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Christina M. Klug, Allan Cardenas, R. Morris Bullock, Molly O'Hagan, and Eric S. Wiedner ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.7b04379 • Publication Date (Web): 07 Mar 2018 Downloaded from http://pubs.acs.org on March 7, 2018

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## Reversing the Tradeoff Between Rate and Overpotential in Molecular Electrocatalysts for H<sub>2</sub> Production

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**ABSTRACT:** A long-standing challenge in molecular electrocatalysis is to design catalysts that break away from the tradeoff between rate and overpotential arising from electronic scaling relationships. Here we report an inversion of the rate-overpotential correlation through system-level design of  $[Ni(P^R_2N^{R'}_2)_2]^{2+}$  electrocatalysts for the production of H<sub>2</sub>. The overpotential is lowered by an electron-withdrawing ligand, while the turnover frequency is increased by controlling the catalyst structural dynamics, using both ligand design and solvent viscosity. The cumulative effect of controlling each of these system components is an electrocatalyst with a turnover frequency of 70,000 s<sup>-1</sup> and an overpotential of 230 mV, corresponding to a 100-fold rate enhancement and a 170 mV reduction in overpotential compared to the parent nickel catalyst. Molecular Tafel plot analysis reveals that the new catalysts reported here are substantially more efficient than other leading molecular electrocatalysts for production of H<sub>2</sub>.

Keywords: electrocatalysis, hydrogen, scaling relation, overpotential, nickel, proton relay, viscosity

#### Introduction

There is a growing need for electrocatalysts that efficiently interconvert electrical and chemical energy due to the expanded use of solar and wind energy.1-2 A key measure of efficiency for an electrocatalytic reaction is the overpotential, defined as the additional potential beyond the thermodynamic potential needed to drive a reaction at a certain rate. Balancing the tradeoff between increasing the reaction rate (or current density) and decreasing the overpotential (wasted electrical energy) is a pervasive challenge in the search for improved electrocatalysts. In heterogeneous electrocatalysis, scaling relationships between the catalytic rate and the binding energies of catalytic intermediates have emerged as an effective tool for understanding catalytic activity and predicting new catalyst materials.3-5 Scaling relationships can also be transformative in guiding the design of molecular electrocatalysts. In this study, we demonstrate that the rate-overpotential correlation of a molecular electrocatalyst can be shattered if the chemistry that governs its scaling relationships is well understood, and therefore controllable.

Scaling relationships are manifested differently in heterogeneous and molecular electrocatalysis due to differences in how their catalytic activity is measured and reported. Heterogeneous electrocatalysts show an exponential increase in current at higher overpotential according to the Tafel equation, and different catalysts are often compared at either a defined overpotential or current density.<sup>6</sup> Molecular electrocatalysis is initiated by a discrete redox event of the catalyst. For an ideal catalyst, the catalytic current increases over a narrow potential range before reaching a constant value due to steady-state catalytic turnover. The potential-independent turnover frequency (TOF) of a molecular catalyst is determined by the rate-limiting chemical steps of catalysis,<sup>7-8</sup> while the overpotential is frequently reported at the catalytic half-wave potential,  $E_{cat/2}$ , which is a well-defined point in the voltammogram.<sup>9-12</sup> Free-energy correlations between TOF and overpotential are ubiquitous in molecular electrocatalysis, such that catalysts with a larger TOF also display a higher overpotential. This correlation has been observed in molecular electrocatalysts for H<sup>+</sup> reduction,<sup>13-16</sup> CO<sub>2</sub> reduction,<sup>17-19</sup> and O<sub>2</sub> reduction.<sup>20-21</sup>

Electronic scaling relationships lie at the root of this tradeoff between rate and overpotential. Multiple studies have demonstrated that the reduction potential of a catalyst is correlated to the thermodynamics of substrate binding and activation.<sup>20, 22-26</sup> As a result, lowering the overpotential by changing the electronics of the catalyst also leads to a decrease in the TOF. The pervasiveness of electronic scaling relationships presents an obstacle to designing molecular electrocatalysts that display a high TOF and a low overpotential. Catalysts that break away from the rateoverpotential correlation are fairly limited and, similar to enzymes, often contain functional groups in the second coordination sphere to lower the activation barrier for substrate binding to the metal center. Pendant proton relays,<sup>27</sup> hydrogen bonding groups,<sup>28</sup> electrostatic groups,<sup>18</sup> and bimetallic catalysts<sup>29</sup> have all been used to move away from

the TOF-overpotential correlation. Alternatively, the rateoverpotential correlation of a catalyst can be changed by controlling the reaction medium, such as careful selection of the organic acid<sup>30</sup> or addition of water to an organic solvent.<sup>31</sup>

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In designing new catalysts, it is recognized that the relationship between TOF and overpotential can be governed by complex factors. For the well-known  $[Ni(P_2^R N_2^{R'})_2]^{2+}$  electrocatalysts for production of H<sub>2</sub>, the mechanism of catalysis has several branching points arising from multiple protonation sites, as well as competing sequences of proton and electron transfer.<sup>32-34</sup> Recently, we demonstrated that incorporation of long alkyl chains onto the pendant amines of  $[Ni(P_2^R N_2^{R'})_2]^{2+}$  complexes increases the TOF by three orders of magnitude with only a minimal increase in overpotential (70 mV).35 This dramatic rate enhancement results from slowing the formation of inactive "exo-pinch" isomers that arise from exo-protonation at a single pendant amine, followed by chair-boat isomerization of the ligand arms (Scheme 1). Incorporation of the alkyl chains slows the chair-boat ring flip that is necessary to form the thermodynamically and kinetically stabilized exo-pinch isomer. Importantly, this result demonstrated that the correlation between rate and overpotential of  $[Ni(P_{2}^{R}N_{2}^{R'})_{2}]^{2+}$  complexes could be broken by modifying the outer coordination sphere of the catalyst.

Scheme 1. One of the branching points in the catalyst cycle.<sup>*a*</sup>



<sup>*a*</sup> Each protonation step is a branch point leading to either an active endo or an inactive exo pathway. The first protonation step, protonation of Ni(I) (not shown), can also occur at the exo site, resulting in additional branching that leads to a doubly exo-pinched species.

Despite the tremendous gains in TOF, the  $[Ni(PR_2NR'_2)_2]^{2+}$  catalysts continue to suffer from large overpotentials (> 400 mV). In this paper, we demonstrate that the overpotential of  $[Ni(PR_2NR'_2)_2]^{2+}$  catalysts can be lowered while maintaining high TOF's for H<sub>2</sub> production. We combine electron-withdrawing ligands and controlled ligand dynamics, achieved with long-alkyl chains on the pendant amines and viscous dinitrile solvents. By controlling

all of these system components, we can simultaneously lower the overpotential by ~200 mV and increase the TOF by two orders of magnitude, relative to the parent catalyst. This change in performance is an *inversion* of the typical rate-overpotential correlation. This accomplishment results from a detailed mechanistic understanding leading to precise control over the structure and function of the catalyst. Analysis of the electronic scaling relationships of these catalysts demonstrates the need for a system-level approach to catalyst design, where the catalytic properties are controlled all the way from the first coordination sphere of the catalyst to the bulk properties of the reaction medium.

#### **Results and Discussion**

Synthesis and Characterization. Complexes 1, 1-C6, and 1-C14 are  $[Ni(P_2^R N_2^{R'})_2]^{2+}$  complexes containing a phenyl group on the phosphorus ligand and have been previously reported.<sup>35-36</sup> The two new complexes, 2 and 2-C14, contain electron-withdrawing CF<sub>3</sub> groups in the para position of the phenyl groups on the phosphorus atoms (Chart 1). Synthesis of complexes 2 and 2-C14 started with the preparation of diethyl (4-(trifluoromethyl)phenyl)phosphonate using a copper-catalyzed variant of the Michaelis-Arbuzov reaction.37 The phosphonate was converted into the new  $P^{R}_{\ _{2}}N^{R'}_{\ _{2}}$  ligands using standard methods,  $^{15,\ 38}$  and subsequent metalation with  $[Ni(CH_3CN)_6](BF_4)_2$  afforded 2 and 2-C14. A cyclic voltammogram of 2 displays two fully reversible one-electron couples at -0.74 and -0.85 V versus Cp<sub>2</sub>Fe<sup>+/o</sup>, assigned to the Ni(II/I) and Ni(I/o) oxidation states. The electron-withdrawing CF<sub>3</sub>-groups of 2 shift the Ni(II/I) and Ni(I/o) couples more positive than 1 by 70 mV and 200 mV, respectively. The Ni(II/I) and Ni(I/o) couples of 2-C14 are observed at -0.75 and -0.86 V, indicating the alkyl chain on the pendant amine has only a minor effect on the electronics of nickel.

# Chart 1. Structures of the nickel complexes used in this study.



Effect of Solvent Viscosity on Structural Dynamics. To examine the impact of solution viscosity on the structural dynamics, we measured the boat-chair isomerization rate of **1-C6** in mixed solvent systems containing either acetonitrile or butyronitrile and a second, more viscous, solvent or analyte. The nickel(II) complexes reversibly bind acetonitrile to afford a trigonal bipyramidal complex with two inequivalent phosphorus

environments, which interconvert through dissociation of the acetonitrile ligand, chair-boat isomerization of the pendant amines, and re-coordination of acetonitrile.<sup>39</sup> The rate constant for this isomerization process was measured for **1-C6** in the different solvent mixtures by lineshape analysis of variable temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectra as previously described.<sup>39</sup> The microviscosity<sup>40-41</sup> of each solvent system was determined from the inverse of the translational diffusion coefficient (1/*D*) of **1-C6**, as measured by <sup>1</sup>H-DOSY NMR spectroscopy. Notably, the rate of boat-chair isomerization of **1-C6** decreased as the microviscosity of the solution was increased (Figure 1), thereby confirming that solvent can be used to control the structural dynamics of the catalyst.



**Figure 1.** Plot of the chair-boat isomerization rate (298 K) of **1-C6** versus the microviscosity for different solvent mixtures. In order of increasing microviscosity, the solvents are 20% (v/v) CD<sub>3</sub>CN in CD<sub>2</sub>Cl<sub>2</sub>,<sup>35</sup> 190 mM tetrabutylammonium tetrakis(pentafluorophenyl)borate in CH<sub>3</sub>CN, 50:45:5% (v/v) butryonitrile:dibutylformamidium bis(trifluoromethanesulfonyl)imide:H<sub>2</sub>O,<sup>35</sup> 20% (v/v) CD<sub>3</sub>CN in 2-propanol,<sup>35</sup> and 20% (v/v) butyronitrile in 2,6-dimethyl-4-heptanol.

Electrocatalytic Measurements. Electrocatalytic experiments were performed in organic solvent with 0.2-1.3 M H<sub>2</sub>O and the organic acid *N*,*N*-dimethylformamidium triflate, [DMF(H)][OTf]. The addition of water has been previously shown to enhance the catalytic rate by decreasing the steric penalty of protonation and deprotonation.<sup>42-43</sup> Classical "S-shaped" catalytic waves were observed using scan rates (u) of 0.2-2.0 V s<sup>-1</sup> and low catalyst concentrations of 10-70  $\mu$ M (Figure 2a). Appearance of this "S-shaped" wave indicates that catalysis is occurring under steady-state conditions in the electrochemical diffusion layer. The catalytic turnover frequency, TOF, was measured using equation 1, where *D* is the diffusion coefficient

$$\text{TOF} = \frac{1}{D} \left( \frac{i_{\text{cat}}}{2FA[\text{Cat}]_T} \right)^2 \tag{1}$$

of the catalyst,  $i_{cat}$  is the potential-independent catalytic current, *F* is Faraday's constant, *A* is the geometric surface area of the electrode, and  $[Cat]_T$  is the total concentration

of the catalyst in solution.<sup>44</sup> As typical for  $[Ni(P_2NF_2)_2]^{2+}$  electrocatalysts, each catalyst displayed an initial dependence of the TOF on the concentration of both [DMF(H)][OTf] and water, and became independent of [DMF(H)][OTf] and water at higher concentrations (Figure 2b-2c). Therefore the maximum turnover frequency,  $TOF_{max}$ , is defined at the acid and water concentration that results in the highest TOF for each catalyst (Figure 2c). The TOF<sub>max</sub> values for each catalyst, as well as other catalytic data, are given in Table 1.

a)



**Figure 2.** a) Cyclic voltamograms of 10  $\mu$ M **1-C14** in hexanedinitrile (0.2 M [Bu<sub>4</sub>N][BF<sub>4</sub>]) with increasing concentrations of [DMF(H)][OTf], followed by increasing concentration of H<sub>2</sub>O. b) Plot of TOF of **1-C14** versus concentration of [DMF(H)][OTf]. c) Plot of TOF of **1-C14** versus concentration of H<sub>2</sub>O. The dashed line indicates the maximum turnover frequency, TOF<sub>max</sub>.

Butanedinitrile (succinonitrile) and hexanedinitrile (adiponitrile) were used as the solvent in electrocatalytic studies to increase the solution viscosity relative to acetonitrile without substantially changing the other bulk properties.<sup>45</sup> Butanedinitrile is a solid at room temperature and was Table 1. Turnover frequencies and overpotentials for  $H_2$  production by  $[Ni(P_2^R N_2^{R'})_2]^{2+}$  catalysts.

Catalyst	Solvent <sup>a</sup>	Microviscosity, 1/D (×10 <sup>9</sup> s m <sup>-2</sup> )	TOF <sub>max</sub> (s <sup>-1</sup> )	E°' <sub>BH+/H2</sub> (V vs Fc <sup>+/o</sup> ) <sup>b</sup>	$E_{\text{cat/2}}$ (V vs Fc <sup>+/o</sup> )	η at E <sub>cat/2</sub> (mV)
1	acetonitrile <sup>c</sup>	1.0	720	-0.43 <sup>d</sup>	-0.83	400
1-C6	acetonitrile <sup>e</sup>	1.3	740	-0.43 <sup>d</sup>	-0.79	360
1-C14	acetonitrile <sup>f</sup>	1.6	98,000	-0.43 <sup>d</sup>	-0.83	400
2	acetonitrile	o.8	160	-0.43 <sup>d</sup>	-0.74	310
2-C14	acetonitrile	1.7	11,000	-0.43 <sup>d</sup>	-0.69	260
1-C6	80% butanedinitrile	12.5	7,700	-0.39	-0.69	300
1-C14	80% butanedinitrile	13.3	400,000	-0.39	-0.72	330
1-C6	hexanedinitrile	26.3	4,800	-0.49	-0.77	280
1-C14	hexanedinitrile	30.3	1,500,000	-0.49	-0.79	300
2-C14	hexanedinitrile	25.6	70,000	-0.49	-0.72	230

<sup>*a*</sup> Conditions: 0.2 M [Bu<sub>4</sub>N][BF<sub>4</sub>], 0.2-0.6 M [DMF(H)][OTf], 0.2-1.3 M H<sub>2</sub>O, 298 K. <sup>*b*</sup> Open-circuit potential of 1:1 DMF:[DMF(H)]OTf with 0.2-1.3 M H<sub>2</sub>O and 1 atm H<sub>2</sub>. <sup>*c*</sup> Reference 31. <sup>*d*</sup> Reference 46. <sup>*e*</sup> Reference 47. <sup>*f*</sup> Reference 35.

used as a mixed acetonitrile/butanedinitrile solvent system. Hexanedinitrile is a liquid at room temperature and was used as a neat solvent. To report overpotentials in these dinitrile solvents, the equilibrium potential of 1:1 DMF:[DMF(H)][OTf] was measured in the presence of 0.2-1.3 M  $H_2O$  and 1 atm of  $H_2$  using a previously reported opencircuit potential method.<sup>46</sup>

Using **1-C6** as the catalyst in acetonitrile/butanedinitrile solvent, little change in TOF<sub>max</sub> is observed at low butanedinitrile concentrations (<25 mol%) compared to pure acetonitrile (TOF<sub>max</sub> = 740 s<sup>-1</sup>).<sup>47</sup> A marked increase in TOFmax is observed at butanedinitrile concentrations greater than 25 mol%. TOF<sub>max</sub> was determined to be 4100 s<sup>-1</sup> with 50 mol% of butanedinitrile and 7700 s<sup>-1</sup> at 80 mol% butanedinitrile (Figure 3). This equates to a 10-fold rate enhancement in 80 mol% butanedinitrile compared to acetonitrile under similar conditions. We were unable to quantify the change in structural dynamics of **1-C6** in acetonitrile/butanedinitrile due to the relatively high melting



**Figure 3.** Plot of  $TOF_{max}$  for **1-C6** versus microviscosity (298 K) in acetonitrile / butanedinitrile solvent mixtures. In order of increasing microviscosity, the solvents are 0%, 25%, 50%, and 80% butanedinitrile in acetonitrile.

point of the solvent mixture which does not afford the temperature range necessary to measure the dynamic process. However, it can be inferred from the studies above, with data summarized in Figure 1, that the rate of chair-boat isomerization of **1-C6** slows by an order of magnitude upon moving from pure acetonitrile to 80 mol% butanedinitrile, based upon the change in the microviscosity of **1-C6** in those solvents.

Catalyst 1-C14 was also studied in the 80 mol% butanedinitrile solution using [DMF(H)][OTf] as the acid. A TOF<sub>max</sub> of 400,000 s<sup>-1</sup> was measured at an initial water concentration of 0.28 M, corresponding to a 4-fold increase in the catalytic rate compared to acetonitrile/water under similar acid concentrations. TOF<sub>max</sub> decreased at water concentrations above 500 mM, possibly resulting from a decrease in the solubility of 1-C14 due the hydrophobic alkyl chains. Therefore hexanedinitrile, a less polar dinitrile, was investigated to improve the solubility of 1-C14 at high water concentrations. In hexanedinitrile, the TOF of 1-C14 increases with increasing water concentration (0.27 M -1.34 M), resulting in a TOF<sub>max</sub> of 1,500,000 s<sup>-1</sup> (Figure 2a-b). This data represents a 15-fold enhancement in catalytic rate compared to acetonitrile. Similarly, 2-C14 displayed a TOFmax of 70,000 s<sup>-1</sup> in hexanedinitrile, corresponding to a 7fold increase in rate over acetonitrile.

**2-C14** was found to be substantially less stable in the presence of acid than **1-C14**. Cyclic voltammetry experiments of **2-C14** were kept under one hour in length due to slow decomposition of **2-C14** in the bulk solution. In controlled potential electrolysis experiments, the stability of **2-C14** appeared to be electrode-dependent. With an untreated carbon foam electrode, a rapid decrease in current was observed over 10 minutes during electrolysis of **2-C14** in acetonitrile with  $[DMF(H)]^+$  and  $H_2O$ , resulting in an average turnover number  $(TON_{avg})$  of 6 and a Faradaic efficiency of 75 ± 5% for production of  $H_2$ . The electrolysis

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**Figure 4.** Plot of  $\log(\text{TOF}_{max})$  versus overpotential at  $E_{\text{cat/2}}$  showing the different scaling relationships that dictate catalytic performance. (A) describes catalysts that differ in the identity of the phosphorus substituent, R. (B) describes catalysts that differ by the length of the alkyl chain on the pendant amine. (C) describes the electronic scaling relationship of **1-C14** and **2-C14** in acetonitrile. (D) describes the electronic scaling relationship of **1-C14** and **2-C14** in hexanedinitrile.

performance was significantly improved by pretreating the carbon foam electrode at 850 °C under a N<sub>2</sub> atmosphere to reduce the quantity of oxygen functionalities on the carbon surface.<sup>48</sup> Using the pretreated electrode, **2-C14** afforded a sustained electrolysis current over 1 hour with TON<sub>avg</sub> = 36 and Faradaic efficiency = 93 ± 5%. These results suggest that oxygen functionalities on the electrode surface play a role in decomposition of **2-C14** under cathodic conditions.

Scaling Relationships. Rate-overpotential correlations can be circumvented through mechanistic understanding that guides system-level control. This result is clearly illus-trated by the evolution of TOF<sub>max</sub> and overpotential for sev-eral catalysts under different conditions, which can be dis-sected into four different scaling relationships (Figure 4). In order of increasing level of control over the catalyst structure and dynamics, these scaling relationships are: (A) changing the electronics of nickel through variation of the phosphorus substituent, (B) slowing the structural dynam-ics using long alkyl chains on the pendant amines, (C) combining electronics and structural dynamics by chang-ing the phosphorus group while using a C14-alkyl chain, and (D) increasing the solvent viscosity while using the com-bined electronics and structural dynamics. Qualitative in-sight into the origin of these relationships can be gained from prior computational studies of  $[Ni(P_2^R N_2^{R'})_2]^{2+}$  cata-lysts. In a microkinetic modeling study of 1, the main cata-lytic intermediates in the electrochemical diffusion layer were found be the nickel hydride complex, [HNi<sup>II</sup>(P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)<sub>2</sub>]<sup>+</sup>, and two different exo-protonated spe-cies (Scheme 1 and Figure 5).33 TOF<sub>max</sub> could be increased by either accelerating the rate of protonation of the nickel hydride complex, or by increasing the rate of deprotona-

tion of the catalytically incompetent exo-protonated species. In the following discussion, each scaling relationship is analyzed within the context of these two rate-limiting processes.



**Figure 5.** Plot of the  $pK_a^{MeCN}$  for the protonated pendant amine versus  $E_{1/2}$  of the Ni(II/I) couple for two intermediates of different  $[Ni(PR_2NPh_2)_2]^{2+}$  complexes. The  $pK_a^{MeCN}$  for values were determined using previously reported thermodynamic correlations derived from computations.<sup>24</sup>

Incorporation of the electron-withdrawing group on phosphorus for 2 leads to a 90 mV decrease in the overpotential relative to 1. This decrease in overpotential is accompanied by a decrease in the TOF<sub>max</sub> from 720 s<sup>-1</sup> for 1 to 160 s<sup>-1</sup> for 2. These findings are consistent with other  $[Ni(P_2^RN_2^{Ph})_2]^{2+}$  catalysts in which the Ni(II/I) couples are controlled by the identity of the phosphorus substituent. A very shallow slope of  $m_A = 1/200$  mV is obtained when  $log(TOF_{max})$  is plotted versus the overpotential for various

catalysts in acetonitrile (Figure 4, black circles), and this correlation can be considered as the "parent" electronic scaling relationship of  $[Ni(P_2^RN_2^{R'_2})_2]^{2+}$  catalysts.

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In addition to increasing the overpotential, shifting the Ni(II/I) couple to more negative potentials also leads to an increase in the pendant amine basicity due to inductive effects.<sup>24</sup> This is illustrated in Figure 5 for two key catalytic intermediates, the active endo-protonated nickel hydride and the inactive exo-exo intermediate. Because of the inductive effect, complexes that have a higher overpotential will have a greater thermodynamic driving force and lower kinetic barrier for protonation of the nickel hydride, leading to an increase in the rate of H<sub>2</sub> formation from this intermediate. The effect is counter-balanced by slower recovery from the inactive exo-pinch species at higher overpotential, resulting from an increased  $pK_a^{MeCN}$  of the exopinched intermediates. The shallow slope for the scaling relation ( $m_A = 1/200$  mV) results from the tradeoff between endo-protonation and exo-deprotonation as the catalyst electronics are varied.

The second method used to control the rate-overpotential correlation is slowing the structural dynamics of the pendant amines by adding long alkyl chains into the outer coordination sphere of the catalyst. As described previously, this modification increases  $TOF_{max}$  by orders of magnitude with only a small increase in the overpotential (Figure 4, red squares).<sup>35</sup> The alkyl chains slow the chair-boat flip that leads to the thermodynamically stabilized exopinch isomers, thereby allowing the acidic non-pinched exo-isomers to be deprotonated (Scheme 1). This is purely a kinetic effect that does not change the electronics of the catalyst, resulting in a very steep slope of  $m_B = 1/2$ omV in the plot of log(TOF<sub>max</sub>) versus overpotential. In other words, it only costs 20 mV (0.9 kcal mol<sup>-1</sup>) in extra driving force to increase TOF<sub>max</sub> by an order of magnitude.

Complex 2-C14 combines electronic effects and a long alkyl chain in a single catalyst. As a result, 2-C14 does not fall within either of the individual rate-overpotential correlations for electronics or structural dynamics in acetonitrile. Instead, 2-C14 should be considered as part of a new scaling relation in which the size of the alkyl chain is held constant and the electronics of the group on phosphorus are varied (Figure 4, blue squares). Strikingly, the new electronic scaling relation of  $1-C_{14}$  and  $2-C_{14}$  has a slope of  $m_C$ = 1/120 mV, which is a steeper tradeoff between TOF<sub>max</sub> and overpotential than the parent electronic scaling relation  $(m_{\rm A} = 1/200 {\rm mV})$ . Thus, by slowing the formation of the exopinch, the new electronic scaling relation is less influenced by the rate of exo-deprotonation than the parent relation. As a result of the steeper scaling relation, the alkyl-chain effect is much less pronounced for catalysts having both a lower overpotential and a diminished basicity of the pendant amines. Catalyst 1-C14 features a 130-fold rate enhancement compared to 1, while the electron-deficient catalyst 2-C14 only displays a 70-fold rate enhancement compared to 2.

By using the solvent viscosity to further slow the structural dynamics of complexes with long alkyl chains, the impact of exo-protonation on the rate-overpotential correlation is further diminished. The electronic scaling relation of **1-C14** and **2-C14** in hexanedinitrile displays a slope of  $m_D$ = 1/5omV (Figure 4, green diamonds), which is steeper than for the same catalysts in acetonitrile ( $m_C = 1/120mV$ ). As a result, TOF<sub>max</sub> increases more rapidly in hexanedinitrile than in acetonitrile as the overpotential is increased. Raising TOF<sub>max</sub> by an order of magnitude in hexanedinitrile only requires an extra 50 mV (2.3 kcal mol<sup>-1</sup>) of driving force for the net conversion of  $2H^+/2e^-$  to H<sub>2</sub>.

Controlling the system components of  $[Ni(P_2^R N_2^{R'})_2]^{2+}$ has an extraordinary impact on the catalytic performance. Complex 1, the first  $[Ni(P^{R_2}N^{R'_2})_2]^{2+}$  complex reported as an electrocatalyst for production of  $H_{2,36}$  displays a TOF<sub>max</sub> of 720 s<sup>-1</sup> and an overpotential of 400 mV in acetonitrile using [DMF(H)][OTf] as the acid.<sup>31</sup> In complex 2-C14, electron withdrawing groups were added to phosphorus to lower the overpotential, and TOF<sub>max</sub> was increased by adding long alkyl chains to the pendant amines and using a viscous dinitrile solvent, both of which slow the chair-boat flip that leads to the inactive exo-pinch isomers. These system-level changes result in a TOF<sub>max</sub> of 70,000 s<sup>-1</sup> at an overpotential of 230 mV, corresponding to a 100-fold increase in  $TOF_{max}$  and a 170 mV decrease in the overpotential compared to 1. This inversion of the rate-overpotential correlation was only possible by understanding the influence of the inactive exo-pinch intermediates on the electronic scaling relations of  $[Ni(P_2^R N_2^R)_2]^{2+}$  catalysts, as well as understanding the detailed mechanism of exo-pinch formation.

**Molecular Tafel Plots.** Molecular Tafel plots can be used to readily compare **2-C14** to previously reported electrocatalysts (Chart 2, Figure 6).<sup>49</sup> The potential-dependent turnover frequency ( $TOF_E$ ) of an electrocatalyst can be determined (equation 2) through application of the Nernst

$$\text{TOF}_{E} = \frac{\text{TOF}}{1 + \exp\left[\frac{F}{RT}\left(E_{H^{+}} - \eta - E_{cat/2}\right)\right]}$$
(2)

equation, where TOF is the potential-independent TOF measured from  $i_{cat}$ , F is Faraday's constant, R is the gas constant, T is the temperature,  $E_{H+}$  is the thermodynamic potential for reduction of the acid,  $E_{cat/2}$  is the catalytic half-wave potential, and  $\eta$  is the overpotential.<sup>7</sup> The TOF at zero-overpotential (TOF<sub>o</sub>) is obtained by extrapolation of the Tafel plot to  $\eta = o V$ . Similar to the exchange current density in heterogeneous electrocatalysis, TOF<sub>o</sub> corresponds to the forward rate of proton reduction at  $\eta = o V$ , but not the rate of the reverse reaction. As a result, there is zero net current at  $\eta = o V$  even for large values of TOF<sub>o</sub>.

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**Figure 6.** Molecular Tafel plots for selected electrocatalysts for H<sub>2</sub> production. [FeFe]-H<sub>2</sub>ase at pH 7.0 in H<sub>2</sub>O. **2-C14**: [DMF(H)]<sup>+</sup> in hexanedinitrile/water. Co(dmgH)<sub>2</sub>py: [HNEt<sub>3</sub>]<sup>+</sup> in DMF, extrapolated to 1M acid. Co(dmgBF<sub>2</sub>)<sub>2</sub>: 4-trifluoromethoxyanilinium in acetonitrile. **1**: [DMF(H)]<sup>+</sup> in acetonitrile/water. [Ni( $7P^{Ph}_2N^{Ph})_2$ ]<sup>2+</sup>: [DMF(H)]<sup>+</sup> in acetonitrile/water.

The Tafel plots further highlight the net gain in electrocatalytic efficiency resulting from the system-level design approach.  $TOF_0$  of **2-C14** in hexanedinitrile is nearly 5 orders of magnitude larger than for 1 in acetonitrile. This difference is much larger than the difference in  $TOF_{max}$  for these compounds (2 orders of magnitude), and reflects the positive shift in the electrocatalytic wave of 2-C14 relative to 1. Comparison of 2-C14 to  $[Ni(7P^{Ph}_2N^{Ph})_2]^{2+}$ , the landmark catalyst from Helm and co-workers,50 reveals a very large difference of more than 7 orders of magnitude in TOF<sub>0</sub>. The 7P<sup>Ph</sup><sub>2</sub>N<sup>Ph</sup> ligand was an early attempt to improve the  $[Ni(P_2^R N_2^{R'})_2]^{2+}$  catalysts by eliminating the possibility of exo-pinch formation. However, the ligand had two unintended consequences for catalysis. First, the smaller bite angle of the  $7P_{2}^{Ph}N^{Ph}$  ligand leads to a large negative shift in the Ni(II/I) couple, resulting in much larger overpotentials. Second, with only a single pendant amine on each ligand, the probability of the amine being properly positioned relative to the nickel center is substantially decreased.51-52 Conformations with the pendant amine pointed away from nickel do not allow the amine to serve as a proton relay, leading to lower TOF values than desired.

Cobaloximes are one of the most studied families of molecular electrocatalysts for  $H_2$  production.<sup>53-55</sup> The molecular Tafel plot of the proton-bridged variant,

 $Co(dmgH)_2(py)$ , was previously reported by Artero and Savéant.<sup>49</sup> It is worth noting that the TOF<sub>o</sub> value of Co(dmgH)<sub>2</sub>(py) was obtained by extrapolating kinetic data measured at low acid concentrations to 1M acid, which assumes that catalysis remains first-order in acid over this large range of acid concentrations. Dempsey and co-workers observed a switch in the acid dependence for the BF<sub>2</sub>bridged variant,  $Co(dmgBF_2)_2$ , leading to measurement of an acid-independent TOF.<sup>56</sup> A molecular Tafel plot can be constructed for Co(dmgBF<sub>2</sub>)<sub>2</sub> using the literature data (see Supporting Information for details). Interestingly, both cobaloximes give a similar TOF<sub>o</sub> despite the difference in reaction conditions (Figure 6). The low overpotential at  $E_{cat/2}$ is likely related to the low Co-H bond dissociation free energies of the cobaloxime hydride intermediates,57-58 such that making and breaking the Co-H bond during catalysis does not come with a large thermodynamic penalty. Despite their high efficiency, the cobaloxime catalysts are outperformed by 2-C14 by more than 2 orders of magnitude in TOF<sub>o</sub>. Artero has proposed that the ligand oxygen atoms in cobaloximes function as a proton relay during electrocatalytic production of H<sub>2</sub>.53, 59-60 The superior performance of 2-C14 indicates that precise control over the positioning of the proton relay is critical.

[FeFe]-hydrogenase<sup>61</sup> is a primary inspiration for the use of proton relays in molecular electrocatalysis. Accurate kinetic measurements of the enzyme are complicated by the need to determine the surface coverage of electroactive enzyme molecules that display good interfacial electron transfer with the electrode.<sup>62</sup> In a single-molecule imaging study of CaHydA [FeFe]-hydrogenase, the TOF for H<sub>2</sub> production was estimated to be 21,000 s<sup>-1</sup> at an overpotential of 90 mV.63 This value can be used to estimate a TOF<sub>0</sub> of 630 s<sup>-1</sup> by assuming the same Nernstian Tafel slope as found with molecular electrocatalysts. Comparison of [FeFe]-hydrogenase to 2-C14 in this manner reveals that the enzyme is more efficient by nearly 2 orders of magnitude in TOF<sub>0</sub>. Thus, while 2-C14 represents an extraordinary advancement in the design of energy-efficient molecular electrocatalysts, it does not reach the enzymatic level of performance.

#### Conclusions

Discovery of efficient electrocatalysts that store electrical energy in chemical bonds is critical for expanding the use of renewable energy. The structure of a molecular catalyst is highly customizable, affording opportunities for precise control over the catalyst performance. The traditional approach for designing a molecular electrocatalysts is to modify the first coordination sphere of ligands bound to the metal. However, this strategy leads to an undesirable tradeoff between rate and overpotential due to electronic scaling relationships of the catalyst. We employed a system-level design approach for controlling each catalyst component from the first coordination sphere all the way to the bulk solvent. In addition to tuning the first and second coordination spheres, we use the outer coordination sphere and the solvent viscosity to control the dynamics of the pendant amines in the second coordination sphere. The resulting catalyst system shows an enhanced turnover frequency at a significantly reduced overpotential, thus circumventing the rate-overpotential correlation of parent catalyst.

This study illustrates that efficient proton delivery demands a high level of cooperativity beyond the first and second coordination spheres. In the synthetic systems of this study, as in [FeFe]-hydrogenase, the positioning of the pendant amine needs to be precisely controlled for efficient proton transfer. It is a formidable task to control the positioning of the relay through ligand design alone without adversely affecting the catalyst thermodynamics or blocking protonation altogether. Designing the catalyst beyond the ligand set at a system level parallels the intricate macromolecular structures of hydrogenases and other enzymes. Notably, the catalyst system presented here comes closer to matching the efficiency of [FeFe]-hydrogenase than any other synthetic catalyst reported to date. These findings suggest that system-level control over the catalyst structure and function will be required to develop next generation electrocatalysts for energy transduction between electricity and chemical bonds.

#### **Experimental Section**

#### General Procedures.

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All manipulations were performed under a dinitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres glovebox. Protio solvents were deoxygenated by sparging with nitrogen and dried by passage through neutral alumina columns in an Innovative Technology, Inc., PureSolv solvent purification system. Acetonitrile- $d_3$  (CD<sub>3</sub>CN) was dried over P<sub>2</sub>O<sub>5</sub> and purified by vacuum transfer. Butanedinitrile was sublimed prior to use. Dichloromethane- $d_2$  (CD<sub>2</sub>Cl<sub>2</sub>) was dried over 3 Å molecular sieves and purified by vacuum transfer. Hexanedinitrile was deoxygenated by sparging with nitrogen and passed through a neutral alumina column. All other reagents from commercial sources were used as received. <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F NMR spectra were recorded on a 500 MHz <sup>1</sup>H frequency Agilent spectrometer. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced to an external phosphoric acid standard. <sup>19</sup>F NMR spectra were referenced to an external  $\alpha, \alpha, \alpha$ -Trifluorotoluene standard at -63.72 ppm. All <sup>1</sup>H chemical shifts were referenced to the residual protio solvent, and all J values are given in Hz.  $[Bu_4N][B(C_6F_5)_4]^{64}$  [DMF(H)][OTf],<sup>65</sup>  $[Ni(CH_3CN)_6](BF_4)_2$ ,<sup>66</sup> 1-C6,<sup>47</sup> and 1-C14<sup>35</sup> were synthesized as previously described.

A 300 MHz 'H frequency Agilent VNMRS system equipped with a direct detect dual band probe was used for diffusion experiments. The standard VNMRJ 4.0 'H Diffusion Ordered Spectroscopy (DOSY) pulse sequence was used.<sup>67</sup> A 500 MHz 'H frequency Agilent VNMRS system was used to record variable temperature <sup>31</sup>P{'H} NMR spectra, and lineshape analysis of the resulting spectra was used to determine the kinetics of the structural dynamics exchange process.<sup>39</sup>

Electrochemical measurements were recorded using a CH Instruments 620D potentiostat equipped with a standard three-electrode cell. The working electrode was a 1 mm PEEK-encased glassy carbon disc, the counter electrode was a glassy carbon rod, and the pseudo-reference electrode was a silver wire suspended in a 0.2 M [Bu<sub>4</sub>N][BF<sub>4</sub>] solution of the solvent mixture and separated from the analyte solution by a Vycor frit. Prior to the collection of each voltammogram, the working electrode was polished using 0.25  $\mu$ m diamond paste on a polishing pad lubricated with ethylene glycol, then rinsed with acetonitrile. Ferrocene was used as an internal reference and all potentials are referenced to the ferrocenium/ferrocene couple at o V. Open circuit potential measurements were performed as previously described.<sup>46</sup>

#### Synthesis

(4-(trifluoromethyl)phenyl)diethylphosphonate. In a modification of a previously described procedure,37 a 100 mL Schlenk flask was charged with Cs<sub>2</sub>CO<sub>3</sub> (24.3 g, 75 mmol) and 40 mL of toluene. To remove residual water from the Cs<sub>2</sub>CO<sub>3</sub>, a Dean-Stark trap and a condenser were added to the flask under a stream of dinitrogen, and the mixture was brought to reflux. The mixture was cooled to room temperature after 1 hour of refluxing, and the liquid contained in the Dean-Stark trap was discarded. Cul (0.353 g, 3.9 mmol), triethylphosphite (3.2 mL, 3.1 g, 19 mmol), and 4-trifluoromethyliodobenzene (2.65 mL, 4.90 g, 18.4 mmol) were added and the reaction was brought to reflux. After five days, the reaction was cooled to room temperature and filtered. The resulting filtrate was washed with 100 mL of water and extracted with dichloromethane  $(3 \times 100)$ mL). The organic layers were combined, dried over  $MgSO_4$ , and the solvent was removed under vacuum. The resulting yellow oil was purified by column chromatography (silica, 2:1 hexanes: ethyl acetate,  $R_f = 0.25$ ). The desired fractions were combined and the solvent removed under reduced pressure, resulting in a light yellow oil (3.35 g, 11.8 mmol, 66% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.9 (dd, 2 H, *J*= 7.9, 13 Hz), 7.73 (dd, 2 H, J = 3.4, 8.0 Hz), 4.14 (m, 4 H), 1.33 (t, 6 H, J = 7.0 Hz).  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>):  $\delta$  15.6.  ${}^{19}F$  NMR (CDCl<sub>3</sub>):  $\delta$  – 63.3.

(4-(trifluoromethyl)phenyl)phosphine. A 50 mL Schlenk flask was charged with 20 mL of THF, prechilled to -35 °C, then LiAlH<sub>4</sub> (270 mg, 7 mmol, 3.8 eq) was added and cooled to -35 °C for 1 hour. Me<sub>3</sub>SiCl (0.9 mL, 7 mmol, 3.8 eq) was added to the flask and the reaction was further cooled to -78 °C. A solution of (4-(trifluoromethyl)phenyl)diethylphosphonate (0.53 g, 1.9 mmol) in 5 ml of THF was slowly added to the reaction over 10 minutes. The mixture was allowed to stir at -78 °C for an additional 10 minutes, then at room temperature for 45 minutes. The mixture was cooled to 0 °C, then 8 mL of deoxygenated wa-

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ter was added and allowed to stir for 5 minutes. The reac-1 tion was filtered with an inline Schlenk frit and washed 2 with 15 mL of THF. The solution of phosphine was used in 3 subsequent reactions without isolation. <sup>31</sup>P NMR (THF):  $\delta$ 4 -126.0 (t,  $J_{PH} = 203.7$  Hz). 5 Bis(hydroxymethyl)(4-(trifluoromethyl)phenyl)phos-6

phine. In a 50 mL Schlenk flask, paraformaldehyde (220 mg, 7.3 mmol) was added to a solution of (4-(trifluoromethyl)phenyl)phosphine (334 mg, 1.9 mmol) in 20 mL of THF. The reaction was heated at 60 °C for 18 hours. The 10 solution was filtered and dried over MgSO<sub>4</sub> for 10 minutes. The solution was decanted and the solvent removed under 12 reduced pressure. The resulting yellow oil was used in sub-13 sequent reactions without further purification. <sup>31</sup>P{<sup>1</sup>H} 14 NMR (THF):  $\delta$  –19.6. <sup>19</sup>F NMR (THF):  $\delta$  –66.0.

15 PArCF3<sub>2</sub>N<sup>Ph</sup><sub>2</sub>. In a 100 mL Schlenk flask, bis(hydroxyme-16 thyl)(4-(trifluoromethyl)phenyl)phosphine (373 mg, 1.6 17 mmol) and aniline (102 mg, 0.1 mL, 1.1 mmol) were com-18 bined and dissolved into 30 mL of absolute ethanol. The 19 reaction was stirred under dinitrogen at 70 °C for 16 hours, 20 during which time a white precipitate formed. The solid 21 was isolated by vacuum filtration, washed with 10 mL of 22 cold absolute ethanol, and dried under vacuum for 1 hour. Yield = 78 mg (0.13 mmol, 24% yield).  ${}^{31}P{}^{1}H$  NMR 23  $(CD_2Cl_2): \delta -50.3.$  <sup>19</sup>F NMR  $(CD_2Cl_2): \delta -64.8.$ 24

25 P<sup>ArCF3</sup><sub>2</sub>N<sup>ArC14</sup><sub>2</sub>. In a 100 mL Schlenk flask, bis(hydroxyme-26 thyl)(4-(trifluoromethyl)phenyl)phosphine (447 mg, 1.9 27 mmol) and 4-tetradecylaniline (543 mg, 1.9 mmol) were 28 combined and dissolved into 30 mL of absolute ethanol. 29 The reaction was stirred at 70 °C for 16 hours, during which time a white precipitate formed. The solid was isolated by 30 vacuum filtration, washed with 20 mL of cold absolute eth-31 anol, and dried under vacuum for 1 hour. Yield = 480 mg 32 (0.49 mmol, 52% yield).  ${}^{31}P{}^{1}H}$  NMR (THF):  $\delta$  -51.5.  ${}^{19}F$ 33 NMR (THF): δ -64.2. 34

 $[Ni(P^{ArCF_{3}}N^{Ph}_{2})_{2}(CH_{3}CN)](BF_{4})_{2}$  (2). A solution of 35 36  $[Ni(CH_3CN)_6](BF_4)_2$  (29 mg, 0.06 mmol) in 5 mL of acetoni-37 trile was combined with a solution of PArCF32NPh2 (78 mg, 0.13 mmol) in 5 mL of THF. The reaction was stirred at 38 room temperature for 18 hours. The solution was filtered 39 through a Celite plug and the solvent removed under re-40 duced pressure to obtain a red solid. Crystals were grown 41 from an acetonitrile/toluene solvent mixture. Yield = 73 mg 42 (0.05 mmol, 84% yield). <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 7.65 (d, 8 H, 43 J = 7.6 Hz, 7.48 (t, 4 H, J = 7.5 Hz), 7.33-7.21 (m, 24 H), 4.31 44 (d, 8 H, J = 4.3 Hz), 4.05 (br s, 8H). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN): 45  $\delta$  1.8. <sup>19</sup>F NMR (CD<sub>3</sub>CN):  $\delta$  -62.39, -151.65 (<sup>10</sup>BF<sub>4</sub>), -151.70 46 ("BF4). 47

 $[Ni(P^{ArCF_3}N^{ArC_{14}})_2(CH_3CN)](BF_4)_2$  (2-C14). A solution of 48 [Ni(CH<sub>3</sub>CN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> (123 mg, 2.5 mmol) in acetonitrile (10 49 mL) was added to a suspension of PArCF32NArC142 (480 mg, 50 4.9 mmol) in toluene (10 mL). The solution was allowed to 51 stir at room temperature for 2 days, during which time the 52 solution became dark red in color. The solution was fil-53 tered through a Celite plug and the solvent removed under 54

reduced pressure. The resulting solid was dissolved in acetonitrile (10 mL), filtered, and the solvent removed under reduced pressure. This solid was dissolved in toluene (10 mL), filtered and the solvent removed under reduced pressure. The solid was triturated with hexanes (20 mL) to obtain a free flowing brick-red solid. Yield = 494 mg (0.22 mmol, 91 % yield). The product contained ~5%  $[Ni(P^{ArCF_3}N^{ArC_{14}})_2Cl]^+$  as indicated by additional resonances centered at 23.2 and -10.3 ppm in the  ${}^{31}P{}^{1}H$  NMR spectrum (Supporting Information, Figures S7 and S8). The source of Cl<sup>-</sup> is unknown; chloride sources, such as chlorinated solvents, were not used during the synthesis and workup. We were unable to purify 2-C14 further due the high solubility of the two complexes. Control experiments demonstrate that the catalytic current decreases in the presence of added [Bu<sub>4</sub>N][Cl] (Supporting Information, Figure S9), indicating that the [Ni(PArCF32NArC142)2Cl]+ impurity is not responsible for the catalytic current of 2-C14. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  7.48 (bs, 8 H), 7.44 (d, 8 H, J = 8.1 Hz), 7.21 (d, 8 H, J = 8.4 Hz), 7.16 (d, 8 H, J = 8.4 Hz), 4.26 (d, 8 H, J = 14.0 Hz), 3.93 (d, 8 H, J = 13.8 Hz), 2.59 (t, 8 H, J = 7.5 Hz), 1.59 (t, 8 H, J = 6.6 Hz), 1.29 (s, 16 H), 1.22 (s, 72 H), 0.86 (t, 12 H, J = 6.9 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$  5.95. <sup>19</sup>F NMR (CD<sub>3</sub>CN):  $\delta$  – 64.48, –151.65 (<sup>10</sup>BF<sub>4</sub>), –151.70 (<sup>11</sup>BF<sub>4</sub>).

#### **Determination of Diffusion Coefficients.**

A 300 MHz 'H frequency Agilent VNMRS system equipped with a direct detect dual band probe was used for diffusion experiments. The standard VNMRJ 4.0 <sup>1</sup>H Diffusion Ordered Spectroscopy (DOSY) pulse sequence was used.<sup>67</sup> Experimental parameters included 4-32 scans, 2.0-4.0 ms gradient pulse lengths, and 50-400 ms diffusion delays. The diffusion coefficient (D) for 1-C6 in electrocatalytic conditions was determined using similar electrolyte, acid, and water concentrations as the electrocatalytic experiments. Due to the limited solubility and spectral overlap of acid resonances and aryl resonances for 1-C14 and 2-C14, the diffusion coefficients were determined in neat solvents for those complexes. Based on differences in D for 1-**C6** in neat hexanedinitrile ( $D = 0.39 \pm 0.01 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) and with the addition of electrolyte, acid, and water (D = 0.36 $\pm$  0.02 × 10<sup>-10</sup> m<sup>2</sup> s<sup>-1</sup>), these additives are expected to have little influence on *D* for 1-C14 and 2-C14.

#### NMR Line Shape and Kinetic Analysis.

The gNMR program<sup>68</sup> was used to analyze the exchange process observed in the variable temperature <sup>31</sup>P{<sup>1</sup>H} spectra. The spectra were processed in gNMR using a Lorentzian function with line broadening up to 6 Hz. A twosite exchange model was used to determine the rates of nuclei exchange by iteration of the simulated line widths, using both manual and gNMR algorithm methods. Eyring parameters were determined using the equation:

$$k = \frac{k_B T}{h} e^{\Delta H^{\ddagger}/_{RT}} e^{\Delta S^{\ddagger}/_{R}}$$

Error bars of 15% were determined for each data point based on visual inspection of the overlaid experimental

and simulated spectrum from gNMR. Nonlinear regression was done using Profit software with the error applied to the individual data points. The sample temperature in the NMR spectrometer was calibrated using a methanol standard sample with an estimated error of 0.5 K. The error in the activation parameters were determined by the error propagation method described by Girolami et al.<sup>69</sup>

## Electrocatalytic Experiments.

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Aliquots of a [DMF(H)][OTf] stock solution were added to an electrolyte solution of the catalyst until a constant value of *i*<sub>cat</sub> was achieved. A similar procedure was followed for water concentration by adding known volumes of water to the electrochemical cell containing the electrolyte, acid, and catalyst. Upon achievement of acid concentration and water concentration independence, the independence of the scan rate on the catalytic current was determined. The performance under optimal conditions was cross-checked by adding the catalyst to a fresh solution of the electrolyte, acid, and water. Experiments using **2-C14** were kept under one hour in length due to catalyst decomposition over time.

## **Controlled Potential Electrolysis.**

Electrocatalytic hydrogen production for 2-C14 was confirmed by controlled potential electrolysis in acetonitrile. A 30 mL three compartment bulk electrolysis cell was charged with 8.3 mL of a solution containing 0.2 M [Bu<sub>4</sub>N][BF<sub>4</sub>], 0.1 M [DMF(H)][OTf], 0.8 M water, 50 μM 2-C14, and ferrocene. The working electrode was a cylinder of reticulated vitreous carbon fixed to a copper wire using conductive silver epoxy. In some experiments, the carbon electrode was pretreated by heating to 850 °C under a flow of N<sub>2</sub> for 4 hours. The pseudo-reference electrode was a silver wire suspended in a 0.2 M [Bu<sub>4</sub>N][BF<sub>4</sub>] solution of the solvent mixture and separated from the analyte solution by a Vycor frit. The counter electrode was a nichrome wire suspended in a 0.2 M [Bu<sub>4</sub>N][BF<sub>4</sub>] acetonitrile solution separated by an ultrafine frit. Experiments were performed at -1 V vs Cp<sub>2</sub>Fe<sup>+/o</sup>. Samples of the headspace were removed via gastight syringe upon completion of the experiment and analyzed by gas chromatography. Gas analysis for hydrogen and nitrogen were performed using an Agilent 6850 gas chromatograph fitted with a 10 ft long Supelco 1/8" Carbosieve 100/120 column equipped with a thermal conductivity detector. The percentage of hydrogen and nitrogen in the headspace were determined by calibration using gas standards of known composition.

## ASSOCIATED CONTENT

**Supporting Information**. Synthetic scheme, NMR spectra, diffusion coefficient and structural dynamics analysis, electrochemical data, additional details of Tafel plot analysis. (pdf)

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#### ACKNOWLEDGMENT

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. The authors thank Dr. Abhijeet Karkamkar for thermal activation of the carbon foam electrodes. Pacific Northwest National Laboratory is operated by Battelle for DOE.

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#### Table of Contents Graphic



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