Catalysis toward Utilization of Renewable Resources:

Ligand Contribution to the Group 9 Metal Mediated H_2 Addition/Elimination Reactions

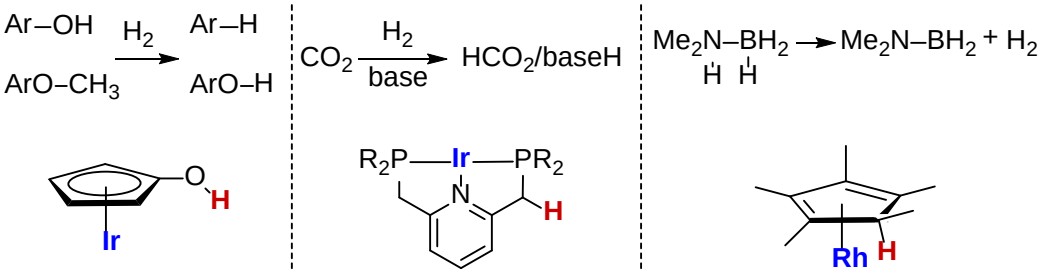
Kyoko Nozaki

Department of Chemistry and Biotechnology,

The University of Tokyo

When organometallic species mediate chemical transformations, ligands often play a major role for catalysis by interaction between a part of a ligand and a substrate. Here in this presentation, an essential role played by the metal–ligand cooperation will be discussed in group 9 metal mediated H_2 addition/elimination reactions which possibly contribute for the utilization of renewable carbon resources.

1. Hydrogenolysis of sp^2 C–OH and sp^3 C–O bonds:[1] The direct and selective hydrogenolysis of sp^2 C–OH bonds in substituted phenols and naphthols catalyzed by hydroxycyclopentadienyl iridium complexes. The same catalysts were applied to the unprecedented selective hydrogenolysis of the sp^3 C–O bonds in aryl methyl ethers. Furthermore, the hydrodeoxygenation of vanillylacetone, a lignin model compound, afforded alkylbenzenes as the major products via triple deoxygenation. As a mechanism, cooperative effect between the metal and the hydroxy group in the ligand is suggested.
2. Hydrogenation of CO_2:[2] Hydrogenation catalyzed by PNP/Ir complex in the presence of KOH afforded a salt of formic acid in TON of 3,50,000. For the use of organic base, the use of PC(II)P ligand was successful. The contribution of the protic hydrogen in the ligand to the hydrogenation will be discussed.
3. Dehydrogenation of amine-borane:[3] Cp*Rh served as a catalyst for dehydrogenation of Me_2NHBH_3 with TON of 2630 in 48 h. The robustness of the catalyst is notable. A non-inocent behavior of the Cp* will be discussed.



References

1. Kusumoto, S.; Nozaki, K. *Nat. Commun*. **2015**, 6, 7296.
2. (a) Tanaka, R.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14168–14169. (b) Tanaka, R.; Yamashita, M.; Chung, L. W.; Morokuma, K.; Nozaki, K. *Organometallics* **2011**, *30*, 6742–6750. (c) Aoki, W.; Wattanabinin, N.; Kusumoto, S.; Nozaki, K. *Bull. Chem. Soc. Jpn.* **2016**, *89*, 113–124. (d) Takaoka, S.; Eizawa, A.; Kusumoto, S.; Nakajima, K.; Nishibayashi, Y.; Nozaki, K. To be submitted.
3. Pal, S.; Kusumoto, S.; Nozaki, K. *Submitted for publication.*