

Research Highlight from the Group of Dr. Swadhin Mandal

One of the major concerns for today's World has been the development of processes, which are sustainable without destroying our limited resources and environment. In this regard, the development of environmentally benign and cost-effective catalysts is ideal. The major concerns on the industrially used catalytic systems have been: i) high expense of catalysts; ii) toxicity of transition metals; iii) difficulties in removal of trace amount of toxic-metal residues from the desired products which are in particular pharmaceutically important; and finally iv) the large consumption of heavier and rare transition metals which do not meet the requirement of sustainable development. As an example, worldwide total annual production of palladium is about 200 metric tons, which costs around 50 billion USD (3 lakh 40 thousand crores Rs approx.), mostly used by different chemical industries for preparation of drugs, natural products and various commodity materials. This high demand of palladium is mainly due to its unique potential to catalyze various coupling reactions, which are key steps involved in almost every organic synthetic process. Not surprisingly, in 2010 the process of palladium catalyzed C-C coupling reaction was recognized with Nobel prize to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki.

However, very low abundance of palladium in the earth crust (63 ppm) raises concern over excess use of such precious and rare metal. As a result, there has been an enormous urge to develop a new synthetic protocol by avoiding the use of palladium or other rare earth metals for coupling reactions. The recent research article from the group of Dr Swadhin Mandal at Department of Chemical Sciences, IISER Kolkata addresses one such problem. The article is published in the prestigious American Chemical Society Journal *J. Am. Chem. Soc.* entitled, "Integrating Organic Lewis Acid and Redox Catalysis: The Phenalenyl Cation in Dual Role" which is coauthored by Dr Mandal's PhD student, Mr. Jasimuddin Ahmed. The article describes how one can avoid precious metal like palladium and even go forward without using any metal in the C-C coupling at mild conditions for the first time. The research also demonstrates that a billion dollar agrochemical (fungicide), boscalid marketed by the multinational company BASF can be prepared without using any palladium based coupling catalyst. This work conceptualizes on the fundamental understanding of organometallic chemistry how typically a metal works during a coupling catalysis and the major steps in such catalysis are termed as oxidative addition (when metal looses two electrons) and reductive elimination (when metal gains back its two electron). Dr. Mandal's group capitalizes on this concept to build an organic molecule (named as phenalenyl based molecule) which can accept electrons, store it and delivers the way a typical transition metal such as palladium functions in a coupling reaction. Dr. Mandal has pioneered this concept and his group is currently engaged in applying such concept to replace many such coupling catalysis reactions without using rare and precious metals. Dr Mandal describes this approach as "Transition Metal Mimicking Catalysis".

Reference:

Ahmed, J., Chakraborty, S., Jose, A., P., Sreejyothi & Mandal, S. K. Integrating Organic Lewis acid and Redox Catalysis: The Phenalenyl Cation in Dual Role. *J. Am. Chem. Soc.* (2018) DOI:10.1021/jacs.8b04786.

Link: https://pubs.acs.org/doi/10.1021/jacs.8b04786