

# BES014. Bio-Inspired Molecular Catalysts for Hydrogen Oxidation and Hydrogen Production

R. Morris Bullock and Daniel L. DuBois  
(Principal Investigators)  
Chemical and Materials Sciences Division  
Pacific Northwest National Laboratory  
P.O. Box 999, K2-57  
Richland, WA 99352  
Phone: (509) 372-6589 (Bullock)  
(509) 375-2331 (DuBois)  
E-mails: morris.bullock@pnl.gov; daniel.dubois@pnl.gov

DOE Program Officer: Raul Miranda  
Division of Chemical Sciences, Biosciences and  
Geosciences  
Office of Basic Energy Sciences

## 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

The Basic Energy Sciences workshop report, *Basic Research Needs for the Hydrogen Economy*, emphasized the need for “developing catalysts that rely less on noble metals, which will become a limiting resource in large-scale hydrogen energy systems.” Because of limited supplies and the high cost of platinum, alternatives that use abundant, inexpensive metals are being studied in our research. We seek an understanding of how molecular complexes of nickel, cobalt and manganese can function as catalysts for oxidation of H<sub>2</sub> and for production of H<sub>2</sub> by reduction of protons. The challenges involve 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.

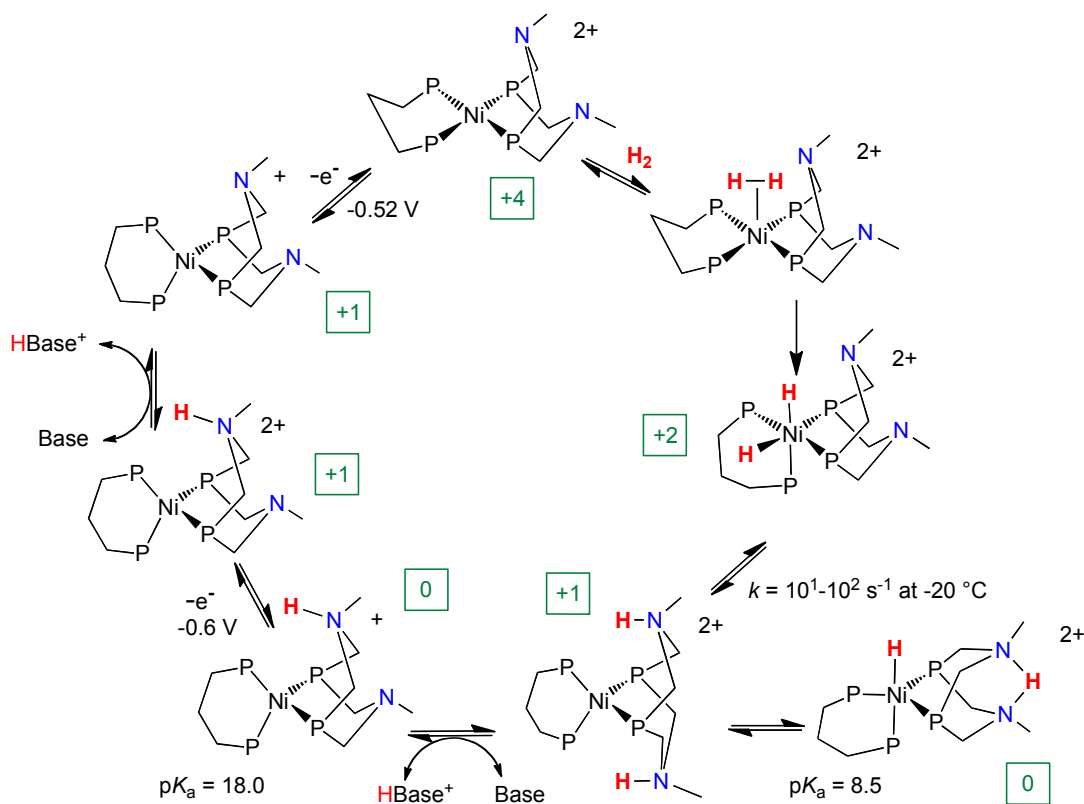
## Abstract, Progress Report and Future Directions

Renewable energy sources such as solar, wind, or geothermal provide the possibility of large amounts of carbon-free energy, but the temporal variation

in electricity output from these sources will require energy storage. Studies of H<sub>2</sub> are a critical part of efforts to rationally design electrocatalysts for energy storage as fuels. Low-temperature proton exchange membrane (PEM) fuel cells require platinum, an expensive noble metal of low abundance. Lower costs for fuel cells are expected to lead to broader and more diverse applications of fuel cells for conversion of H<sub>2</sub> to electricity. The cost of Ni, Co, or Mn is typically about three or four orders of magnitude less than the cost of Pt, so dramatic cost savings may be obtained by development of catalysts using these inexpensive, earth-abundant metals. This goal has already been achieved by biological systems that oxidize and produce H<sub>2</sub> using iron and nickel under exceedingly mild conditions.

Our objective is to synthesize *biologically inspired functional models* that provide high catalytic activity with low overpotentials, by recognizing that some of the most salient features enabling the remarkable capabilities of Nature’s catalysts can be replicated synthetically. In the [FeFe] enzyme, it is thought that an N atom near the iron assists in the heterolytic cleavage of H<sub>2</sub>, and that this pendant amine shuttles protons from the catalytically active metal site to the proton conduction channel. Our efforts focus on the design of biologically inspired complexes that use abundant metals and have a pendant amine; we seek *functional* rather than *structural* models of the [FeFe] or [FeNi] hydrogenases. Our work has demonstrated that complexes based on nickel, an inexpensive, abundant metal, can be used as electrocatalysts for H<sub>2</sub> production with rates (up to about 800 s<sup>-1</sup> at 22 °C) comparable to those of [NiFe] hydrogenase enzymes, and with overpotentials of 100-300 mV. Another important need is for catalysts with improved tolerance to CO, since the Pt catalyst in fuel cells is sensitive to CO impurities at the ppm level. The nickel-based hydrogen oxidation catalysts developed by our group have been demonstrated to have remarkable tolerance to CO; they function under 5% CO, with no detectable loss of activity.

Pendant amines in the diphosphine ligand can lead to a profound acceleration of the catalytic rates in nickel electrocatalysts for oxidation of H<sub>2</sub> and production of H<sub>2</sub>. In our series of electrocatalysts for oxidation of H<sub>2</sub>, the thermodynamic driving force for the addition of H<sub>2</sub> increases in the order [Ni(P<sup>Cy</sup><sub>2</sub>N<sup>Bz</sup><sub>2</sub>)<sub>2</sub>]<sup>2+</sup> < [Ni(dppp)(N<sup>Ph</sup><sub>2</sub>P<sup>Bz</sup><sub>2</sub>)]<sup>2+</sup> < [Ni(PNP)<sub>2</sub>]<sup>2+</sup> (PNP = Et<sub>2</sub>PCH<sub>2</sub>N(Me)CH<sub>2</sub>PEt<sub>2</sub>). The turnover frequencies, which correspond to the rates of H<sub>2</sub> addition, show the reverse order. These rates correlate with the *number of amines positioned near the metal ion in the second coordination sphere of each complex* (not the total number of



Numbers in green squares indicate the relative energies in kcal/mol

The Figure above shows the proposed mechanism for oxidation of  $\text{H}_2$  by  $[\text{Ni}(\text{dppp})(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bz}}_2)]^{2+}$ . (dppp =  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ ; benzyl groups on the N atoms, and phenyl groups on the P atoms are not shown.)

pendant amines). These comparisons indicate that *two positioned* pendant bases are important for achieving the fast catalytic rates observed for  $[\text{Ni}(\text{P}^{\text{Cy}}_2\text{N}^{\text{Bz}}_2)]^{2+}$  in the oxidation of  $\text{H}_2$ , and for  $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)]^{2+}$  in the production of  $\text{H}_2$ . The role of the two amines positioned in close proximity to the metal serves to stabilize, through hydrogen bonding interactions, both the binding of the dihydrogen ligand on nickel and the heterolytic cleavage of  $\text{H}_2$ .

Nickel catalysts for reduction of oxygen to water were also discovered, again with pendant amines on the ligands facilitating these reactions involving transfers of multiple protons and electrons. No activity for catalytic reduction of oxygen was found for related complexes lacking the proton relay in the ligand.

Our progress on cobalt complexes shows that our approach of using pendant amines in the second coordination sphere of nickel complexes can lead to the development of new classes of catalysts based on other earth-abundant, inexpensive first row metals. Catalytic reduction of protons by  $[\text{Co}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Ph}}_2)(\text{CH}_3\text{CN})_3]^{2+}$  occurs with a turnover frequency of  $90 \text{ s}^{-1}$  for production of  $\text{H}_2$  and essentially 100% current efficiency. This

reaction occurs at the half-wave potential of the Co(II/I) couple ( $-1.00 \text{ V}$  vs.  $\text{Cp}_2\text{Fe}^+/\text{Cp}_2\text{Fe}$ ). The overpotential of this reaction was calculated to be 285 mV, so this cobalt catalyst operates at a fast rate and with a relatively low overpotential. In contrast to the nickel complexes, where two relays were found to be optimal, the cobalt catalysts need only one ligand containing a positioned pendant amine. Much remains to be done in terms of future catalyst development. These discoveries point to new directions that we propose to study in detail, since our knowledge of the mechanistic details of these cobalt complexes is scant compared to the understanding we now have for the nickel complexes.

We recently began a new study of manganese complexes. Manganese is not normally even considered in studies of catalytic oxidation of  $\text{H}_2$  or for production of  $\text{H}_2$ , but we believe that with appropriate ligands, a new class of catalysts could result. We have synthesized a series of Mn complexes of general formula  $[(\text{P}-\text{P})(\text{P}'-\text{P}')(\text{CO})\text{Mn}]^+$  and have studied their binding of  $\text{H}_2$ . The reaction of  $\text{H}_2$  with  $[(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bz}}_2)(\text{dppm})(\text{CO})\text{Mn}]^+$  produces an  $\eta^2\text{-H}_2$  complex. A related complex with electron-withdrawing aromatic groups on the second

diphosphine reacts with H<sub>2</sub> (1 atm) to give *heterolytic cleavage of H<sub>2</sub> at room temperature*, with the H<sup>-</sup> being located on the Mn and the H<sup>+</sup> being transferred to the N.

In proposed future work, we will focus on the design and development of Co, Mn, and Fe complexes; we seek to obtain an understanding of the molecular reactivity that will allow us to design and discover new, robust, highly active catalysts for oxidation and production of H<sub>2</sub>. We propose new studies of how changes in the first and second coordination spheres will alter catalytic activity and the mechanism. New studies on iron complexes are being initiated; iron is a very attractive metal since it is cheap, non-toxic, and the metal used by the biological catalysts that have the highest rates for H<sub>2</sub> production/oxidation. We propose the synthesis of a new series of ligands with enhanced hydrogen bonding capabilities.

### Publications acknowledging DOE Hydrogen Fuel Initiative Funding

1. Jacobsen, G.M.; Yang, J.Y.; Twamley, B.; Wilson, A.D.; Bullock, R.M.; Rakowski DuBois, M.; DuBois, D.L., "Hydrogen production using cobalt-based molecular catalysts containing a proton relay in the second coordination sphere," *Energy Environ. Sci.* **2008**, *1*, 167-174. (invited article)
2. Rakowski DuBois, M.; DuBois, D.L., "The Role of Pendant Bases in Molecular Catalysts for H<sub>2</sub> Oxidation and Production," *Comptes Rendus Chimie* **2008**, *11*, 805-817. (invited review)
3. Wilson, A.D.; Frazee, K.; Twamley, B.; Miller, S.M.; DuBois, D.L.; Rakowski DuBois, M., "The Role of the Second Coordination Sphere of [Ni(P<sup>Cy</sup><sub>2</sub>N<sup>Bz</sup><sub>2</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> in Reversible Carbon Monoxide Binding," *J. Am. Chem. Soc.* **2008**, *130*, 1061-1068.
4. Nimlos, M.R.; Chang, C.H.; Curtis, C.J.; Miedaner, A.; Pilath, H.M.; DuBois, D.L., "Calculated Hydride Donor Abilities of Five-Coordinate Transition Metal Hydrides [HM(diphosphine)<sub>2</sub>]<sup>+</sup> (M = Ni, Pd, Pt) as a Function of the Bite Angle and Twist Angle of Diphosphine Ligands," *Organometallics* **2008**, *27*, 2715-2722.
5. Yang, J.Y.; Bullock, R.M.; Shaw, W.J.; Twamley, B.; Frazee, K.; Rakowski DuBois, M.; DuBois, D.L., "Mechanistic Insights into Catalytic H<sub>2</sub> Oxidation by Ni Complexes Containing a Diphosphine Ligand with a Positioned Amine Base," *J. Am. Chem. Soc.* **2009**, *131*, 5935-5945.
6. Rakowski DuBois, M.; DuBois, D.L., "Development of Molecular Electrocatalysts for CO<sub>2</sub> Reduction and H<sub>2</sub> Production/Oxidation," *Acc. Chem. Res.* **2009**, *42*, 1974-1982 (invited).
7. Rakowski DuBois, M.; DuBois, D.L., "The Roles of the First and Second Coordination Spheres in the Design of Molecular Catalysts for H<sub>2</sub> Production and Oxidation," *Chem. Soc. Rev.* **2009**, *38*, 62-72. (invited review)
8. 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 (invited paper).
9. Rakowski DuBois, M.; DuBois, D.L., "A Modular Approach to the Development of Molecular Electrocatalysts for H<sub>2</sub> Oxidation and Production Based on Inexpensive Metals," In "Catalysis Without Precious Metals:" R.M. Bullock, Ed.; Wiley-VCH, Weinheim, Germany, to be published in 2010.
10. Welch, K.D., Dougherty, W.G., DuBois, D.L., Bullock, R.M. "Synthesis, Structures, and Reactions of Manganese Complexes Containing Diphosphine Ligands With Pendant Amines," *submitted*.