II.G.16 Artificial Hydrogenases: Utilization of Redox Non-Innocent Ligands in Iron Complexes for Hydrogen Production

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Objectives

The primary barrier to widescale electrocatalytic production of hydrogen from water is development of efficient catalysts for this transformation using only earth abundant transition metals. The objective of this project is to employ chemical principles gleaned from hydrogenases, biological hydrogen production catalysts, to construct fast and efficient hydrogen production catalysts based on iron.

Technical Barriers

Iron-based molecular proton reduction catalysts usually require substantial basicity at the metal site for fast catalysis. However, the price for this basicity is electrochemical overpotential, i.e. high activation energy, for the electrocatalysis. In this project, we have sought to break this link by constructing bio-inspired complexes employing redox non-innocent, chelating and sterically demanding ligands.

Abstract

Here we report the synthesis and characterization of functional models of hydrogenases for electrocatalytic prouduction of hydrogen from weak acids. The complexes employ iron in bio-inspired coordination environments yielding catalysts that are fast and require very little electrochemical overpotential to support turnover.

Progress Report

Electrocatalysis by an Asymmetrically Disubstituted Diiron Complex with a Redox-Active 2,2'-bipyridyl Ligand

Organometallic complexes of the (μ-$S(CH_2)_3S$) $Fe_2(CO)_4L_2$ family of biomimetic models of [FeFe]-hydrogenases are capable of electrocatalytic production of hydrogen from weak acids, but they typically require substantial overpotential to achieve the catalytically competent Fe(I)Fe(0) redox state. This is especially true if L is a strongly donating ligand that enhances the basicity of the coordinated metal.

In this project, we have employed the chelating, strongly electron donating, redox active 2,2'-bipyridyl (bpy) ligand to construct (μ-$S(CH_2)_3S$)$Fe_2(CO)_4(\kappa^2$-bpy) (**1**) as shown in Figure 1. At room termperature in the presence of excess HBF_4-OEt_2, an acetonitrile solution of **1** changes color from green to light brown. As shown in Figure 2, the reaction was monitored by FTIR spectroscopy. Upon addition of acid, three new bands appeared in the ν_{CO} region at 2098, 2044, and 1970 cm^{-1} with concomitant decrease of the bands associated with **1**. The shift of an average of 92 cm^{-1} to higher wavenumbers is consistent with protonation of the Fe-Fe bond to form a bridging hydride. A ^1H NMR resonance associated with hydride formation could also be detected providing further evidence that $[1H]^+$ is a bridging hydride complex.

Cyclic voltammetry was employed to characterize the redox properties of 1 and the impact of the redox non-innocent ligand on electrocatalytic proton reduction. Controlled potential coulometry showed that a reduction observed as -2.06 V vs. Fc^+/Fc is a two-electron process. By analogy to related complexes and since complexes in this family are not usually able to form an Fe(0)Fe(0) state, we hypothesize that one of the reductions occurs at the metal forming an Fe(I)Fe(0) complex and the

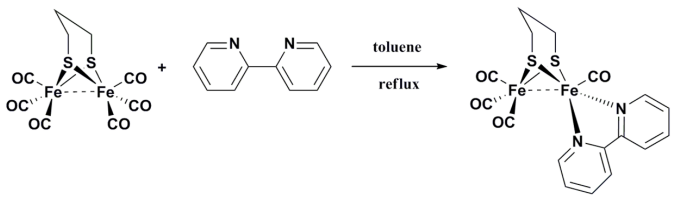

FIGURE 1. Synthetic route to (μ-S(CH2)$_3$S)Fe_2(CO)4(κ^2-bpy).

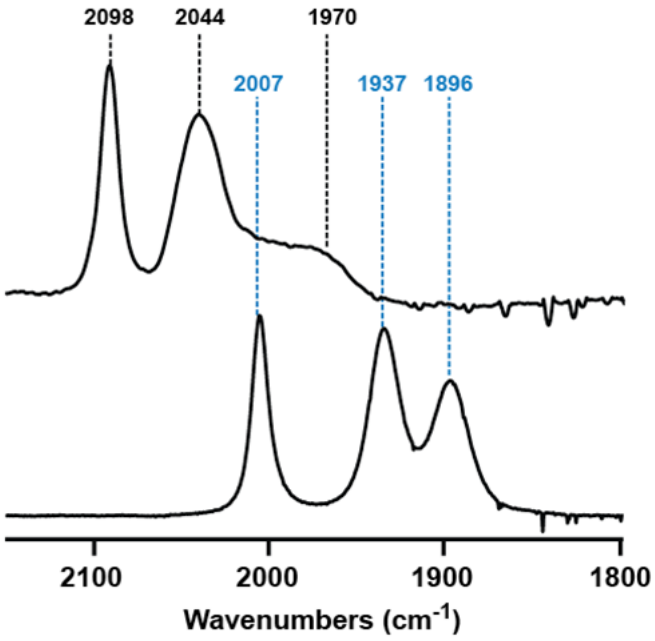

FIGURE 2. FTIR spectra of **1** before (bottom) and after (top) the addition of HBF_4-OEt_2.

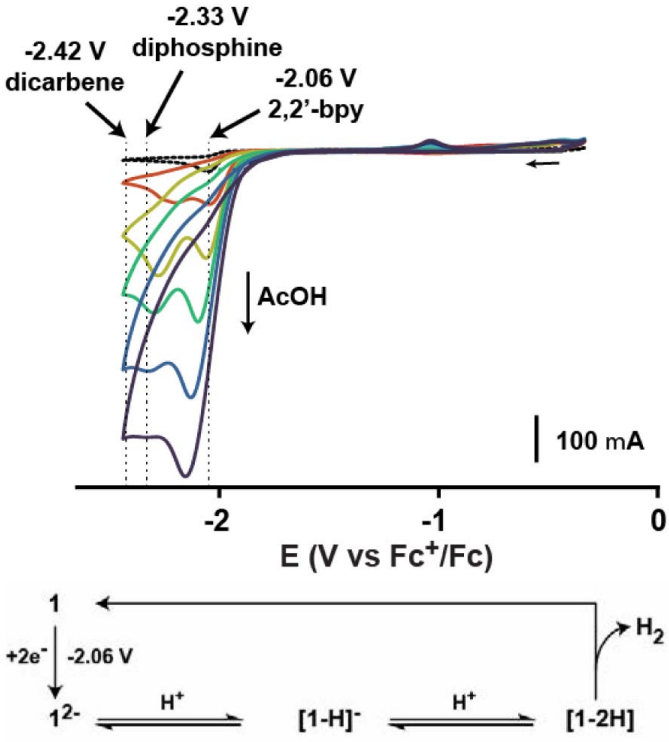

FIGURE 3. Cyclic voltammograms demonstrating electrocatalytic proton reduction by 1 from acetic acid and a hypothetical EECC catalytic scheme that accounts for all data. Dotted lines indicate potentials of electrocatalysis by related complexes with different chelating ligands.

other corresponds to the bpy^0/bpy^{1-} couple. As shown in Figure 3, addition of 1-30 equivalents of the weak acid acetic acid results in a 12-fold enhancement of the reductive current indicating electrocatalytic reduction of protons to hydrogen. The overpotential of this process, defined as the difference between the standard potential for reduction of the acid and the half-wave potential for catalytic proton reduction, was 0.68 V. On the basis of these and other electrochemical results, an EECC mechanism such as that depicted in Figure 3 is thought to be operational. Perhaps most importantly, although this mechanism is not unusual for diiron carbonyl complexes, the low overpotential of the catalysis is. Ordinarily, there is a strong correlation between the CO stretching frequency and the potential of catalysis. For **1**, this connection has been partially broken, and, compared to complexes with similar CO stretching frequencies, catalysis is observed at a less reducing potential. This unexpectedly mild overpotential may be a result of the redox non-innocence of the chelating bpy ligand.

Catalytic Hydrogen Evolution by Fe(II) Carbonyls Featuring a Redox Non-innocent Dithiolate and Chelating Phosphine

Figure 4 shows the synthetic route to two new pentacoordinate Fe(II) complexes: (κ^2-dppf)Fe(CO)(κ^2-bdt) (**2**) and (κ^2-NP_2)Fe(CO)(κ^2-bdt) (**3**) where dppf is 1,1'-bis(diphenylphosphino)ferrocene, bdt is benzene-1,2-dithiol, and NP_2 is methyl-2-{bis(diphenylphosphinomethyl) amino}-acetate. The bdt ligand was employed both for its strong donating propensity and its redox non-innocence. The dppf and NP_2 ligands are both chelating phosphines, but dppf has an extraordinarily large bite angle and comparatively little flexibility. The structures of **2** and **3** were determined by single-crystal X-ray diffraction. Suprisingly, **2** features a trigonal bipyramidal geometry with phosphorous and sulfur in the apical positions. On the other hand, **3** is in a distorted square pyramidal geometry with an axial CO ligand. Importantly, in both structures, the C-C bond lengths of the bdt show an alternating pattern of two shorter C-C bonds and four longer ones. Similarly, the two C-S bonds are not equivalent. This suggests that the C-S bond orders are greater than one and the bdt possesses substantial 1,2-dithiobenzosemiquinonate, π-radical character. The structural results could also be confirmed via DFT calculations of the electronic structure of the complexes.

To establish whether the open coordation site of complexes **2** and **3** is available for external ligand binding, the reactions of **2** and **3** with CO were studied. Although coordinatively unsaturated, both complexes display only weak, reversible binding of CO (data not shown). However, ligand centered protonation of **2** by HBF_4-OEt_2 triggers

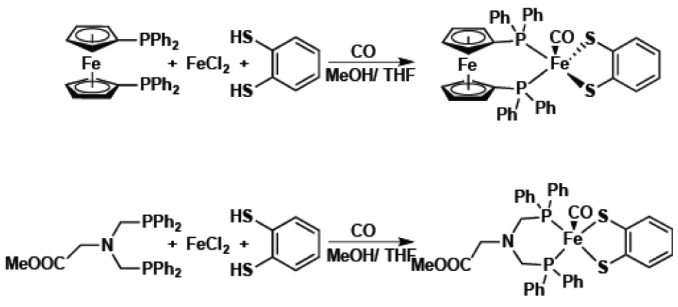

FIGURE 4. Synthetic route to Fe(II) carbonyl complexes.

quantitative, reversible uptake of CO. This reactivity is very similar to that observed for [FeFe]-hydrogenases. DFT calculations suggest that ligand protonation disrupts the extensive electronic delocalization between the Fe and bdt of **2** making it more susceptible to ligand uptake.

As shown in Figure 5, electrochemical investigation shows that both complexes catalyze electocatalytic proton reduction from acetic acid at mild overpotentials, 0.17 and 0.38 V for **2** and **3**, respectively. The unusually low overpotential for catalysis by **2** is likely a result of the geometric strain imposed by dppf and the stabilization of significant electron density at the iron site by the redox non-innocence of bdt.

Future Directions

Future research will investigate the impact of redox non-innocent ligands on proton reduction catalysts employing other first row transition metals including nickel. Decreasing the overpotential to even more energetically favorable values will be attempted by tuning the electron donating propensities of the ligands.

Publication list

1. Jones, Anne K.; McIntosh, Chelsea L.; Dutta, Arnab; Kwan, Patrick; Roy, Souvik; Yang, Sijie. Bioelectrocatalysis of hydrogen oxidation/production by hydrogenases, In *Enzymatic Fuel Cells: From Fundamentals to Applications*. Edited by H. Luckarift, G Johnson, and P. Attanasov, Wiley-VCH, Weinheim, Germany, **2014**.

2. Roy, Souvik; Groy, Thomas; Jones, Anne K. Biomimetic model for [FeFe]-hydrogenase: Asummetrically disubstituted diiron complex with a redox-active 2,2'-bipyridyl ligand. *Dalton Trans.* **2013**, *42*.

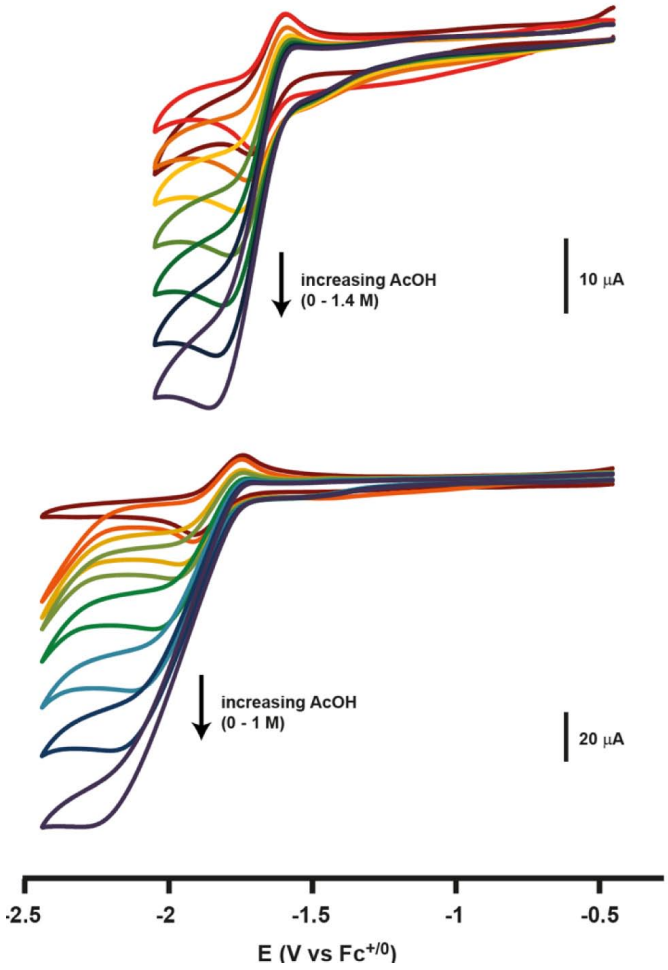

FIGURE 5. Cyclic voltammograms demonstrating proton reduction electrocatalysis by **2** (top) and **3** (bottom).

3. Dutta, Arnab; Flores, Marco; Roy, Souvik; Schmitt, Jennifer; Hamilton, George A.; Hartnett, Hilairy E.; Shearer, Jason; Jones, Anne K. Sequential Oxidation of Thiolates and the Cobalt Metallocenter in a Synthetic Metallopeptide: Implications for the Biosynthesis of Nitrile Hydratase, *Inorg. Chem.*, **2013**, *52*.

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