Hydrogen Catalysis

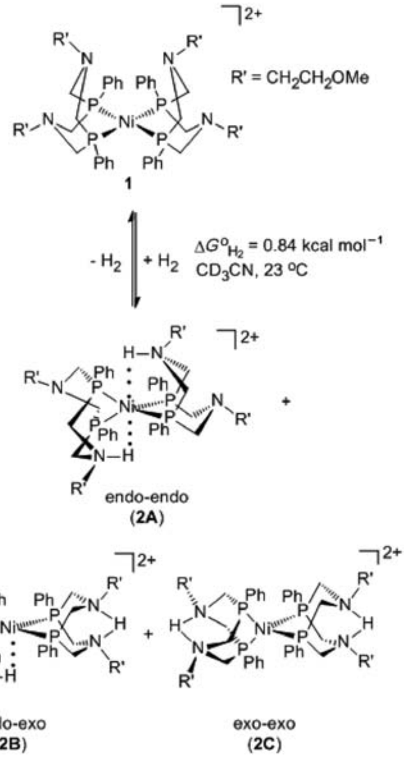
DOI: 10.1002/ange.201108461

Reversible Electrocatalytic Production and Oxidation of Hydrogen at Low Overpotentials by a Functional Hydrogenase Mimic**

Stuart E. Smith, Jenny Y. Yang, Daniel L. DuBois, and R. Morris Bullock**

Interest in the use of hydrogen for energy storage, transportation fuel, and as a reductant to generate other chemical fuels has grown rapidly in recent years.[1,2] This has led to the investigation of new catalysts composed of abundant and inexpensive metals that can produce and use hydrogen efficiently. In nature, hydrogen is also used as a fuel and is an important source of energy in the microbial world.[3] Hydrogen metabolism in nature is mediated by hydrogenase enzymes, which operate at ambient conditions and pressures, using the abundant metals nickel and iron in their active sites.[4] One of the hallmarks of these enzymes is their ability to reversibly catalyze the oxidation of hydrogen to protons and electrons with high efficiency.[5] This capability indicates that addition and release of hydrogen is nearly thermoneutral and kinetically accessible.

Previous studies in our laboratory have focused on the synthesis and catalytic performance of functional hydrogenase mimics.[6] Our studies have focused on iron,[7] cobalt,[8] and nickel[9] complexes with the diphosphine ligand $P^{R}_{2}N^{R'}_{2}$ shown in Scheme 1, where R is the substituent on phosphorous, and R′ is the substituent on nitrogen. From our experimental and theoretical[10] studies on $[Ni(P^{R}_{2}N^{R'}_{2})_2]^{2+}$ derivatives, we have established how steric and electronic properties of the R and R′ substituents affect the hydride acceptor and proton acceptor abilities of these complexes. These two quantities determine the free-energy of hydrogen addition to these complexes. The ability to vary these properties by varying substituents on the ligand has led to the design of catalysts that are biased towards hydrogen production[9] or hydrogen oxidation[11] by adjusting the free-energy for hydrogen addition to be either positive or negative, respectively.



Scheme 1. Reaction of complex **1** with hydrogen (1 atm) in [D$_3$]acetonitrile at 23 °C.

We present here the complex $[Ni(P^{Ph}_{2}N^{R'}_{2})_2](BF_4)_2$, **1**, ($R' = CH_2CH_2OCH_3$) the hydrogen addition product of which is nearly isoenergetic with the starting materials, **1** and free H_2 (Scheme 1).

Additionally, this catalyst displays reversible electrocatalytic hydrogen oxidation and production activity with high efficiency. Previously, only one synthetic molecular hydrogen production catalyst has been shown to also oxidize hydrogen, although the reaction was slow and this reaction was not shown to be catalytic.[12] An electrode modified by physisorption of a molecular catalyst was shown to perform reversible hydrogen catalysis.[13] However, this is the first example of electrocatalysis which comprises reversible hydrogen oxidation and production and is shown by a nonenzymatic complex under homogeneous conditions.

The $P^{Ph}_{2}N^{R'}_{2}$ ligand was synthesized by the condensation of phenylphosphine, paraformaldehyde, and 2-methoxyethylamine, in a procedure similar to those reported previously for related cyclic ligands.[14] Reaction of the unpurified ligand with 0.5 equivalents of $[Ni(CH_3CN)_6](BF_4)_2$ resulted in the

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[*] Dr. S. E. Smith, Dr. J. Y. Yang,[+] Dr. D. L. DuBois, Dr. R. M. Bullock
Center for Molecular Electrocatalysis
Pacific Northwest National Laboratory
P.O. Box 999, K2-57, Richland, WA 99352 (USA)
E-mail: morris.bullock@pnnl.gov
Homepage: http://efrc.pnnl.gov/

[+] Current address:
Joint Center for Artificial Photosynthesis
California Institute of Technology, Pasadena, CA 91125 (USA)
E-mail: jyy@caltech.edu

[**] This research was supported as part of the Center for Molecular Electrocatalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. Pacific Northwest National Laboratory is operated by Battelle for the U. S. Department of Energy.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201108461.

formation of a crude sample of **1**. Addition of hydrogen and 2.1 equivalents of the base *N,N,N′,N′*-tetramethylguanidine led to the selective precipitation of the pure Ni^0 complex $Ni(P^{Ph}{}_2N^{R'}{}_2)_2$ ($R' = CH_2CH_2OCH_3$), **2**, from the acetonitrile solution. Complex **2** was oxidized with two equivalents of $Cp_2Fe^+BF_4^-$ to afford analytically pure samples of **1**. These complexes have been characterized by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis, as detailed in the Supporting Information. All data are consistent with their formulations.

The Ni^{II} complex **1** reacts cleanly with H_2 (1 atm) to form an equilibrium mixture of Ni^0 complexes with two protonated amines, isomers **2A**, **2B**, and **2C**, in a ratio of 0.8:1.0:0.1, respectively (Scheme 1). The isomeric products differ in the orientation of the N–H bonds. Isomer **2A**, in which the protons are both in the endo position with respect to the metal center, is the initial product of H_2 addition, but intermolecular proton exchange at room temperature leads to the formation of additional isomers in which one or both protons are in the exo position with respect to the metal and interact with both nitrogen atoms of the ligand (isomers **2B** and **2C**). Characterization of the three isomers has previously been described in detail for related systems.[15] Integration of the ^1H NMR resonances for complex **1** and the sum of the products **2A**, **2B**, and **2C** yields an equilibrium constant of 0.24(2) atm^{-1} at 23 °C and 1 atm H_2, corresponding to $\Delta G° = 0.84\ kcal\,mol^{-1}$ for hydrogen addition. Integration of the $^{31}P\{^1H\}$ spectrum yields a similar value, but because of the broadness of the peaks, the value obtained from the ^1H NMR integration is considered more accurate. In performing this study, we have observed an inverse equilibrium isotope effect for this reaction. Detailed experimental and theoretical studies on this effect will be reported in a future publication.

The cyclic voltammogram of **1** in acetonitrile under N_2, shown as the black trace in Figure 1, displays two reversible one-electron reduction waves at −0.94 V and −1.25 V versus $Cp_2Fe^{+/0}$, and these are assigned to the $Ni^{II/I}$ and $Ni^{I/0}$ couples ($\Delta E_p = 63$ mV and 66 mV, respectively, at a scan rate of 50 $mV\,s^{-1}$). The blue trace in Figure 1 shows the cyclic voltammogram of **1** in acetonitrile with 5.9 mM 4-cyanoanilinium tetrafluoroborate. Addition of acid results in an observed increase in the cathodic current at −0.55 V attributed to catalytic proton reduction to produce hydrogen. The rise and plateau shape of the current is indicative of catalytic activity. Higher concentrations of acid did not result in any further increase in current. Based on the modest current enhancement, the turnover frequency is less than 0.5 s^{-1}.[16] The catalytic activity and H_2 product was confirmed by controlled-potential coulometry followed by gas chromatographic analysis of the head space to measure the hydrogen produced; the current efficiency was determined to be (101 ± 5) %.

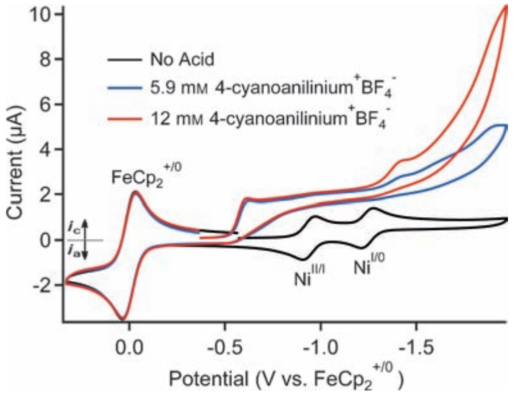
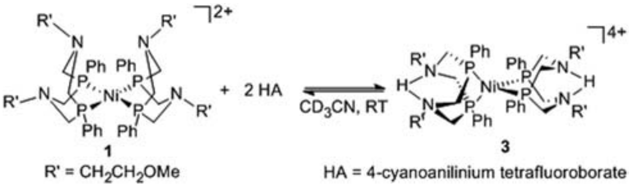


Figure 1. Cyclic voltammograms of a 0.8 mM solution of complex **1** with no acid (black), and in 5.9 mM (blue), and 12 mM (red) 4-cyanoanilinium tetrafluoroborate. Conditions: scan rate, 50 $mV\,s^{-1}$, 0.20 M NEt_4BF_4 in acetonitrile solvent, glassy carbon working electrode. Potentials are referenced to the $Cp_2Fe^{+/0}$ couple, shown at 0.0 V.

The onset potential for catalytic reduction in the acidic solution is shifted about 360 mV positive of the $Ni^{II/I}$ couple observed in the absence of acid. Under catalytic conditions (in the presence of the acid 4-cyanoanilinium tetraflurorоborate, $pK_a = 7.0$ in CH_3CN)[17] the Ni^{II} complex **1** is doubly protonated to form **3**, as shown in Scheme 2. Both ^1H and $^{31}P\{^1H\}$ NMR studies on complex **1** in the presence of acid confirm that double protonation occurs in the "exo" positions, with each proton shared between the pendant amines of their respective ligands (see the Supporting Information). A similar structure has been previously characterized for the protonation of a related Ni^{II} complex.[18] Complex **3** has been characterized by both ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (see the Supporting Information). Addition of less than two equivalents of acid leads to the doubly protonated complex **3** and unprotonated complex **1**; the singly protonated complex is not observed. The pK_a of complex **3** in CH_3CN was determined relative to 4-cyanoanilinium. ^1H NMR spectroscopy was used to determine the ratio of 4-cyanoanilinium and 4-cyanoaniline, and integration of the $^{31}P\{^1H\}$ NMR spectra was used to determine the ratio of **3** to **1**. The two ratios were used to determine an average pK_a value of 7.3 in CH_3CN for the two sequential deprotonations of **3**.



Scheme 2. Complex **1** is protonated in the exo position on each ligand upon addition of 4-cyanoanilinium tetrafluoroborate.

Formation of **3** under acidic conditions results in a positive shift of 360 mV for the onset of the catalytic current for proton reduction. Positive shifts of up to 440 mV have been observed for related $[Ni(P^R{}_2N^{R'}{}_2H)_2]^{4+}$ complexes compared to their unprotonated analogs.[18] The observed potential is dependent on the pK_a of the solution, indicating a proton-coupled electron transfer. This large positive shift corresponds to a lower overpotential for proton reduction. The overpotential for this catalyst is 140[19] or 68 mV,[20] depending on the literature value used for the standard potential for proton reduction in the calculation for the thermodynamic potential.

The low free-energy for hydrogen addition and the small overpotential for catalytic hydrogen production indicate the possibility for reversible electrocatalytic hydrogen production and oxidation. The cyclic voltammograms shown in Figure 2 were performed in a buffered solution. In nitrogen (green trace), catalytic proton reduction is observed at potentials negative of −0.55 V. When the same solution is sparged with H_2 (red trace), an oxidation current is observed, indicating oxidation of H_2. Additionally, the reductive current is decreased because of product (H_2) inhibition. Sparging the solution with nitrogen gives a cyclic voltammogram similar to the initial recorded voltammogram (blue trace). The dotted black line in Figure 2 indicates the thermodynamic reduction potential of the H^+/H_2 couple expected under these conditions, using the thermodynamic proton reduction potential determined by the group of DuBois[19a] and by Artero and coworkers[19b] (−0.48 mV at pH 7 versus the ferrocenium/ferrocene couple at 25 °C and 1 atm H_2). The current for proton reduction is greater than for hydrogen oxidation, indicating the catalytic bias towards proton reduction. This is consistent with the small positive free-energy for hydrogen addition.

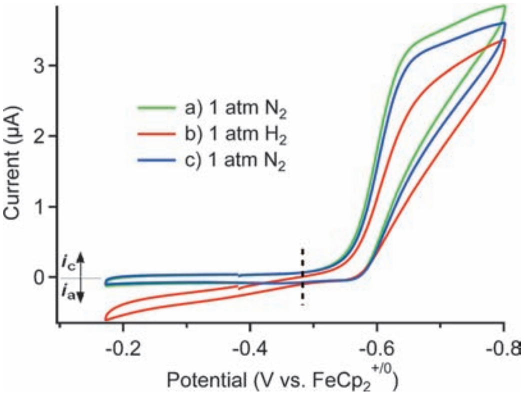


Figure 2. Cyclic voltammograms of a 1.3 mM solution of **1** in 7.8 mM 4-cyanoanilinium tetrafluroroborate and 7.3 mM 4-cyanoaniline in acetonitrile at 1 atm of N_2 (green), 1 atm of H_2 (red), and re-exposure to 1 atm of N_2 (blue). The dotted line indicates the formal reduction potential of the H^+/H_2 couple expected under these conditions[19] (−0.48 V at pH 7, 25 °C, 1 atm H_2). Conditions: scan rate, 50 mV s^{-1}, 0.20 M NEt_4BF_4 in acetonitrile solvent, glassy carbon working electrode. Potentials are referenced to the $Cp_2Fe^{+/0}$ couple.

Catalytic activity for hydrogen oxidation was confirmed by chemical oxidation because the slow rate of reaction makes bulk electrolysis difficult to perform in a timely manner. An excess of 2,6-lutidine and $Cp_2Fe^+BF_4^-$ was added to a solution of **1** in CH_3CN, and D_2 was sparged through the solution. C_6D_6 was used as an internal standard to measure the amount of conjugate acid generated, giving eight turnovers after five minutes. A control reaction showed that the D_2 oxidation did not occur from the $Cp_2Fe^+BF_4^-$.

In summary, the new nickel complex reported here, $[Ni(P^{Ph}{}_2N^{R'}{}_2)_2]^{2+}$ ($R' = CH_2CH_2OCH_3$, **1**) possesses a low $\Delta G°$ for H_2 addition, and an equilibrium mixture with H_2 is readily observed by NMR spectroscopy. Furthermore, the complex electrocatalytically produces and oxidizes hydrogen close to the thermodynamic potential. This is the first example of a synthetic homogeneous electrocatalyst capable of performing this task, which is otherwise most commonly observed in the hydrogenase enzymes.

Received: December 1, 2011

Keywords: catalysis · electrochemistry · homogeneous catalysis · hydrogen · hydrogenase enzymes

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