

Mimicking Biological Reduction

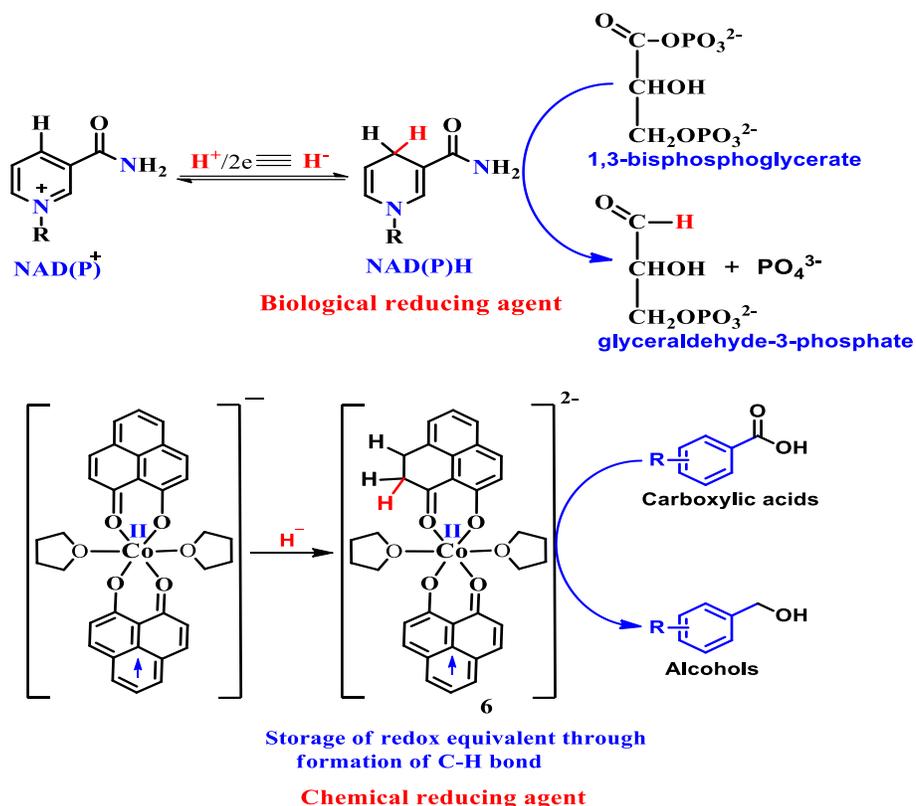
By Dr. Mrinal Bhunia



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Storing and transferring electrons for multielectron reduction process is considered as the key step in various important chemical and biological transformations. Nature has pioneered strategy in storing and transferring electrons through C-H bond via dearomatization of pyridine ring present in nicotinamide adenine dinucleotide (phosphate) [NAD(P)⁺]. The Nature often displays pioneering activities in this direction, such as reducing equivalents created in Photosystem II are stored in organic backbone, in the form of nicotinamide adenine dinucleotide (phosphate), NAD(P)H. The NAD(P)H, which is the reduction currency in biology is generated by 2e/H⁺ transfer to NAD(P)⁺ by a reductive dearomatization and stores reducing equivalent in the form of a hydride on an sp³-carbon center (Scheme below, top). A plethora of biological processes are known where NAD(P)H acts as the primary vehicle for electron and hydride delivery. For example, NAD(P)H reduces 1,3-bisphosphoglycerate to glyceraldehyde-3-phosphate in the photosynthetic production of carbohydrates in Calvin cycle.

In this work, we report a conceptually similar phenomena by using a redox active phenalenyl (PLY) based ligand backbone in consonance with an appropriate transition metal to accomplish multielectron reduction. Herein we show a complex, Co(PLY)₂(THF)₂ which upon two electron injection to the redox active ligand backbone, effectively executes reduction of carboxylic acid to alcohol via hydrosilylation pathway. This reduction proceeds by a single electron transfer (SET) housed in the ligand backbone leading to the cleavage of the Si-H bond. Several important intermediates along the catalytic reduction have been isolated and well characterized to prove that the redox equivalent is stored in the form of a C-H bond in the PLY backbone via a dearomatization process and the reduction closely mimics nature's strategy of using organohydride in the form of NAD(P)H.



Bhunia *et al.* "Storing redox equivalent in the phenalenyl backbone towards catalytic multi-electron reduction" *Chem. Sci.* **2019**, *10*, DOI: 10.1039/c9sc02057h.

Way to success: We discovered the first result on this project during the first quarter of 2016. The work took shape when I serendipitously observed that PLY-dimer can be leached out where one of the two PLY rings got dearomatized. This result was surprising at the beginning and led us to our understanding that the hydride is being stored in the PLY ring at the expense of aromaticity just like the NADP stores hydride by losing its aromaticity.