A DFT Study of PNP-Mn Catalyzed Acceptorless Dehydrogenative Coupling of Primary Alcohols with Hydrazine to Give Alkene or Azine

Abstract: Acceptorless dehydrogenative coupling (ADC) is an atom-economy and environmentally friendly method to use readily available feedstock (e.g., alcohol) to synthesize value-added compounds, because the method does not use oxidant or hydrogen acceptor and only produces hydrogen or water as by-product. Accordingly, we performed a DFT mechanistic study of the ADC reactions of primary alcohols with hydrazine to afford alkene or azine, catalyzed by **PNP-Mn** pincer catalyst. The study shows that the reaction proceeds via three stages: alcohol dehydrogenation to give aldehyde (stage I), the coupling of the aldehyde with hydrazine to give hydrazone (stage II) and further coupling of hydrazones with the aldehyde to afford alkene or azine (Stage III). For alcohol dehydrogenations, the BDHT (bifunctional double hydrogen transfer) pathway is more favorable than β-hydride elimination. In stage III, the N–H addition of hydrazone to **PNP-Mn** gives a nucleophilic [Mn]–N^1H–N^2=C^1HR intermediate (i.e., **IM7** or **IM7a**) featuring two nucleophilic sites at N^1 and C^1. The nucleophilic attack of aldehyde at C^1 leads to an alkene, while the attack at N^1 gives azine. The kinetic competition between the two pathways controls the chemoselectivity of the reaction. If the alcohol is aromatic such as benzyl alcohol, the pathway initiated by a nucleophilic attack at C^1 is kinetically more favorable, leading to an alkene. For aliphatic alcohol, the pathway with the attack at N^1 wins, resulting in azine. Our computed mechanism is energetically more favorable than mechanism postulated by the experimentalist, which is consistent with the acceptorless dehydrogenative coupling (ADC) reactions.

Key words: Acceptorless dehydrogenative coupling (ADC), **PNP-Mn** pincer catalyst, DFT