

Supramolecular approaches to control selectivity in transition metal catalysis

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The interface between supramolecular chemistry and transition metal catalysis has received surprisingly little attention in contrast to the individual disciplines. It provides, however, novel and elegant strategies that lead to new tools for the search of effective catalysts, and as such this has been an important research theme in our laboratories. In this presentation I will focus on supramolecular strategies to control activity and selectivity in transition metal catalysis, which is especially important for reactions that are impossible to control using traditional catalyst development. For substrates with functional groups we use substrate orientation effects to control selectivity. We demonstrate that hydrogen bonding is a versatile tool to control the substrate orientation at the metal center, and that this is an excellent tool to achieve highly enantioselective hydrogenation catalysts, highly regioselective hydroformylation, Heck and CH borylation catalysts.

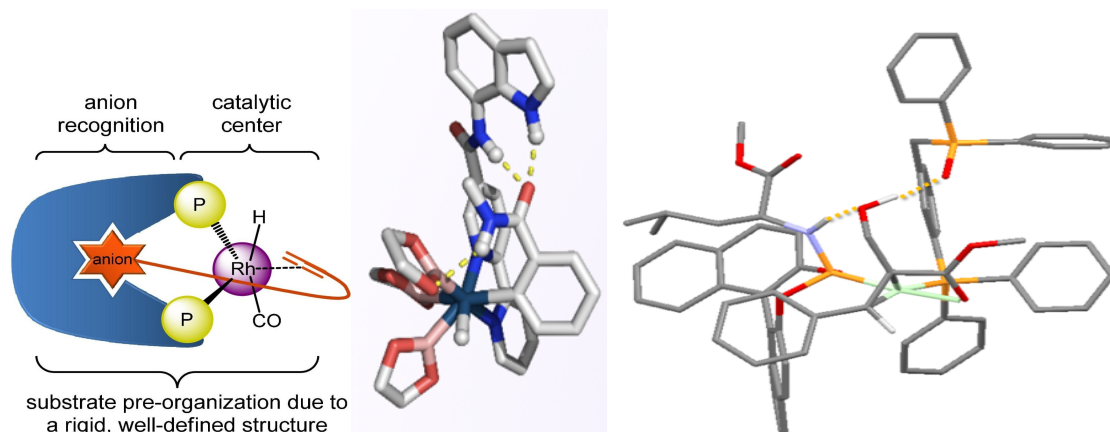


Figure 1. An schematic example of substrate pre-organization at the metal complex for selective hydroformylation and substrate pre-organization for CH borylation and asymmetric hydrogenation.

For reviews see: 1) Reek et al “New directions in supramolecular catalysis,” *Nature Chemistry*, **2010**, 2, 615. 2) Reek et al , “Supramolecular control of selectivity in transition-metal catalysis through substrate preorganization” *Chem. Sci*, **2014**, 5, 2135. 3) Reek et al, ‘Supramolecular Approaches To Control Activity and Selectivity in Hydroformylation Catalysis” *ACS Catal.* **2018**, 8, 3469–3488

Substrate preorganization: Reek et al. *Angew. Chem. Int. Ed.*, **2013**, 52, 3878; *Angew. Chem., Int. Ed.* **2011**, 50, 396– 400.; *Nature Protocols*, **2014**, 9, 1183 *J. Am. Chem. Soc.* **2013** 135, 10817; *Angew. Chem. Int. Ed.*, **2017**, 56, 13056-13060