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$[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ as an Electrocatalyst for H_2 Production

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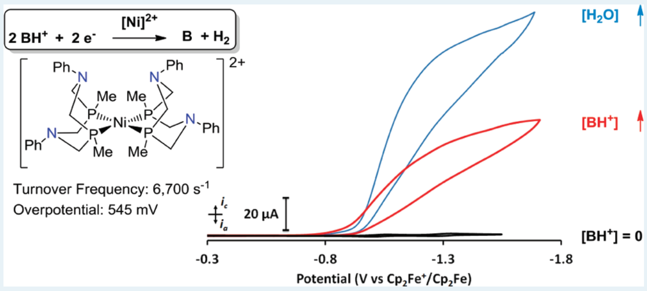
ABSTRACT: A nickel(II) bis(diphosphine) complex, $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ ($P^{Me}{}_2N^{Ph}{}_2$ = 1,5-diphenyl-3,7-dimethyl-1,5-diaza-3,7-diphosphacyclooctane), has been synthesized and characterized. This complex, which contains pendant amines in the diphosphine ligand, is an electrocatalyst for hydrogen production by proton reduction. Using [(DMF)H]OTf as the acid, a turnover frequency of 1,540 s^{-1} was obtained with no added water, and a turnover frequency of 6,700 s^{-1} was found with 1.0 M water added. Thermochemical studies show that the hydride donor ability of $[HNi(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)$ is $\Delta G°_{H^-}$ = 54.0 kcal/mol, and we estimate a driving force for H_2 elimination of 13.8 kcal/mol. $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ is the fastest H_2 production catalyst in the $[Ni(P^{R}{}_2N^{R'}{}_2)_2](BF_4)_2$ family of complexes.



KEYWORDS: *hydrogen, electrocatalysis, proton relay, pendant amine, proton reduction, nickel*

■ INTRODUCTION

Increasing the viability of sustainable, nonfossil fuel energy sources, such as wind and solar, requires the development of improved methods for energy storage to compensate for the temporal variations of energy generation. Storing and releasing electrical energy from chemical bonds is a promising solution because of the high energy density of chemical fuels. The simplest form of energy storage in a chemical bond is the reduction of two protons to form H_2, as shown in eq 1. Platinum is a fast and efficient catalyst for the storage and release of energy from H_2, but the high cost of platinum and its limited abundance make its use as an electrocatalyst on a global scale problematic.[1]

$$2H^+ + 2e^- \underset{\text{Energy Release}}{\overset{\text{Energy Storage}}{\rightleftharpoons}} H_2 \tag{1}$$

Earth-abundant, inexpensive metals such as nickel and iron are found in hydrogenase enzymes, which regulate hydrogen metabolism in nature.[2] For example, [FeFe]-hydrogenase enzymes catalyze H_2 production from water with turnover frequencies as high as 9,000 s^{-1} at 30 °C.[3] On the basis of structural and spectroscopic studies of the [FeFe]-hydrogenase enzyme, it has been proposed that a positioned pendant amine is present in the [FeFe]-hydrogenase active site (structure **1** in Figure 1).[2,4−6]

Iron complexes containing pendant bases in the second coordination sphere have been reported as models for the [FeFe]-hydrogenase.[7−22] In addition, hydrogen production electrocatalysis has been reported for cobalt,[23−33] iron,[34−37] and molybdenum[38−40] complexes that do not contain proton relays. Work from our laboratories has focused on a family of $[Ni^{II}(P^{R}{}_2N^{R'}{}_2)_2](BF_4)_2$ complexes, where $P^{R}{}_2N^{R'}{}_2$ are diphosphine ligands that contain two noncoordinating pendant amines (Structure **2** of Figure 1).[41−44] These studies have shed light on the roles of pendant amines in multiproton, multielectron processes. The pendant amines function as proton relays, dramatically increasing the rates of intra- and intermolecular proton transfer, and assisting in the heterolytic cleavage/formation of the H−H bond. As a result, complexes containing these pendant bases are much faster electrocatalysts for both H_2 production and oxidation and operate at much lower overpotentials than analogous complexes without pendant amines.

Derivatives of $[Ni(P^{R}{}_2N^{R'}{}_2)_2](BF_4)_2$ have been probed for H_2 production and oxidation. The free energy of hydrogen addition to the various catalysts determines whether they favor hydrogen oxidation or production. Complexes that have negative free energies of hydrogen addition are better hydrogen oxidation catalysts,[45−47] while complexes that have positive free energies of hydrogen addition are biased toward hydrogen production catalysis.[45,48−53] This driving force can be controlled by varying the substituents on N, which control the acidity of the protonated amine, and the substituents on P, which control the hydride donor abilities of proposed proton-hydride intermediates such as structure **3** of Figure 1. In addition to controlling the bias for H_2 oxidation or addition, these parameters also influence the catalytic rates for H_2 oxidation and production. For example, aryl-substituted complexes with the general formula $[Ni(P^{Ph}{}_2N^{C6H4X}{}_2)_2](BF_4)_2$

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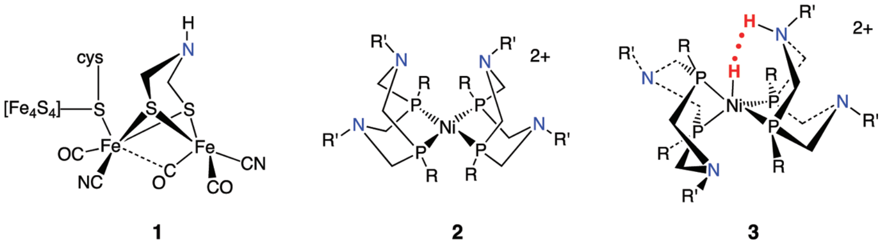
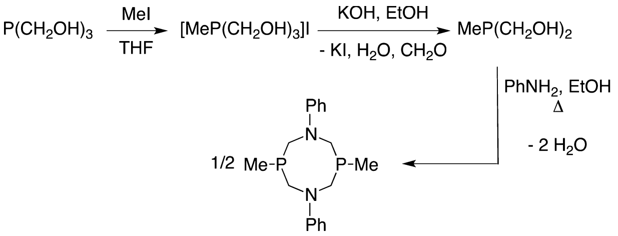


Figure 1. Proposed structure of [FeFe]-hydrogenase enzyme active site, **1**. $[Ni^{II}(P^{R}{}_2N^{R'}{}_2)_2]^{2+}$ catalyst structure with positioned pendant amines adjacent to a vacant coordination site on nickel, **2**. Proposed structure of proton-hydride intermediate, **3**.

(X = CF_3, Br, H, Me, OMe) all have positive free energies of hydrogen addition, and they are H_2 production catalysts. For these complexes the catalytic rates increase as the acidity of the protonated pendant amines increase.[51] Similarly, a series of $[Ni^{II}(P^{R}{}_2N^{Ph}{}_2)_2](BF_4)_2$ complexes were studied in which the N-Ph group maintained a nearly constant acidity, while the hydride donor ability was varied by changing substituents on P.[53] It was found that the catalytic rates increased as the hydride donor abilities of the Ni complexes increased, with the exception of sterically encumbered phosphine substituents. Of the $[Ni(P^{R}{}_2N^{Ph}{}_2)_2](BF_4)_2$ complexes studied, $[Ni(P^{n\text{-}Bu}{}_2N^{Ph}{}_2)_2](BF_4)_2$ is the fastest H_2 production electrocatalyst, with a maximum turnover frequency of 1,820 s^{-1} and an overpotential of 500 mV. The recently reported synthesis[54] of the $P^{Me}{}_2N^{Ph}{}_2$ ligand and the corresponding Ni complex, $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](OTf)_2$, prompts us to extend our studies on electrocatalytic H_2 production to $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$. The smaller methyl substituent compared to *n*-Bu should result in a more negative redox potential for the Ni(II/I) couple and an increase in the hydride donor abilities of important nickel hydride intermediates. These changes would then be expected to lead to faster catalysis. In this work, we report that $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ is the fastest H_2 production catalyst in the $[Ni(P^{R}{}_2N^{R'}{}_2)_2](BF_4)_2$ family of complexes, with a turnover frequency of 6,700 s^{-1} and an overpotential of 545 mV.

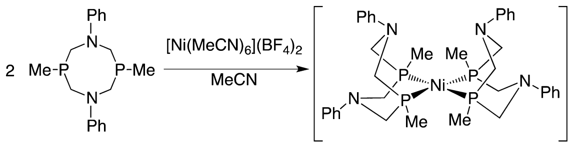
RESULTS

Synthesis and Characterization of $P^{Me}{}_2N^{Ph}{}_2$ and $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$. The diphosphine ligand $P^{Me}{}_2N^{Ph}{}_2$ was prepared in a three-step synthesis (eq 2) that is a modification of the recently reported preparation.[54] In the first step, the reaction of tris(hydroxymethyl)phosphine with methyl iodide gave the iodide salt of tris(hydroxymethyl)methylphosphonium. Upon addition of KOH, bis(hydroxymethyl)methylphosphine forms. Aniline was then added to bis(hydroxymethyl)methylphosphine in hot ethanol, and $P^{Me}{}_2N^{Ph}{}_2$ precipitated as a white solid, which was isolated in 88% yield.



(2)

The corresponding Ni(II) complex, $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$, can be prepared by addition of 2 equiv of $P^{Me}{}_2N^{Ph}{}_2$ to $[Ni(MeCN)_6](BF_4)_2$ in acetonitrile (eq 3). The complex was characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry and elemental analysis, all of which are consistent with the indicated structure. The $^{31}P\{^1H\}$ NMR spectrum of this complex shows a singlet resonance at 1.3 ppm, shifted 59 ppm downfield from the free ligand. The ^1H and $^{31}P\{^1H\}$ NMR spectra are similar to the previously reported[51] $[Ni(P^{Ph}{}_2N^{C6H4X}{}_2)_2](BF_4)_2$ complexes and nearly identical with the recently reported triflate salt, $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](CF_3SO_3)_2$,[54] which has been characterized by an X-ray diffraction study and shown to have a square planar geometry.



(3)

Electrochemical Studies of $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$. The cyclic voltammogram of $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ shows two distinct reversible one-electron waves (Figure 2). The wave at −1.03 V has a peak to peak separation (ΔE_p) of 64 mV and is assigned to the Ni(II/I) couple, and the wave at −1.29 V (ΔE_p = 66 mV) is assigned to the Ni(I/0) couple. All potentials are reported versus the Cp_2Fe^+/Cp_2Fe couple at 0 V. The Ni(II/I) and Ni(I/0) couples are more negative than those of the previously reported $[Ni(P^{Ph}{}_2N^{C6H4X}{}_2)_2(BF_4)_2$ complexes, which range from −0.74 to −0.88 V for Ni(II/I) couple and −0.89 to −1.07 V for Ni(I/0) couple.

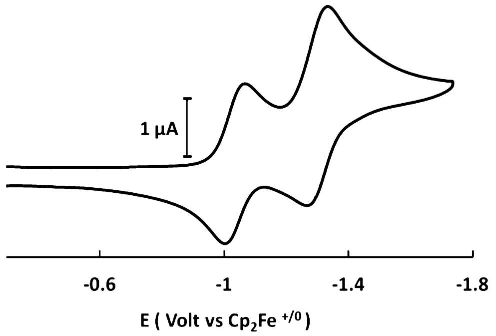


Figure 2. Cyclic voltammogram of 1 mM $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ in MeCN/0.2 M NEt_4BF_4 with a 1 mm glassy carbon working electrode; scan rate = 0.1 V s^{-1}.

Catalytic Production of Hydrogen in the Absence of Added H_2O. Cyclic voltammograms of $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ in the absence (black trace) and presence (blue, green, and red traces) of increasing concentrations of the Brønsted acid [(DMF)H]OTf are shown in Figure 3. [(DMF)H]OTf is the acid resulting from the protonation of dimethylformamide with triflic acid.[55] This acid was chosen because its pK_a value of 6.1

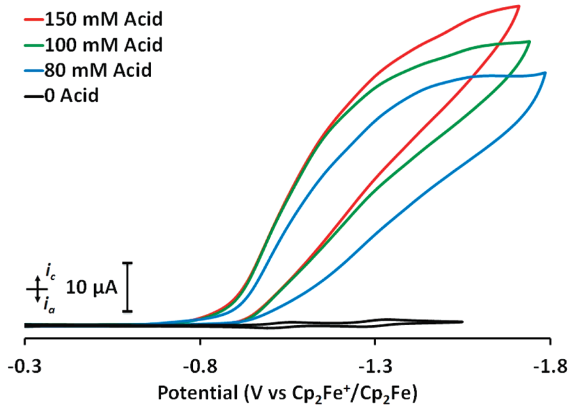


Figure 3. Cyclic voltammograms of 0.6 mM $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ in MeCN/0.2 M Et_4NBF_4 with a 1 mm glassy carbon working electrode. The black trace was taken in the absence of acid, and the blue, green, and red trace traces were recorded in the presence of increasing concentrations of [(DMF)H]OTf at a scan rate of 0.1 V s^{-1}.

in acetonitrile[56] is well-matched to the estimated pK_a values (approximately 6)[57] of protonated reduced forms of $[Ni^0(P^R{}_2N^{Ph}{}_2H)_2](BF_4)_2$ complexes. It can be seen in Figure 3 that the addition of acid results in a large increase in the current at the potential of the Ni(II/I) couple, and this enhanced current is attributed to the catalytic reduction of the protons of [(DMF)H]OTf to form H_2. To confirm the production of H_2, a controlled potential coulometry experiment was performed at −1.50 V, and the gases in the headspace of the electrochemical cell were determined by gas chromatography. The quantity of H_2 produced corresponds to a current efficiency for this catalyst of 94 ± 5%, confirming selective catalytic production of H_2 with no detectable catalyst decomposition.

Figure 4 shows the results of a study in which the acid concentration was gradually increased until the ratio (i_{cat}/i_p) of the catalytic current (i_{cat}, measured at −1.3 V) to the peak current of the Ni(II/I) reduction wave in the absence of acid (i_p) remained constant. The linear dependence of the catalytic current on acid concentration up to approximately 0.12 M indicates a second-order dependence of the catalytic rate on acid. The acid-independent region above 0.12 M acid implies a zero-order dependence on acid. This transition from a region of second-order dependence on acid to a region of no acid dependence is interpreted in terms of a pre-equilibrium step involving the transfer of two protons to reduced Ni species $[Ni^I(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)$ and $[HNi(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)$, followed by a rate-determining intramolecular process that could involve H_2 elimination.

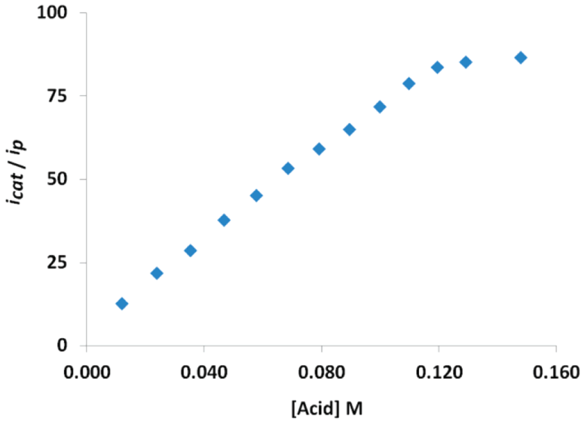


Figure 4. Plot of i_{cat}/i_p vs concentration of [(DMF)H]OTf for $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ catalyst at 23 °C at a scan rate of 0.1 V s^{-1} in acetonitrile/0.2 M Et_4NBF_4 at a 1 mm glassy carbon working electrode.

The experimentally determined value of i_{cat}/i_p in the acid-independent region can be used in eq 4[58−61] to calculate an observed turnover frequency for this catalyst of 1,540 s^{-1} under dry conditions. This is twice as fast as the previously reported $[Ni(P^{Ph}{}_2N^{C6H4Br}{}_2)_2](BF_4)_2$ complex, which has a turnover frequency of 740 s^{-1} under similar conditions.[51] In eq 4, n is the number of electrons involved in the reaction (2 for catalytic production of H_2), R is the gas constant, T is the temperature in K, F is Faraday constant, and υ is the scan rate in V/s.

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463}\sqrt{\frac{RTk_{obs}}{F\upsilon}} \tag{4}$$

Using the potential where the current is half its maximum value (the half-peak potential, $E_{p/2}$), the overpotential for $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ was determined to be 545 mV using the method of Evans et al.[62] This overpotential is higher than the overpotentials previously reported for $[Ni(P^{Ph}{}_2N^{C6H4X}{}_2)_2](BF_4)_2$ complexes, which did not exceed 340 mV under these conditions.

Catalytic Studies in the Presence of Added H_2O. We have previously shown that the addition of water to acidic solutions of $[Ni(P^{Ph}{}_2N^{C6H4X}{}_2)_2](BF_4)_2$ and $[Ni(P^R{}_2N^{Ph}{}_2)_2](BF_4)_2$ complexes can significantly increase the observed turnover frequencies of these catalysts.[51,53] To determine if this also occurs for $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$, water was added in increments to a solution containing 0.15 M [(DMF)H]OTf to reach a final concentration of 0.14 M acid and 1.0 M water (see Figure 5). The addition of water caused an increase in turnover frequency to 6,700 s^{-1}, which is the fastest H_2 production rate observed for any electrocatalyst in the $[Ni(P^R{}_2N^{R'}{}_2)]^{2+}$ family. The fastest previously reported $[Ni(P^R{}_2N^{R'}{}_2)_2]^{2+}$ catalyst, $[Ni(P^{Ph}{}_2N^{C6H4CH2P(O)(OEt)2}{}_2)_2]^{2+}$ showed a maximum catalytic

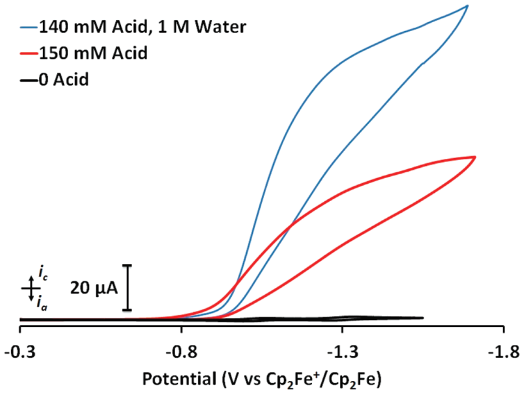


Figure 5. Cyclic voltammograms of 0.6 mM $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ in MeCN/0.2 M Et_4NBF_4 using a 1 mm glassy carbon working electrode at a scan rate of 0.1 V s^{-1}. The black trace was recorded in the absence of acid and water. The red trace was recorded in the presence of acid only, and the blue trace was recorded in the presence of 1.0 M water and 0.14 M [(DMF)H]OTf.

rate of 1,850 s^{-1} under similar conditions,[51] approximately 3.5 times slower.

Thermodynamic Studies. Previous studies of $[Ni(P^{R}_{2}N^{Ph}_{2})_{2}]^{2+}$ catalysts have shown that their TOFs correlate with the hydride donor abilities of the corresponding $[HNi(P^{R}_{2}N^{Ph}_{2})_{2}](BF_4)$ complexes.[53] The thermodynamic cycle shown in Scheme 1 was used to determine the hydride donor ability of $[HNi(P^{Me}_{2}N^{Ph}_{2})_{2}](BF_4)$. In this experiment, collidine was used as the base shown in eq 5 to act as the proton acceptor during the heterolytic cleavage of H_2. After allowing the reaction to reach equilibrium over 24 h and verifying that no change in the equilibrium constant was observed, ^{1}H NMR spectroscopy was used to determine the relative concentration of collidine and collidinium, and the ratios of $[HNi(P^{Me}_{2}N^{Ph}_{2})_{2}]^{+}$ and $[Ni(P^{Me}_{2}N^{Ph}_{2})_{2}]^{2+}$ were determined by integration of the corresponding $^{31}P\{^{1}H\}$ spectra. These ratios were used to calculate the equilibrium constant (K_{eq} = 13.9) for eq 5, as described in the Experimental Section. This equilibrium constant, together with the pK_a value for collidinium (14.98 in acetonitrile),[63] and the reported value for the heterolytic cleavage of H_2 in MeCN (76 kcal/mol)[64] were used in eq 8 to determine a hydride donor ability of $\Delta G^{\circ}_{H^-}$ = 54.0 kcal/mol for $[HNi(P^{Me}_{2}N^{Ph}_{2})_{2}](BF_4)$ in acetonitrile. This value can be used to calculate a homolytic bond dissociation energy of 54.5 kcal/mol for $[HNi(P^{Me}_{2}N^{Ph}_{2})_{2}](BF_4)$ and a pK_a value of 22.5 using well-established thermodynamic cycles[57,64−66] and the potentials of the Ni(II/I) and Ni(I/0) couples of $[Ni(P^{Me}_{2}N^{Ph}_{2})_{2}]^{2+}$. These values can also be used to estimate a driving force for H_2 elimination of 13.8 kcal/mol from the doubly protonated Ni(0) complex, $[Ni(P^{Me}_{2}N^{Ph}_{2}H)_{2}]^{2+}$, as shown in Scheme 2. In this calculation a pK_a value of 6.0 is used for $[Ni(P^{Me}_{2}N^{Ph}_{2}H)_{2}]^{2+}$ as described previously for closely related $[Ni(P^{R}_{2}N^{Ph}_{2}H)_{2}]^{2+}$ complexes.[53,57]

Scheme 1. Thermodynamic Cycle for Determination of $\Delta G^{\circ}_{H^-}$

$$[HNi(P^{R}_{2}N^{R'}_{2})_{2}]^{+} + BH^{+} \rightleftharpoons [Ni(P^{R}_{2}N^{R'}_{2})_{2}]^{2+} + H_2 + B \qquad (5) \qquad -RT\ln K$$

$$B + H^{+} \rightleftharpoons BH^{+} \qquad (6) \qquad -1.364pK_a$$

$$H_2 \rightleftharpoons H^{+} + H^{-} \qquad (7) \qquad 76\ \text{kcal / mol}$$

$$[HNi(P^{R}_{2}N^{R'}_{2})_{2}]^{+} \rightleftharpoons [Ni(P^{R}_{2}N^{R'}_{2})_{2}]^{2+} + H^{-} \qquad \Delta G^{o}_{H-}$$

$$\Delta G^{o}_{H-} = -RT\ln K - 1.364pK_a + 76.0\ \text{kcal / mol} \qquad (8)$$

Scheme 2. Thermodynamic Cycle for Estimation of ΔG°_{H2}

$$[Ni(P^{R}_{2}N^{R'}_{2})_{2}]^{2+} + H^{-} \rightleftharpoons [HNi(P^{R}_{2}N^{R'}_{2})_{2}]^{+} \qquad (9) \qquad -\Delta G^{o}_{H-}$$

$$[HNi(P^{R}_{2}N^{R'}_{2})_{2}]^{+} + H^{+} \rightleftharpoons [Ni(P^{R}_{2}N^{R'}_{2}H)_{2}]^{2+} \qquad (10) \qquad -1.364pK_a$$

$$H_2 \rightleftharpoons H^{+} + H^{-} \qquad (11) \qquad 76\ \text{kcal / mol}$$

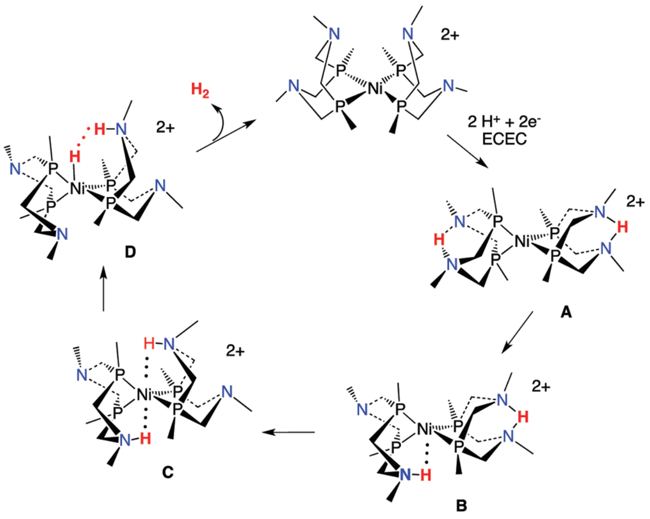
$$[Ni(P^{R}_{2}N^{R'}_{2})_{2}]^{2+} + H_2 \rightleftharpoons [Ni(P^{R}_{2}N^{R'}_{2}H)_{2}]^{2+} \qquad (12) \qquad \Delta G^{o}_{H2}$$

$$\Delta G^{o}_{H2} = -\Delta G^{o}_{H-} - 1.364pK_a + 76.0\ \text{kcal/mol} \qquad (13)$$

■ DISCUSSION

Previous investigations of electrocatalysts for H_2 production and oxidation in our laboratory[45,51,53] have shown that during H_2 production, the $[Ni^{II}(P^{R}_{2}N^{R'}_{2})_{2}]^{2+}$ complexes undergo two sequential electron and proton transfer reactions (ECEC) to form doubly protonated Ni^{0} complexes,[52,67] followed by H_2 elimination as shown in Scheme 3. The doubly protonated Ni^{0} intermediates[52,67] can exist in three isomeric forms, as shown by structures **A**−**C**, with the kinetically preferred isomer being the exo-exo isomer **A**. However, only the endo-endo isomer **C** can evolve H_2 from the proton-hydride intermediate[68] **D**.

Scheme 3. Proposed Mechanism for Catalytic Production of H_2[a]



[a]Me groups on P and Ph groups on N not shown.

The overall driving force for the catalytic production of H_2 is determined by the hydride donor ability of $[HNi(P^{R}_{2}N^{R'}_{2})_{2}]^{+}$ intermediates and the acidity of the doubly protonated Ni^{0} complexes, isomers **A**−**C** as discussed above. Isomers **A**−**C** have been shown to have nearly equal energies, and therefore pK_a values, by virtue of the fact that they exist in equilibrium with each other.[69,70] As the driving force for the catalytic reaction increases by increasing the hydride donor abilities and acidities of the nickel complexes, the catalytic rate should increase, as observed previously for $[Ni(P^{R}_{2}N^{Ph}_{2})_{2}]^{2+}$ and $[Ni(P^{Ph}_{2}N^{C6H4X}_{2})_{2}]^{2+}$ complexes.[51,53] The hydride donor abilities of $[HNi(P^{R}_{2}N^{R'}_{2})_{2}]^{+}$ complexes increase linearly as the Ni(II/I) couple becomes more negative, and the potential of the Ni(II/I) couple depends on two factors: the electron donor ability of the substituent R on phosphorus and the planarity of the four-coordinate Ni^{II} complex.[71,72] More electron donating substituents result in more negative potentials and better hydride donors as expected. Larger phosphorus substituents increase steric interactions that cause tetrahedral distortions and stabilize the lowest unoccupied molecular orbital (LUMO) of $[Ni(P^{R}_{2}N^{R'}_{2})_{2}]^{2+}$ complexes by reducing the antibonding overlap between the phosphorus σ orbitals and the $d_{x^2-y^2}$ orbital of nickel.[73] As a result of the stabilization of the LUMO, $[Ni(P^{R}_{2}N^{R'}_{2})_{2}]^{2+}$ complexes with large substituents on phosphorus are more easily reduced (i.e., have more positive Ni(II/I) couples) and are better hydride acceptors than complexes with small substituents on phosphorus. For example, $[Ni(P^{Ph}_{2}N^{Ph}_{2})_{2}]^{2+}$ has a Ni(II/I) couple at −0.84 V and a $\Delta G^{\circ}_{H^-}$ value of 59.0 kcal/mol,[57] compared to $[Ni(P^{Cy}_{2}N^{Ph}_{2})_{2}]^{2+}$ (Cy = cyclohexyl) which has a Ni(II/I) couple at −0.62 V and a $\Delta G^{\circ}_{H^-}$ value of 63.7 kcal/

Table 1. Values of $\Delta G°_{H^-}$ for $[HNi(P^R{}_2N^{Ph}{}_2)_2]^+$, $E_{1/2}$ for Ni(II/I) Couples, Turnover Frequencies (TOF), and Overpotentials[a]

catalyst	$\Delta G°_{H^-}$ of $[HNi(P^R{}_2N^{Ph}{}_2)_2]^+$ (kcal/mol)	Ni(II/I) (V vs $Cp_2Fe^{+/0}$)	TOF (s^{-1}) [DMF(H)]OTf (overpotential, mV)	TOF (s^{-1}) [DMF(H)]OTf + water (overpotential, mV)	ref
$[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2]^{2+}$	59.0	−0.84	590 (300)	720 (320)	51
$[Ni(P^{n\text{-}Bu}{}_2N^{Ph}{}_2)_2]^{2+}$	57.1	−0.93	46 (450)	1,820 (500)	53
$[Ni(P^{Me}{}_2N^{Ph}{}_2)_2]^{2+}$	54.0	−1.03	1,540 (500)	6,700 (545)	this work

[a] In parentheses, in mV.

mol.[74] Smaller $\Delta G°_{H^-}$ values indicate better hydride donors. On the basis of electron donor abilities, the cyclohexyl derivative would be expected to have a more negative Ni(II/I) couple and a less positive $\Delta G°_{H^-}$ value, the opposite of what is actually observed. Clearly, steric interactions play a major role in the thermodynamic properties of these complexes as previously discussed in more detail.[75,76] Because of the small size of the methyl substituent, $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2]^{2+}$ is expected to have more negative redox potentials than $[Ni(P^{n\text{-}Bu}{}_2N^{Ph}{}_2)_2]^{2+}$, which was the fastest catalyst of this class previously reported, and the corresponding hydride, $[HNi(P^{Me}{}_2N^{Ph}{}_2)_2]^+$, is expected to be a better hydride donor than $[HNi(P^{n\text{-}Bu}{}_2N^{Ph}{}_2)_2]^+$. As can be seen from Table 1, these expectations are confirmed, and $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2]^{2+}$ is the fastest catalyst for H_2 production of this class of complexes. This increase in rate comes at the expense of a larger overpotential (545 mV) that is a result of the more negative Ni(II/I) couple.

In addition to increasing the rate by increasing the driving force for the catalytic process, it is clear from Table 1 that addition of water also dramatically increases the catalytic rates from 1,540 s^{-1} to 6,700 s^{-1}. This acceleration of the catalytic rate was anticipated from previous studies, which have shown similar rate increases upon addition of water.[51,53] On the basis of previous NMR studies, this enhancement is attributed to an increase in the rate of conversion of isomer **A** in Scheme 3 to isomer **C**.[67] Theoretical studies suggest the enhanced rate of isomer conversion is the result of water forming a hydrogen bond that weakens the NH···N hydrogen bond of the pinched exo-exo isomer **A**. Cleavage of this bond allows easier access of the conjugate base in solution to the NH proton, which facilitates deprotonation and reprotonation to first form isomer **B** and then **C**. Once isomer **C** is formed, H_2 evolution is facile. It has also been suggested in previous studies[53] of $[Ni(P^R{}_2N^{Ph}{}_2)_2]^{2+}$ complexes that the size of the P substituent can influence the rate of protonation at the endo position, with larger substituents retarding this protonation step and slowing catalysis. All of these considerations suggested that the small methyl substituent should facilitate rapid protonation at the desired endo position and enhance catalytic rates compared to previously reported catalysts of this class. This expectation is clearly supported by the data shown in Table 1. To the best of our knowledge, only the complex $[Ni(P^{Ph}{}_2N^{Ph})_2]^{2+}$ (where $P^{Ph}{}_2N^{Ph}$ is 1,3,6-triphenyl-1-aza-3,6-diphosphacycloheptane) exhibits higher turnover frequencies (106,000 s^{-1} in the presence of 0.43 M [(DMF)H]OTf and 1.2 M water, scan rate 10 V/s)[77] than $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2]^{2+}$. This results from an even larger driving force (due to an even more planar structure resulting from the smaller seven-membered ring of the diphosphine ligand) and avoiding pinched exo forms of the catalyst by redesigning the ligand structure.

SUMMARY AND CONCLUSION

This work describes catalytic and thermodynamic studies of $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2]^{2+}$ and its derivatives. On the basis of the results of previous studies and the measured hydride donor ability of $[HNi(P^{Me}{}_2N^{Ph}{}_2)_2]^+$ ($\Delta G°_{H^-}$ = 54.0 kcal/mol), this complex was anticipated to have the highest turnover frequency for catalytic H_2 production of any complex of this class reported to date. The measured turnover frequencies for H_2 production of 1,540 s^{-1} in the presence of dry [(DMF)H]OTf (6,700 s^{-1} in the presence of [(DMF)H]OTf and water) confirm this expectation and supports our basic understanding of the features controlling the catalytic activity of this class of complexes.

EXPERIMENTAL SECTION

Synthesis and Materials. All reactions and manipulations were performed under an N_2 atmosphere using standard Schlenk techniques or in a glovebox unless otherwise indicated. Solvents were dried using an Innovative Technology, Inc. PureSolv solvent purification system. Acetonitrile-d_3 (Cambridge Isotope Laboratories, 99.5%D) was vacuum distilled from P_2O_5. Chloroform-*d* (Cambridge Isotope Laboratories, 99.5%D) was degassed and stored over molecular sieves. Tetraethylammonium tetrafluoroborate (Alfa-Aesar) was recrystallized twice by vapor diffusion of diethyl ether into an acetonitrile solution; the crystals obtained were dried under vacuum. Dimethylformamide-trifluoromethanesulfonic acid, [(DMF)H]OTf, was prepared by the method of Faviera and Duñach.[55] Tris(hydroxymethyl)phosphine (Strem) was used as received. Water was dispensed from a Millipore Milli-Q purifier and sparged with nitrogen. Ferrocene (Aldrich) was sublimed under vacuum before use. $[Ni(CH_3CN)_6](BF_4)_2\cdot 1/2\ CH_3CN$ was prepared by the literature method.[78]

Synthesis of $P^{Me}{}_2N^{Ph}{}_2$. This is a modification of the preparation of $P^{Me}{}_2N^{Ph}{}_2$ recently reported.[54] A Schlenk flask charged with tris(hydroxymethyl)phosphine (532 mg, 4.29 mmol), and 20 mL of tetrahydrofuran (THF) was cooled to 0 °C. Methyl iodide was added (609 mg, 4.29 mmol) to this solution. The mixture was stirred overnight. The resulting oily mixture was dried under vacuum and dissolved in 10 mL of absolute ethanol. To this solution was added solid KOH (240 mg, 4.3 mmol), and a white precipitate was observed. The precipitate, presumed to be KI, was removed by filtration. The filtrate was then transferred to a Schlenk flask and heated to 60 °C. Aniline (305 mg, 3.27 mmol) in absolute ethanol (~3 mL) was added over the course of 10 min to the solution. Following two days of stirring, the product was collected by filtration and isolated as a white precipitate (460 mg, 1.39 mmol, 88% based on aniline).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.2 MHz): δ −57.7 (s). ^1H NMR ($CDCl_3$, 499.7 MHz): δ 7.21 (m, 4H, Ar*H*); 6.69 (m, 2H, Ar*H*); 6.67 (m, 4H, Ar*H*); 4.15 (t, *J* = 14.3 Hz, 4H, CH_2); 3.42 (dd, *J* = 15.9 Hz, 4.6 Hz, 4H, CH_2); 1.00 (d, *J* = 4.1 Hz, 6H, CH_3).

Synthesis of $[(Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$. To a stirred MeCN solution (10 mL) of $[Ni(CH_3CN)_6](BF_4)_2\cdot 1/2CH_3CN$ (55 mg, 0.11 mmol) was added 2 equiv of $P^{Me}{}_2N^{Ph}{}_2$ (80 mg, 0.24

mmol). The blue solution of $[Ni(CH_3CN)_6](BF_4)_2\cdot 1/2CH_3CN$ rapidly changed to red. The resultant red solution was stirred overnight, then filtered through a plug of Celite. The solvent was removed under vacuum. The red powder was washed with diethyl ether and dried in vacuo (yield 68 mg, 76 mmol, 69%). $^{31}P\{^1H\}$ NMR (CD_3CN, 202.2 MHz): δ 1.3 (s). ^1H NMR (CD_3CN, 499.7 MHz): δ 7.38 (t, J = 7.6 Hz, 8H, Ar*H*); 7.12 (m, 8H, Ar*H*); 7.06 (m, 4H, Ar*H*); 3.75 (m, 16H, PCH_2N); 1.87 (s, 12H, CH_3). ESI-MS: Observed $\{[Ni(P_2N_2)_2](BF_4)\}^+$: 805.2204 Calculated for $\{[Ni(P_2N_2)_2](BF_4)\}^+$: 805.2212. Analysis Calcd for $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2\cdot 2MeCN$, $C_{40}H_{54}B_2F_8N_6NiP_4$: C, 49.27; H, 5.58; N, 8.62. Found C, 49.21; H, 5.78; N, 8.29.

Equilibration of $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ with H_2 and Collidine/Collidinium in Acetonitrile-d_3. In a typical experiment, $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2\cdot 2MeCN$ and collidine (pK_a = 14.98)[79] were accurately weighed into an NMR tube and dissolved in acetonitrile-d_3 (0.5 mL). Hydrogen gas was bubbled through the solution for 10 min. The solution was allowed to sit for 15 min and was monitored by ^1H NMR and ^{31}P NMR spectroscopy. The reaction came to equilibrium within the time of mixing and was monitored every few hours for 2 days to ensure that the ratios had not changed. The ^{31}P NMR resonances assigned to $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ (1.3 ppm) and the corresponding hydride, $[HNi(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)$ (2.1 ppm) were integrated. The ratio of $[HBase^+]/[Base]$ was determined from the observed ^1H NMR chemical shift. These ratios were used to determine the equilibrium constant for the reaction. Three separate experiments were carried out to determine the reproducibility. The equilibrium constant ($K = [NiH^+][HBase^+]/P_{H2}\,[Ni^{2+}][Base]$) was used to calculate the hydride donor ability. The value of $\Delta G^0{}_{H^-}$ is reported as an average of three runs: ΔG_{H^-} = 54.0 kcal/mol with a standard deviation of less than 0.5 kcal/mol. Purging the samples with N_2 gas for 15 min resulted in the observation of only $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$.

Electrochemistry. Voltammetric procedures were conducted in 0.2 M NEt_4BF_4/CH_3CN at ambient temperature (23 °C) under nitrogen using a Vacuum Atmospheres glovebox. A standard three-electrode configuration was employed in conjunction with CH Instruments 660C or 1100C potentiostat interfaced to a computer with CH Instruments 700 D software. All voltammetric scans were recorded using glassy-carbon working electrode disks of 1 mm diameter encased in PEEK (Cypress Systems EE040). The working electrode was treated between scans by polishing with diamond paste (Buehler) in sequence of decreasing sizes (3 to 0.25 μm) interspersed by washings with purified H_2O. A Glassy-carbon rod (Structure Probe, Inc.) and platinum wire (Alfa-Aesar) were used as auxiliary electrodes and quasi-reference electrodes respectively. All glassware for electrochemical experiments was oven-dried overnight and allowed to cool under vacuum. Ferrocene was used as an internal standard, and all potentials reported within this work are referenced to the ferrocenium/ferrocene couple at 0 V.

Catalytic Hydrogen Production Using $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ as Catalyst and $[(DMF)H]OTf$ as Acid. Typical Experimental Conditions: $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2\cdot 2MeCN$ (1 mg, 0.001 mmol) and ferrocene (0.4 mg, 0.002 mmol) were weighed into an 8 mL glass vial and dissolved in 2 mL of a supporting electrolyte solution (0.2 M NEt_4BF_4 in acetonitrile). Purity of the electrolyte medium was confirmed over the available electrochemical window through background scans taken prior to addition of analyte. In a separate vial, 250 mg (1.1 mmol) of $[(DMF)H]OTf$ was dissolved in 1 mL of acetonitrile. Acidic titrant was transferred to the electrochemical solution via volumetric syringe in 20 μL aliquots. Subsequent to each addition of titrant, the working electrode was cleaned by polishing (vide supra) and a cyclic voltammogram was recorded. The catalytic current (i_{cat}) was measured at −1.3 V. Addition of acidic titrant was continued until catalytic current enhancement ceased (ca. 0.12 M $[(DMF)H]OTf$. Subsequent to the completion of acid additions, the described method was repeated using aliquots of purified H_2O as titrant. H_2O was added by Eppendorf automatic micropipeter in 3−10 μL increments until the observed catalytic current enhancement ceased or catalytic current was reduced.

Controlled Potential Coulometry. The bulk electrolysis vessel and its electrode were assembled under a flow of nitrogen. The working electrode consisted of a copper wire attached to a reticulated vitreous carbon cylinder; the reference electrode was a silver wire, and the auxiliary electrode was a nichrome wire, each placed in a glass electrode compartment separated by Vycor frits. The total volume of this setup was determined to be 295 mL. Inside the glovebox an electrolyte stock solution consisting of 0.1 M Et_4NBF_4 in MeCN was prepared. This electrolyte stock solution was used to prepare a 24 mL solution consisting 0.76 mM $[(Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$ (19.7 mg, 0.022 mmol) and ferrocene. This solution was transferred to the bulk electrolysis vessel and a cyclic voltammogram was recorded. An acid solution containing 5 mL of electrolyte solution and $[(DMF)H]OTf$ (750 mg; 3.36 mmol) was prepared inside the glovebox and added by syringe to the bulk electrolysis vessel. The final solution volume was 29 mL consisting of 0.1 M Et_4NBF_4, 0.76 M $[Ni(P^{Me}{}_2N^{Ph}{}_2)_2](BF_4)_2$, 0.12 M $[(DMF)H]OTf$, and ferrocene. The controlled potential coulometry was performed at −1.50 V versus the ferrocenium/ferrocene as an internal reference. After 30.7, 41.3, and 51.7 C of charge had passed, a 1.0 mL sample of the headspace that had a total volume of 266 mL was removed via gastight syringe and analyzed by gas chromatography. Gas analysis for H_2 was performed using an Agilent 6850 gas chromatograph equipped with a thermal conductivity detector and fitted with a 10 ft long Supelco 1/8″ Carbosieve 100/120 column, calibrated with two $H_2/N_2/CO/CO_2$ mixtures of known composition. Using the moles of H_2 produced and the charge passed, an average current efficiency of 94 ± 5% was calculated for H_2 production. Details are provided in Table 2.

Table 2. Experimental Results from Controlled Potential Coulometry Experiments

sample number	1	2	3
Coulombs (C)	30.7	41.3	51.7
Calcd moles H_2 (mmol)	0.159	0.214	0.268
Exptl. moles H_2 (mmol)	0.149	0.197	0.254
turnovers	7	10	12
current efficiency	94%	92%	95%

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Notes

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