

Bio-Inspired Molecular Catalysts for Oxidation of Hydrogen and Production of Hydrogen: Cheap Metals for Noble Tasks

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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 H₂ 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 H₂ 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⁻) acceptor ability of the metal and the basicity (proton acceptor ability) of the amine appropriately matched so that the heterolytic cleavage of H₂ is close to thermoneutral. The facile reversibility of the heterolytic cleavage of H₂ in the active site of enzymes indicates that those systems have balanced thermodynamics.

Progress Report

The iron complexes CpFe(P^{Ph}₂N^{Bn}₂)Cl, CpFe(P^{Ph}₂N^{Ph}₂)Cl, CpFe(P^{Ph}₂C₅)Cl (where P^{Ph}₂N^{Bn}₂ is 1,5-dibenzyl-1,5-diaza-3,7-diphenyl-3,7-diphosphacyclooctane, P^{Ph}₂N^{Ph}₂ is 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane, and P^{Ph}₂C₅ 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^{Ph}₂N^{Bn}₂)H, CpFe(P^{Ph}₂N^{Ph}₂)H, CpFe(P^{Ph}₂C₅)H and Fe(H₂⁺) complexes [CpFe(P^{Ph}₂N^{Bn}₂)(H₂)]BAR^F₄, (where BAR^F₄ is B[(3,5-(CF₃)₂C₆H₃)₄]), [CpFe(P^{Ph}₂N^{Ph}₂)(H₂)]BAR^F₄, and [CpFe(P^{Ph}₂C₅)

$(\text{H}_2)\text{BAR}_4^{\text{F}}$, and $[\text{CpFe}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)(\text{CO})]\text{BAR}_4^{\text{F}}$. 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 $[\text{CpFe}(\text{P}^{\text{Ph}}_2\text{N}^{\text{Bn}}_2)(\text{CO})]\text{BAR}_4^{\text{F}}$. 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 H_2 and 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 H_2* mediated by the pendant amine. The hydrogenase enzymes have been shown to undergo exchange reactions to produce HD under an H_2/D_2 atmosphere. Computational studies for our synthetic complexes indicate a low barrier for heterolytic cleavage of H_2 . These mononuclear Fe^{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 H_2 cleavage at the active site of $[\text{FeFe}]$ -hydrogenases and synthetic catalysts based on Fe are a ferrous (Fe^{II}) center for binding of 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 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 H_2 and heterolytically cleave H_2 , but they were not electrocatalysts for oxidation of 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 H_2 to the Fe^{II} center. An electron-withdrawing C_6F_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 H_2 under 1 atmosphere H_2 in fluorobenzene solution at 22 °C (Fig. 1).

The proposed mechanism for electrocatalytic oxidation of 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

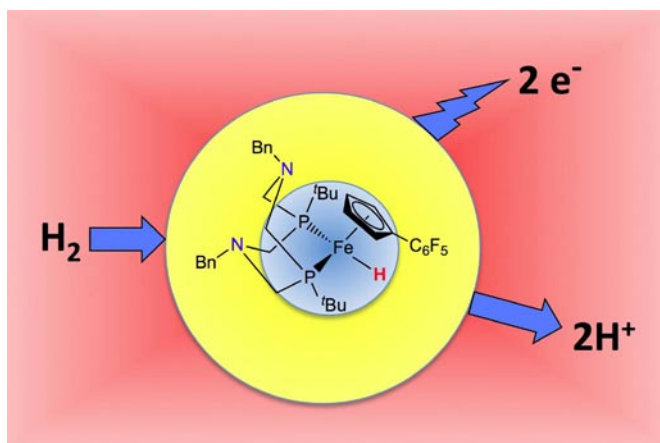


FIGURE 1. Schematic representation of the oxidation of H_2 by $[\text{Cp}^{\text{C}_6\text{F}_5}\text{Fe}(\text{P}^{\text{Bu}}_2\text{N}^{\text{Bn}}_2)\text{H}]$.

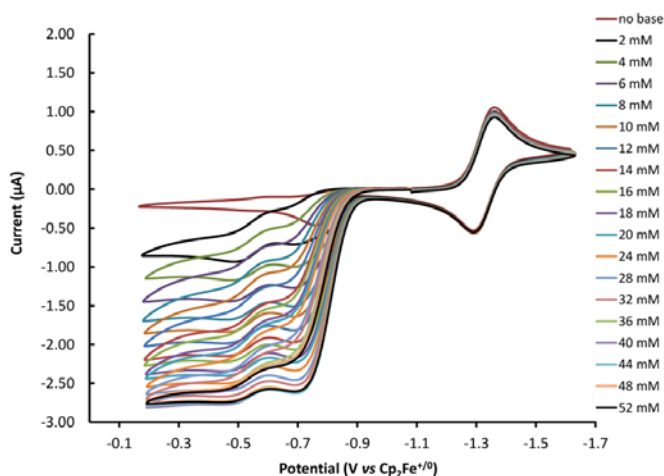


FIGURE 2. Cyclic voltammograms of a fluorobenzene solution of $[\text{Cp}^{\text{C}_6\text{F}_5}\text{Fe}(\text{P}^{\text{Bu}}_2\text{N}^{\text{Bn}}_2)\text{H}]$ (1.0 mM) under 1.0 atm H_2 at 22 °C with increasing concentrations of *N*-methylpyrrolidine, as indicated in the legend. The increase in current at higher concentrations of base indicates that the oxidation of 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.

Molecular Electrocatalysis, an Energy Frontier Research Center, and is focused on increasing the turnover frequency and decreasing the overpotential.

Publications acknowledging DOE-BES Funding (2010-present)

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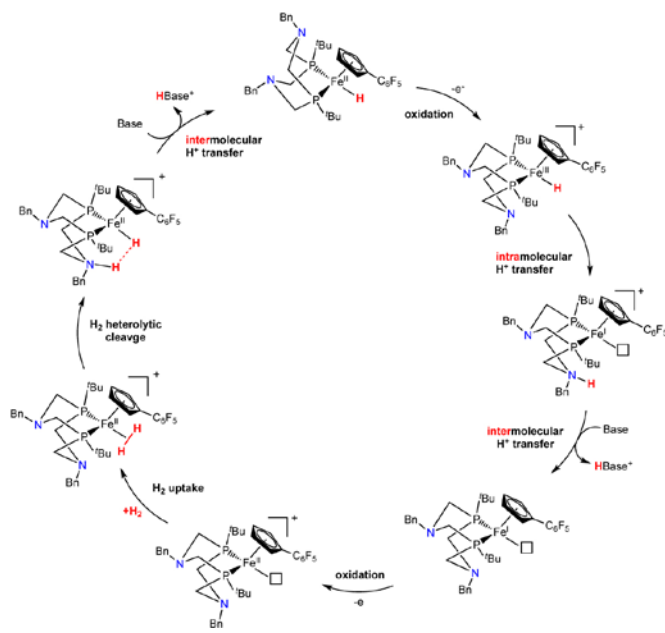


FIGURE 3. Proposed mechanism of electrocatalytic oxidation of H_2 . Oxidation of $\text{Fe}^{\text{II}}\text{-H}$ leads to an increased acidity of the $\text{Fe}^{\text{III}}\text{-H}$ bond. Intramolecular proton transfer from iron to the pendant amine is followed by intermolecular deprotonation of the N-H by the external amine base. Electrochemical oxidation of the iron complex is followed by binding of H_2 , which is heterolytically cleaved, with the hydride being transferred to iron and the proton to the pendant amine. Deprotonation by the external amine base completes the catalytic cycle and regenerates the iron hydride $\text{CpFe}(\text{P}^{\text{Bu}}_2\text{N}^{\text{Bn}}_2)\text{H}$.

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