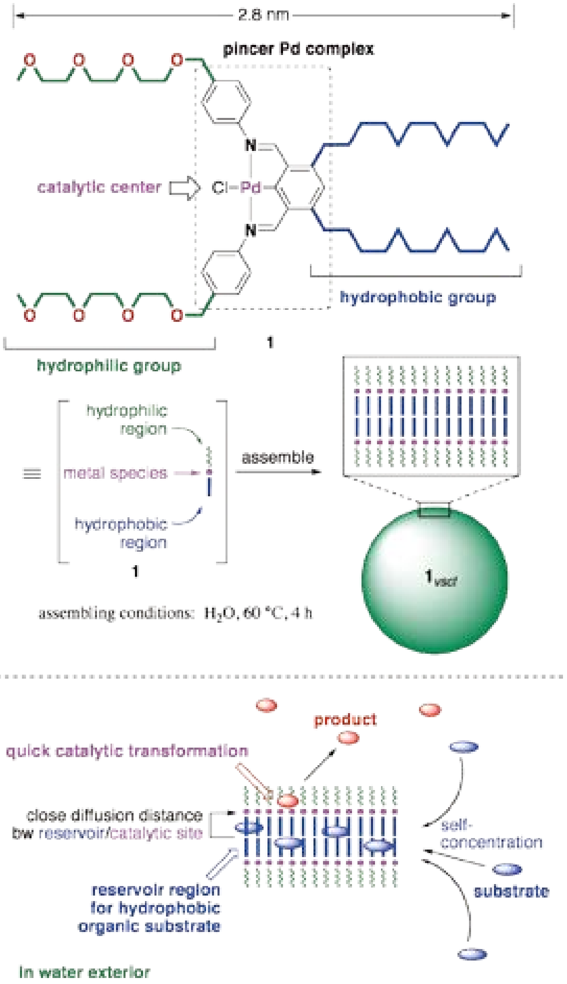
A catalytic tandem olefin migration/aldol condensation process with allylic carbinols and aryl aldehydes was performed with an amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported phosphine-ruthenium complex in water as a single reaction medium under heterogeneous conditions. It is noteworthy that the catalytic performance of the polymeric complex PS-PEG-phosphine-$RuCl_2Cp^*$ in water was much higher than that reported for ruthenium-phosphine complexes (*e.g.* $RuCl_2(PPh_3)_3$) under homogeneous conditions. Thus, 0.5 mol% Ru of the polymeric catalyst promoted the tandem olefin migration/aldol condensation in water at 45 °C within 2 h to give quantitative yields of the corresponding aldols with *syn*-selectivity. Inverse stereoselectivity (*anti*-selectivity) was observed when the reaction was carried out in the presence of K_2CO_3.



Scheme 1. Tandem Olefin Migration-Aldol Condensation in Water with Amphiphilic Resin-Supported Ruthenium Complex.

2. Molecular Architecture-Based Administration of Catalysis in Water via Self-Assembly of an Amphiphilic Palladium Pincer Complex[3)]

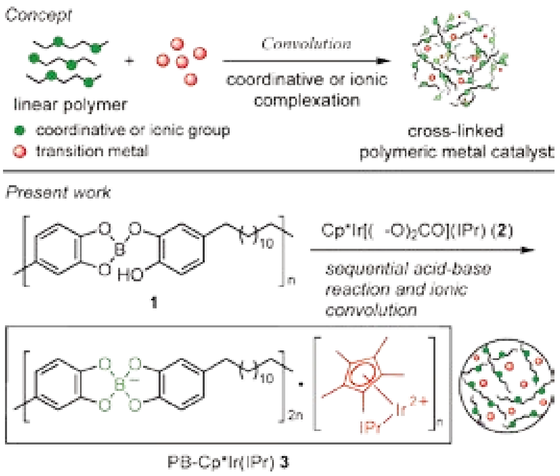
An architecture-based system of transition metal catalysis using an amphiphilic pincer palladium complex bearing hydrophilic and hydrophobic chains was developed, where (i) the self-assembling formation of bilayer vesicles of a palladium complex, (ii) the concentration of organic substrates at the hydrophobic region of the bilayer membrane, (iii) and the catalytic transformation of the substrate with the palladium species, all located in a close diffusion distance, automatically occurred in water. The oxirane ring opening reaction and the Michael reaction, both with arylboron reagents, were found to proceed in water where the vesicle structure of the palladium complex was essential to promote catalysis.



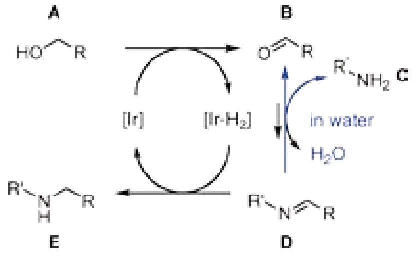
Scheme 2. Formation of Vesicle $\mathbf{1}_{\mathrm{vscl}}$ by Self-Assembly of the Pincer Palladium Complex **1** (top) and Schematic Image of the Concept of Catalysis within the Bilayer membrane of the $\mathbf{1}_{\mathrm{vscl}}$ (bottom).

3. In-Water Dehydrative Alkylation of Ammonia and Amines with Alcohols by a Polymeric Bimetallic Catalyst[4)]

We have previously developed new methodology for the preparation of highly active and reusable polymer-supported catalysts, also known as "molecular convolution," where a soluble linear polymer having multiple ligand groups was convoluted with neutral metals or anionic metal salts via coordinative or ionic complexation to achieve the one-step preparation of the insoluble polymeric metal composite, combining heterogeneity and catalytic activity in one system. A novel convoluted polymeric metal catalyst was designed and prepared for the first time to realize "in-water dehydrative *N*-alkylation." Thus, a boron-iridium heterobimetallic polymeric catalyst was prepared by ionic convolution of a poly (catechol borate) and an iridium complex. The alkylation of ammonia and amines with alcohols, alkylating agents, was performed with 1 mol% Ir of the heterogeneous catalyst in water without the use of organic solvents under aerobic conditions to give the corresponding alkylated amines in up to quantitative yield.



Scheme 3. Concept for the Molecular Convolution (top) and Preparation of PB-Cp*Ir(IPr) (bottom).



Scheme 4. Proposed Mechanism for In-Water Dehydrative *N*-Alkylation with PB-Cp*Ir(IPr).

References

1) Y. Oe and Y. Uozumi, *Adv. Synth. Catal.* **350**, 1771–1775 (2008).
2) Y. Oe and Y. Uozumi, *Synlett* 787–790 (2010).
3) G. Hamasaka, T. Muto and Y. Uozumi, *Angew. Chem., Int. Ed.* **50**, 4876–4878 (2011).
4) H. Ohta, Y. Yuyama, Y. Uozumi and Y. M. A. Yamada, *Org. Lett.* **13**, 3892–3895 (2011).