

# V.N.15 Bio-Inspired Molecular Catalysts for Oxidation of Hydrogen and Production of Hydrogen: Cheap Metals for Noble Tasks

Principal Investigator: R. Morris Bullock

Pacific Northwest National Laboratory

P.O. Box 999, K2-57

Richland, WA 99352

Phone (509) 372-6589

Email: morris.bullock@pnnl.gov

## Names of Team Members

- PNNL Staff Colleagues: Daniel L. DuBois, Mary Rakowski DuBois
- Postdoctoral Research Associates (2010-present): Kevin Welch, Jenny Y. Yang, Eric Wiedner, Tianbiao "Leo" Liu, Elliott Hulley

DOE Program Manager: Dr. Raul Miranda

Office of Basic Energy Sciences

Chemical Sciences, Geosciences, & Biosciences (CSGB)

Division

Email: Raul.Miranda@science.doe.gov

## Objectives

Electrocatalysts based on inexpensive, earth-abundant metals are needed since most fuel cells are based on platinum, an expensive, precious metal. Our objective is to design and synthesize biologically inspired functional model complexes that catalyze the oxidation of hydrogen and the production of hydrogen. Our research focuses on molecular complexes containing ligands bearing pendant amines that function as proton relays.

## Technical Barriers

It is now widely recognized that there is a need to develop catalysts that rely less on noble metals like platinum, particularly for use in large scale energy systems where the high cost and low abundance of precious metals will preclude their use. Our efforts focus on the rational development of new molecular catalysts based on inexpensive, abundant metals such as iron, manganese and cobalt. The technical barriers include synthesis and design of ligands and metal complexes, obtaining an understanding of mechanistic details of the reactions, and development of highly active electrocatalysts with low overpotentials. In addition, we seek to use thermodynamic data to guide the rational design of molecular catalysts. Such thermochemical data can come from equilibrium measurements by spectroscopic measurements (e.g., NMR spectroscopy) as well as electrochemical studies. Together, these measurements provide critical information required for the rational design

of molecular catalysts, including acidity of protonated pendant amines of the ligands and hydride donor ability of metal hydrides. Understanding the thermodynamics allows the rational design of catalysts for oxidation of hydrogen or the reverse, production of H<sub>2</sub> by reduction of protons.

## Abstract

Electrocatalysts for fast, efficient conversion between electrical and chemical energy is needed because of the temporal variations of renewable, carbon-free sources of energy such as solar and wind. Storing energy in the HH bond of hydrogen is attractive since oxidation of hydrogen in a fuel cell provides electricity efficiently and cleanly. Electrocatalysts based on inexpensive, earth-abundant metals are needed since most fuel cells are based on platinum, an expensive, precious metal. The cost of cobalt, manganese or iron is at least a thousand times less expensive than platinum, so dramatic cost savings would result from development of catalysts using these inexpensive, earth-abundant metals. Natural hydrogenase enzymes oxidize and produce H<sub>2</sub> using iron and nickel. Our objective is to design and synthesize biologically inspired functional models that catalyze the oxidation of hydrogen and production of hydrogen with high activity and low overpotentials. A comprehensive knowledge of the thermochemical properties of MH and NH bonds underpins our ability to produce highly active catalysts. Specifically, a key issue for catalysis is the ability to have the hydride (H<sup>-</sup>) acceptor ability of the metal and the basicity (proton acceptor ability) of the amine appropriately matched so that the heterolytic cleavage of H<sub>2</sub> is close to thermoneutral. The facile reversibility of the heterolytic cleavage of H<sub>2</sub> in the active site of enzymes indicates that those systems have balanced thermodynamics.

## Progress Report

The iron complexes CpFe(P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)Cl, CpFe(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)Cl, CpFe(P<sup>Ph</sup><sub>2</sub>C<sub>5</sub>)Cl (where P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub> is 1,5-dibenzyl-1,5-diaza-3,7-diphenyl-3,7-diphosphacyclooctane, P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub> is 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane, and P<sup>Ph</sup><sub>2</sub>C<sub>5</sub> is 1,4-diphenyl-1,4-diphosphacycloheptane) have been synthesized and characterized by NMR spectroscopy, electrochemical studies, and X-ray diffraction. These chloride derivatives are readily converted to the corresponding hydride complexes CpFe(P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)H, CpFe(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)H, CpFe(P<sup>Ph</sup><sub>2</sub>C<sub>5</sub>)H and Fe(H<sub>2</sub>)<sup>+</sup> complexes [CpFe(P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)(H<sub>2</sub>)]BAR<sup>F</sup><sub>4</sub>, (where BAR<sup>F</sup><sub>4</sub> is B[(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>]), [CpFe(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)(H<sub>2</sub>)]BAR<sup>F</sup><sub>4</sub>, and [CpFe(P<sup>Ph</sup><sub>2</sub>C<sub>5</sub>)(H<sub>2</sub>)]BAR<sup>F</sup><sub>4</sub>, and [CpFe(P<sup>Ph</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)(CO)]BAR<sup>F</sup><sub>4</sub>. An attractive interaction was found by x-ray crystallography between the N

atom of the pendant amine and the C atom of the coordinated CO ligand for  $[\text{CpFe}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)(\text{CO})]\text{BAR}^{\text{F}}_4$ . The  $\text{N}\cdots\text{CO}$  distance of 2.848 Å is shorter than the sum of van der Waals radii of N and C atoms (3.25 Å) by ca. 0.4 Å, indicating there is a significant bonding interaction between the N atom of the  $\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2$  ligand and the C atom of the carbonyl ligand.

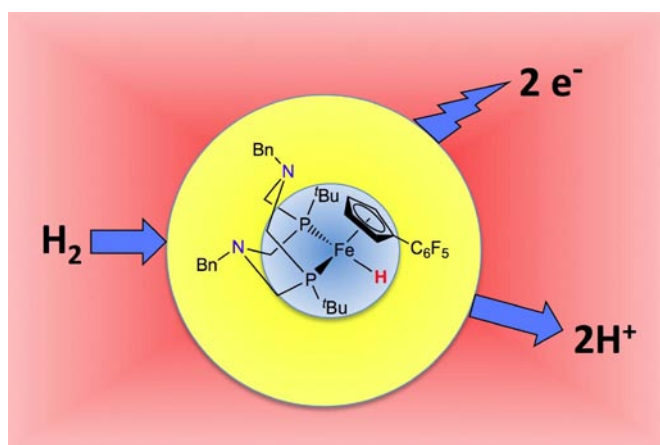
Studies of H/D exchange by the complexes  $[\text{CpFe}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)(\text{H}_2)]^+$ ,  $[\text{CpFe}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{H}_2)]^+$ , and  $[\text{CpFe}(\text{P}^{\text{Ph}}_2\text{C}_3)(\text{H}_2)]^+$  carried out using  $\text{H}_2$  and  $\text{D}_2$  indicate that the relatively rapid H/D exchange observed for  $[\text{CpFe}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)(\text{H}_2)]^+$  and  $[\text{CpFe}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{H}_2)]^+$  compared to  $[\text{CpFe}(\text{P}^{\text{Ph}}_2\text{C}_3)(\text{H}_2)]^+$  is consistent with *intramolecular heterolytic cleavage of  $\text{H}_2$*  mediated by the pendant amine. The hydrogenase enzymes have been shown to undergo exchange reactions to produce HD under an  $\text{H}_2/\text{D}_2$  atmosphere. Computational studies for our synthetic complexes indicate a low barrier for heterolytic cleavage of  $\text{H}_2$ . These mononuclear  $\text{Fe}^{\text{II}}$  dihydrogen complexes containing pendant amines in the ligands mimic crucial features of the distal Fe site of the active site of the  $[\text{FeFe}]$ -hydrogenase required for H-H bond formation and cleavage. Requirements for heterolytic  $\text{H}_2$  cleavage at the active site of  $[\text{FeFe}]$ -hydrogenases and synthetic catalysts based on Fe are a ferrous ( $\text{Fe}^{\text{II}}$ ) center for binding of  $\text{H}_2$ , a properly positioned pendant amine in the ligand framework, and energy matching of the proton acceptor ability of the amine and the hydride acceptor ability of the metal, so that heterolytic cleavage of  $\text{H}_2$  is thermodynamically favored. Our results indicate that suggesting *mononuclear Fe* complexes can be competent models of the active site of  $[\text{FeFe}]$ -hydrogenase enzymes.

The Fe complexes described above were shown to bind  $\text{H}_2$  and heterolytically cleave  $\text{H}_2$ , but they were not electrocatalysts for oxidation of  $\text{H}_2$ . Rational modification of the ligand steric and electronic parameters was carried out by installing an alkyl group with larger steric bulk on phosphorus, with the intent of preventing binding of the external amine base, while still enabling binding of  $\text{H}_2$  to the  $\text{Fe}^{\text{II}}$  center. An electron-withdrawing  $\text{C}_6\text{F}_5$  substituent was added to the Cp ligand, with the intent of increasing the acidity of the  $\text{Fe}(\text{H}_2)^+$  complex. The iron hydride complex  $[\text{Cp}^{\text{C}_6\text{F}_5}\text{Fe}(\text{P}^{\text{Bu}}_2\text{N}^{\text{Bn}}_2)\text{H}]$  was synthesized and fully characterized by spectroscopic measurements as well as by single crystal x-ray crystallography. This complex is an electrocatalyst for oxidation of  $\text{H}_2$  under 1 atmosphere  $\text{H}_2$  in fluorobenzene solution at 22°C (Fig. 1).

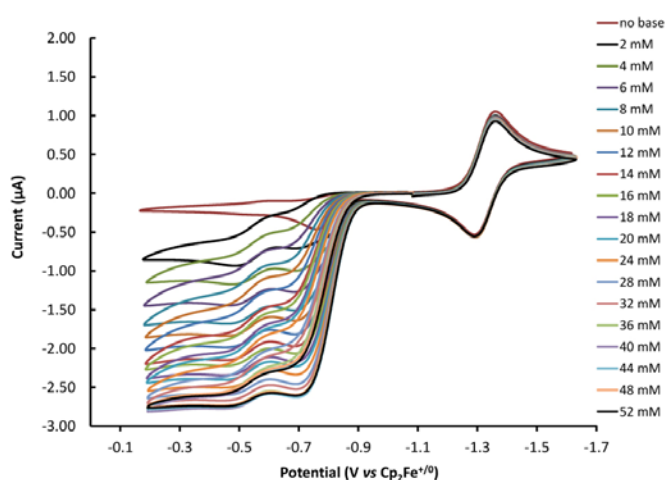
The proposed mechanism for electrocatalytic oxidation of  $\text{H}_2$  by  $\text{CpFe}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)\text{H}$  is shown in Fig. 3.

## Future Directions

Research on iron and manganese electrocatalysts for oxidation of hydrogen is continuing under the Center for Molecular Electrocatalysis, an Energy Frontier Research Center, and is focused on increasing the turnover frequency and decreasing the overpotential.



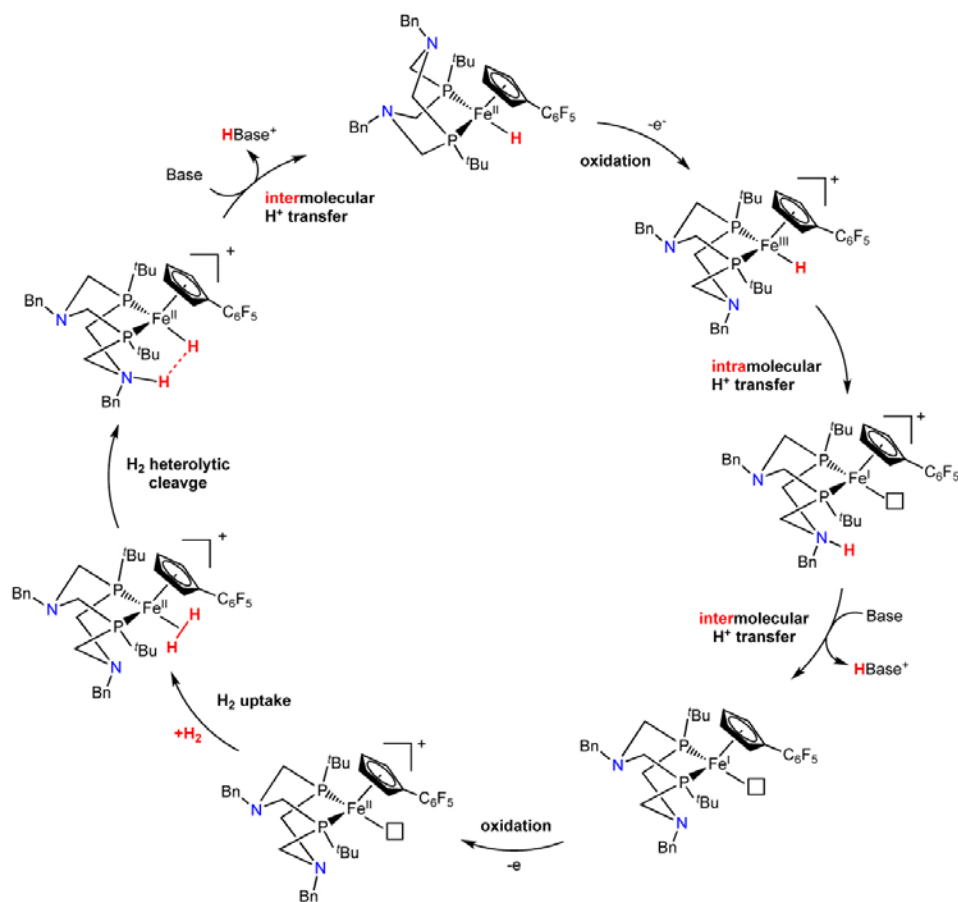
**FIGURE 1.** Schematic representation of the oxidation of  $\text{H}_2$  by  $[\text{Cp}^{\text{C}_6\text{F}_5}\text{Fe}(\text{P}^{\text{Bu}}_2\text{N}^{\text{Bn}}_2)\text{H}]$ .



**FIGURE 2.** Cyclic voltammograms of a fluorobenzene solution of  $[\text{Cp}^{\text{C}_6\text{F}_5}\text{Fe}(\text{P}^{\text{Bu}}_2\text{N}^{\text{Bn}}_2)\text{H}]$  (1.0 mM) under 1.0 atm  $\text{H}_2$  at 22 °C with increasing concentrations of *N*-methylpyrrolidine, as indicated in the legend. The increase in current at higher concentrations of base indicates that the oxidation of  $\text{H}_2$  is catalyzed by the iron complex. Conditions: scan rate, 20 mV/s, 0.1 M  $n\text{-Bu}_4\text{NB}(\text{C}_6\text{F}_5)_4$  supporting electrolyte, glassy carbon working electrode. Potentials are referenced to  $\text{Cp}_2\text{Fe}^{+/0}$  at 0 V, and  $\text{Cp}_2\text{Co}^+\text{PF}_6^-$  (-1.33 V) was used as a secondary internal reference.

## Publications acknowledging DOE-BES Funding (2010-present)

1. Yang, J.Y.; Bullock, R.M.; Dougherty, W.G.; Kassel, W.S.; Twamley, B.; DuBois, D.L.; Rakowski DuBois, M., "Reduction of Oxygen Catalyzed by Nickel Diphosphine Complexes with Positioned Pendant Amines," *Dalton Trans.* **2010**, 39, 3001-3010.
2. "Catalysis Without Precious Metals" R.M. Bullock, Ed.; Wiley-VCH, Weinheim, Germany, 2010; ISBN: 978-3-527-32354-8.
3. Welch, K.D.; Dougherty, W.D.; Kassel, W.S. DuBois, D.L.; Bullock, R.M. "Synthesis, Structures, and Reactions of Manganese



**FIGURE 3.** Proposed mechanism of electrocatalytic oxidation of  $\text{H}_2$ . Oxidation of  $\text{Fe}^{\text{II}}\text{-H}$  leads to an increased acidity of the  $\text{Fe}^{\text{III}}\text{-H}$  bond. Intramolecular proton transfer from iron to the pendent amine is followed by intermolecular deprotonation of the  $\text{N-H}$  by the external amine base. Electrochemical oxidation of the iron complex is followed by binding of  $\text{H}_2$ , which is heterolytically cleaved, with the hydride being transferred to iron and the proton to the pendent amine. Deprotonation by the external amine base completes the catalytic cycle and regenerates the iron hydride  $\text{CpFe}(\text{P}^{\text{Bu}}_2\text{N}^{\text{Bn}}_2)\text{H}$ .

Complexes Containing Diphosphine Ligands With Pendant Amines,” *Organometallics*, **2010**, *29*, 4532-4540.

**4.** Wiedner, E.S.; Yang, J.Y.; Dougherty, W.G.; Kassel, W.S.; Bullock, R.M.; Rakowski DuBois, M.; DuBois, D.L., “Comparison of Cobalt and Nickel Complexes with Sterically Demanding Cyclic Diphosphine Ligands: Electrocatalytic  $\text{H}_2$  Production by  $[\text{Co}(\text{P}^{\text{Bu}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ ,” *Organometallics*, **2010**, *29*, 5390-5401.

**5.** Rakowski DuBois, M.; DuBois, D.L., “A Modular Approach to the Development of Molecular Electrocatalysts for  $\text{H}_2$  Oxidation and Production Based on Inexpensive Metals,” In *Catalysis Without Precious Metals*; R.M. Bullock, Ed.; Wiley-VCH, Weinheim, Germany, 2010.

**6.** Yang, J.Y.; Bullock, R.M. Rakowski DuBois, M.; DuBois, D. “Fast and Efficient Molecular Electrocatalysts for  $\text{H}_2$  Production: Using Hydrogenase enzymes as Guides,” *MRS Bulletin* **2011**, *36*, 39-47. (invited review article).

**7.** DuBois, D.L.; Bullock, R.M., “Molecular Electrocatalysts for the Oxidation of Hydrogen and the Production of Hydrogen

–The Role of Pendant Amines as Proton Relays,” *Eur. J. Inorg. Chem.* **2011**, 1017-1027. (invited review article for special issue on Hydrogenases).

**8.** Bullock, R.M. “A Mercurial Route to a Cobalt Dihydrogen Complex,” *Angew. Chem. Intl. Ed.*, **2011**, *50*, 4050-4052.

**9.** Wiedner, E.S., Yang, J.Y., Chen, S., Raugei, S., Dougherty, W.G., Kassel, S., Helm, M.H., Bullock, R.M., Rakowski DuBois, M., DuBois, D.L., “Stabilization of Nickel Complexes with  $\text{Ni}^0\cdots\text{H-N}$  Bonding Interactions Using Sterically Demanding Cyclic Diphosphine Ligands,” *Organometallics* **2012**, *31*, 144-156.

**10.** Liu, T.; Chen, S.; O’Hagan, M.J.; DuBois, M.R.; Bullock, R.M.; DuBois, D.L. “Synthesis, Characterization and Reactivity of Fe Complexes Containing Cyclic Diazadiphosphine Ligands: The Role of the Pendant Base in Heterolytic Cleavage of  $\text{H}_2$ ” *J. Am. Chem. Soc.* **2012**, *134*, 6257-6272.

**11.** Liu, T.; DuBois, D.L.; Bullock, R.M. “An Iron Complex with Pendant Amines as a Molecular Electrocatalyst for Oxidation of Hydrogen,” *Nature Chemistry*, **2013**, *5*, 228-233.