

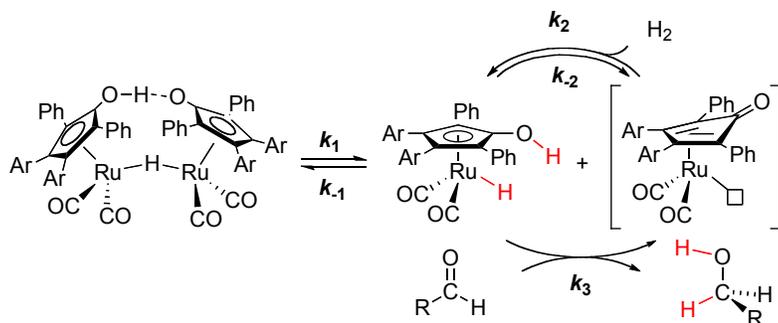
## Final Report for DE-FG-02-85ER13406

### Mechanistic Studies at the Interface Between Organometallic Chemistry and Homogeneous Catalysis

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**Executive Summary.** Our goal was to learn the intimate mechanistic details of reactions involved in homogeneous catalysis and to use the insight we gain to develop new and improved catalysts. Our work centered on the hydrogenation of polar functional groups such as aldehydes and ketones and on hydroformylation. Specifically, we concentrated on catalysts capable of simultaneously transferring hydride from a metal center and a proton from an acidic oxygen or nitrogen center to an aldehyde or ketone. An economical iron based catalyst was developed and patented. Better understanding of fundamental organometallic reactions and catalytic processes enabled design of energy and material efficient chemical processes. Our work contributed to the development of catalysts for the selective and mild hydrogenation of ketones and aldehydes; this will provide a modern green alternative to reductions by  $\text{LiAlH}_4$  and  $\text{NaBH}_4$ , which require extensive work-up procedures and produce waste streams.

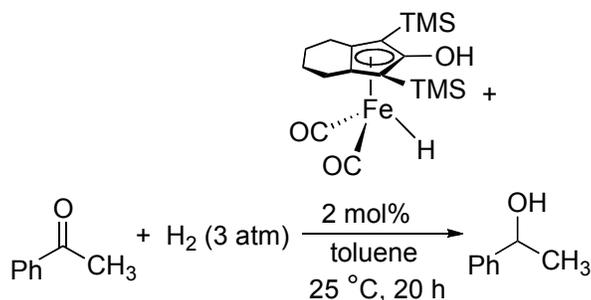
**$(\text{C}_5\text{R}_4\text{OH})\text{Ru}(\text{CO})_2\text{H}$  Hydrogenation Catalysts.** Youval Shvo described a remarkable catalytic system in which the key intermediate  $(\text{C}_5\text{R}_4\text{OH})\text{Ru}(\text{CO})_2\text{H}$  (**1**) has an electronically coupled acidic OH unit and a hydridic RuH unit. Our efforts centered on understanding and improving upon this important catalyst for reduction of aldehydes and ketones. Our mechanistic studies established that the reduction of aldehydes by **1** to produce alcohols and a diruthenium bridging hydride species occurs much more rapidly than regeneration of the ruthenium hydride from the diruthenium bridging hydride species. Our mechanistic studies require simultaneous transfer of hydride from ruthenium to the aldehyde carbon and of a proton from the CpOH unit to the aldehyde oxygen and support reduction of the aldehyde without its prior coordination to ruthenium.



Another important step in the catalysis is the regeneration of **1** from reaction of  $\text{H}_2$  with the stable diruthenium bridging hydride complex **2**. Studies of the microscopic reverse of this process (hydrogen evolution from **1** which occurs at  $80\text{ }^\circ\text{C}$ ) in the presence of alcohol (the product of aldehyde hydrogenation) have shown that a dihydrogen complex is formed reversibly at a rate much faster than hydrogen evolution. Kinetic and theoretical studies in collaboration with Professor Qiang Cui of Wisconsin indicated an important role for alcohol in mediating transfer of hydrogen to ruthenium.

One key to developing more active catalysts was to destabilize the bridging hydride intermediate **2** to prevent its formation or to speed its conversion to a reactive monohydride **1** by reaction with  $\text{H}_2$ . We found several successful ways to destabilize the bridging hydride and to obtain more active catalysts. Most recently, we discovered related iron catalysts for hydrogenation that do not form dimers; the cost advantage of iron catalysts is spectacular.

**Iron Catalysts.** In an exciting development, we found that a related *iron complex* is also a very active ketone hydrogenation catalyst. This hydrogenation catalyst shows high chemoselectivity for aldehydes, ketones, and imines and isolated  $\text{C}=\text{C}$ ,  $\text{C}\equiv\text{C}$ ,  $\text{C}-\text{X}$ ,  $-\text{NO}_2$ , epoxides, and ester functions are unaffected by the hydrogenation conditions. Mechanistic studies have established a reversible hydrogen transfer step followed by rapid dihydrogen activation. The same iron complex also catalyzes transfer hydrogenation of ketones.



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