[Ni(P^2N\textsubscript{2}C\textsubscript{6}H\textsubscript{4}X\textsubscript{2})\textsubscript{2}]\textsuperscript{2+} Complexes as Electrocatalysts for H\textsubscript{2} Production: Effect of Substituents, Acids, and Water on Catalytic Rates


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Supporting Information

ABSTRACT: A series of mononuclear nickel(II) bis(diphosphine) complexes [Ni(P\textsubscript{2}N\textsubscript{2}C\textsubscript{6}H\textsubscript{4}X\textsubscript{2})\textsubscript{2}]\textsuperscript{2+} (P\textsubscript{2}N\textsubscript{2}C\textsubscript{6}H\textsubscript{4}X\textsubscript{2} = 1,5-di(\textit{para}-X-phenyl)-1,5-diaza-3,7-diphosphacyclooctane; X = OMe, Me, P(O)(OEt)\textsubscript{2}, Br, and CF\textsubscript{3}) have been synthesized and characterized. X-ray diffraction studies reveal that [Ni(P\textsubscript{2}N\textsubscript{2}C\textsubscript{6}H\textsubscript{4}Me\textsubscript{2})\textsubscript{2}]\textsuperscript{2+} and [Ni(P\textsubscript{2}N\textsubscript{2}C\textsubscript{6}H\textsubscript{4}OMe\textsubscript{2})\textsubscript{2}]\textsuperscript{2+} are tetracoordinate with distorted square planar geometries. The Ni(II/I) and Ni(I/0) redox couples of each complex are electrochemically reversible in acetonitrile with potentials that are increasingly cathodic as the electron-donating character of X is increased. Each of these complexes is an efficient electrocatalyst for hydrogen production at the potential of the Ni(II/I) couple. The catalytic rates generally increase as the electron-donating character of X is decreased, and this electronic effect results in the favorable but unusual situation of obtaining higher catalytic rates as overpotentials are decreased. Catalytic studies using acids with a range of pK\text{a} values reveal that turnover frequencies do not correlate with substrate acid pK\text{a} values but are highly dependent on the acid structure, with this effect being related to substrate size. Addition of water is shown to dramatically increase catalytic rates for all catalysts. With [Ni(P\textsubscript{2}N\textsubscript{2}C\textsubscript{6}H\textsubscript{4}P(O)(OEt)\textsubscript{2}\textsubscript{2})\textsubscript{2}]\textsuperscript{2+} using [(DMF)\textsubscript{2}H]\textsuperscript{+} OT\textsubscript{f} as the acid and with added water, a turnover frequency of 1850 s\textsuperscript{-1} was obtained.

INTRODUCTION

Controlling the intra- and intermolecular movement of protons is an essential feature of catalytic processes involving multiple protons and electrons. For example, hydrogenase and cytochrome c oxidase enzymes have proton channels consisting of multiple proton relays that facilitate the exchange of protons during the production of only 5 s\textsuperscript{-1}.17 These results clearly indicate that

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the nitrogen substituents of the \( \text{P}^2\text{N}^{2-} \) ligands play an important role in the catalytic activity for these complexes and suggest that more basic amines disfavor catalytic \( \text{H}_2 \) formation. In this study we have prepared a series of \([\text{Ni}(\text{P}^2\text{N}^{2-}\text{C}_6\text{H}_4\text{X})_2] (\text{BF}_4)_2\) derivatives, in which the substituent \( X \) in the para position of the \( \text{N} \) aryl substituent is varied. Such substituent changes are expected to influence the basicity of the pendant amine while minimizing steric and electronic variations at the metal ion. We report here the effect of these substituent variations on the redox potentials of the \( \text{Ni}(II)/I \) and \( \text{Ni}(I/0) \) couples of the complexes and on their catalytic rates for \( \text{H}_2 \) production. Interestingly, the catalytic rates increase as the \( \text{Ni}(II/I) \) potentials become more positive. The overpotentials thus decrease with increasing activity, an unusual but beneficial trend. In addition, we report the effects of acid strength on \( \text{H}_2 \) production rates, and our observation that water enhances the catalytic rates for these complexes. Under the best conditions, turnover frequencies as high as \( 1850 \text{ s}^{-1} \) have been observed for \( \text{H}_2 \) production at room temperature.

## RESULTS

### Synthesis and Characterization of Ligands and Complexes

The new and previously reported ligands used in this study were prepared using a single-flask two-step reaction (eq 1).

In the first step a slight excess of two equivalents of paraformaldehyde was treated with phenylphosphine to form bis-(hydroxymethyl)phenylphosphine. This step was followed by the addition of a solution of two equivalents of a para-substituted aniline in hot ethanol. The desired ligands precipitated as white solids upon cooling, and subsequent workup produced the ligands in reasonable yields and good purity. These ligands were characterized by \( ^1\text{H} \) and \( ^3\text{P} \{^1\text{H}\} \) NMR spectroscopy, elemental analyses, and mass spectroscopy, all of which are consistent with the structures indicated. The data for the new ligands are given in the Experimental Section.

The addition of two equivalents of a \( \text{P}^2\text{N}^{2-}\text{C}_6\text{H}_4\text{X} \) _2_ ligand to an acetonitrile solution of \([\text{Ni}(\text{Me}_3\text{CN})_6](\text{BF}_4)_2\) followed by workup provides a convenient synthesis of \([\text{Ni}(\text{P}^2\text{N}^{2-}\text{C}_6\text{H}_4\text{X})_2] (\text{BF}_4)_2 \) (X = OMe, Me, \( \text{CH}_2\text{P}(\text{O})(\text{OEt})_2 \), H, Br, CF\(_3\); eq 2). The \( ^3\text{P} \{^1\text{H}\} \) NMR spectra of these complexes all consist of one singlet resonance between 3 and 8 ppm, shifted by 50 ppm downfield upon coordination of the ligand to the metal. The simple \( ^1\text{H} \) NMR spectra indicate rapid interconversion between chair and boat conformations of the six-membered \( \text{NiP}_2\text{C}_2\text{N} \) rings. Elemental analyses and mass spectral data are also consistent with the proposed structures.

### Structural Studies

Dark-red crystals of \([\text{Ni}(\text{P}^2\text{N}^{2-}\text{C}_6\text{H}_4\text{OMe})_2] (\text{BF}_4)_2 \) and \([\text{Ni}(\text{P}^2\text{N}^{2-}\text{C}_6\text{H}_4\text{Me})_2] (\text{BF}_4)_2 \) were grown from a 1:3 THF:acetonitrile solution and a 20:1 THF:acetonitrile solution, respectively, by slow evaporation of the solvent under \( \text{N}_2 \) over several days. For \([\text{Ni}(\text{P}^2\text{N}^{2-}\text{C}_6\text{H}_4\text{OMe})_2] (\text{BF}_4)_2 \) the crystals consist of discrete cations, tetrifuoroborate anions, and an unbound acetonitrile molecule. For \([\text{Ni}(\text{P}^2\text{N}^{2-}\text{C}_6\text{H}_4\text{Me})_2] (\text{BF}_4)_2 \) the crystals consist of discrete cations, tetrifuoroborate anions, and two THF molecules. The overall structures are best described as square planes with tetrahedral distortions resulting from a twisting of the diphenyl ligands to mitigate steric interactions between the phenyl groups on phosphorus. The dihedral angles between the \( \text{P}(1)−\text{Ni}(1)−\text{P}(2) \) plane defined by one diphenylphosphine ligand and nickel and the \( \text{P}(3)−\text{Ni}(1)−\text{P}(4) \) plane defined by the other phosphine ligand and nickel are 24.16° for \( X = \text{Me} \) and 29.07° for \( X = \text{OMe} \) (Figure 1). This may be compared to a dihedral angle of 34.88° for \([\text{Ni}(\text{P}^2\text{N}^{2-}\text{C}_6\text{H}_4\text{OMe})_2] (\text{BF}_4)_2 \) (Cy = cyclohexyl, \( Bz = \text{benzyl} \)), for which the steric interactions between adjacent P substituents are expected to be larger, and a dihedral angle of 2.4° for \([\text{Ni}(\text{dmpe})_2] (\text{PF}_6)_2 \) (dmpe = 1,2-bis(dimethylphosphino)ethane), for which these steric interactions are smaller. In both structures, one \( \text{BF}_4^- \) ion is closer to Ni than the other, with one F atom oriented toward the Ni center. However, the Ni–P distances

![Figure 1](Attachment1.png)
(2.98 Å for X = OMe and 2.62 Å for X = Me) are longer than the sum of the covalent radii, 1.88 Å (Figure 1), suggesting that cation–anion interactions in the solid state likely arise from electrostatic/packing effects rather than coordinative interactions. In both structures, the closer BF$_4^-$ anion is accommodated by the conformations of the adjacent six-membered Ni-olate rings, with these rings assuming chair conformations and the opposing rings adopting boat conformations.

**Cyclic Voltammetry Studies of [Ni(PPh$_2$N$_2$H$_4$X)$_2$] (BF$_4$)$_2$ Complexes.** Each of the [Ni(PPh$_2$N$_2$H$_4$X)$_2$] (BF$_4$)$_2$ complexes used in this study shows two distinct and reversible reduction waves assigned to the Ni(II/I) and Ni(I/O) couples. All redox potentials, reported vs the Cp$_2$Fe/Cp$_2$Fe couple, and Δ$E_p$ values are presented in Table 3. Plots of the peak currents ($i_p$) versus the square root of the scan rate are linear for both waves, indicating that these redox reactions are diffusion controlled. As the electron-donating ability of the para substituent increases, as measured by the $pK_a$ values of the corresponding anilinium salt, the $i_p$ and Δ$E_p$ values are increased.

**Catalytic Hydrogen Production.** The complexes [Ni(PPh$_2$N$_2$H$_4$X)$_2$] (BF$_4$)$_2$ (X = OMe, Me, H, CH$_2$P(O)(O-Et)$_2$, Br, CF$_3$) are all active as electrocatalysts for H$_2$ production using Bronsted acid substrates. Their activities were measured by successive cyclic voltammetry of reaction mixtures for which the acid concentrations were systematically increased until the ratio $i_{cat}/i_p$ of the catalytic current ($i_{cat}$) to the peak current of the Ni(II/I) reduction wave in the absence of acid ($i_p$) remained constant (the acid-independent region). Figure 3A shows a typical series of voltammograms obtained with increasing acid concentrations, and Figure 3B shows a corresponding plot of the catalytic current enhancement, $i_{cat}/i_p$ vs [acid]. From Figure 3B it can be seen that $i_{cat}/i_p$ shows a strong dependence on acid concentration at low acid concentrations, but this ratio becomes independent of the acid concentration above approximately 0.2 M. The potential at which $i_{cat}$ was measured was located by finding the potential negative of the potential of the Ni(II/I) couple for which the second derivative of the $i$–$E$ trace was approximately zero. These potentials were sufficiently negative to ensure quantitative reduction of Ni(II) species, 100–150 mV negative of $E_{1/2}$. At these potentials reduction of the acid by the electrode surface, onset of which is observed at $E_{1/2}$, was not a factor. The experimentally observed half-peak potentials for catalytic waves ($E_{cat}^{1/2}$) were within 50 mV of $E_{1/2}$ values for the corresponding Ni(II/I) couples. These results indicate that catalysis proceeds with reduction of the Ni(II) complex followed by protonation of the Ni(I) complex, consistent with the catalytic cycle proposed previously for catalysts of this class.

Turnover numbers were determined using eq 3 from $i_{cat}$/$i_p$ values in the acid-independent region, as shown in Figure 3B.

$$i_{cat} = n \frac{RTK_{obs}}{FV}$$

In eq 3 $i_{cat}$ is the catalytic current measured in the presence of acid, $i_p$ is the peak current for the Ni(II/I) redox couple measured in the absence of acid, $n$ is the number of electrons involved in the reaction, $K_{obs}$ is the observed rate constant, $R$ is the gas constant, $T$ is the temperature, and $F$ is Faraday's constant.

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**Table 1. Selected Bond Distances and Angles for [Ni(PPh$_2$N$_2$H$_4$OMe)$_2$] (BF$_4$)$_2$**

<table>
<thead>
<tr>
<th>bond distances (Å)</th>
<th>bond angles (°)</th>
</tr>
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<tr>
<td>Ni(1)–P(1)</td>
<td>2.1920(12)</td>
</tr>
<tr>
<td>Ni(1)–P(2)</td>
<td>2.264(13)</td>
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<tr>
<td>Ni(1)–P(3)</td>
<td>2.1965(12)</td>
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<tr>
<td>Ni(1)–P(4)</td>
<td>2.2163(13)</td>
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<td>Ni(1)⋅⋅⋅N(1)</td>
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<tr>
<td>Ni(1)⋅⋅⋅N(2)</td>
<td>3.770</td>
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<td>Ni(1)⋅⋅⋅N(3)</td>
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<tr>
<td>Ni(1)⋅⋅⋅N(4)</td>
<td>3.771</td>
</tr>
</tbody>
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**Table 2. Selected Bond Distances and Angles for [Ni(PPh$_2$N$_2$H$_4$Me)$_2$] (BF$_4$)$_2$**

<table>
<thead>
<tr>
<th>bond distances (Å)</th>
<th>bond angles (°)</th>
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<td>Ni(1)–P(1)</td>
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<td>2.1947(4)</td>
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<td>Ni(1)⋅⋅⋅N(2)</td>
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<td>Ni(1)⋅⋅⋅N(3)</td>
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<td>Ni(1)⋅⋅⋅N(4)</td>
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**Table 3. Electrochemical Data for [Ni(PPh$_2$N$_2$H$_4$X)$_2$] (BF$_4$)$_2$ Complexes in Acetonitrile (0.2 M Et$_4$N$^+$BF$_4^-$)***

<table>
<thead>
<tr>
<th>X</th>
<th>$E_{1/2}$ (V)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$E_{1/2}$ (V)</th>
<th>$\Delta E_p$ (mV)</th>
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</thead>
<tbody>
<tr>
<td>OMe</td>
<td>$-0.88$</td>
<td>67</td>
<td>$-1.07$</td>
<td>74</td>
</tr>
<tr>
<td>Me</td>
<td>$-0.84$</td>
<td>74</td>
<td>$-1.05$</td>
<td>73</td>
</tr>
<tr>
<td>CH$_2$P(O)(OEt)$_2$</td>
<td>$-0.84$</td>
<td>73</td>
<td>$-1.02$</td>
<td>76</td>
</tr>
<tr>
<td>H</td>
<td>$-0.83$</td>
<td>71</td>
<td>$-1.02$</td>
<td>76</td>
</tr>
<tr>
<td>Br</td>
<td>$-0.79$</td>
<td>63</td>
<td>$-0.97$</td>
<td>74</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>$-0.74$</td>
<td>78</td>
<td>$-0.89$</td>
<td>64</td>
</tr>
</tbody>
</table>

*Referenced to the Cp$_2$Fe$^+/Cp$_2$Fe couple.**
Figure 3. (A) Cyclic voltammograms of $[\text{Ni}(\text{PPh}_2\text{NPh}_2\text{CH}_2\text{P(O)}\text{OEt})_2]\text{(BF}_4\text{)}_2$ (0.7 mM) in the absence of acid (black trace) and with varying concentrations of acid (acid = 1:1 DMF: [(DMF)H]+ OTf−; red traces) in acetonitrile (0.2 M Et,N'BF4−). Scan rate $\nu = 50$ mV/s. (B) Corresponding plot of $i_{\text{cat}}/i_p$ vs acid concentration.

catalytic production of H₂. R is the gas constant, T is the temperature in K, F is the Faraday constant, $\nu$ is the scan rate in V/s, and $k_{\text{obs}}$ is the observed rate constant. In the acid-independent region, the overall rate is first order in catalyst but independent of acid, and $k$ is a first-order rate constant with units of s$^{-1}$ equivalent to the turnover frequency of the catalyst. The rate law under these conditions indicates that an intramolecular process is rate determining. Because NMR spectroscopy studies have shown that intramolecular proton exchange is fast (10$^{-8}$–10$^{-9}$ s$^{-1}$ at 22 °C) for hydrogen oxidation catalysts of this class,7,9 we have interpreted this slower intramolecular process to be associated with the elimination of H₂ from the nickel catalyst. The turnover frequencies determined for the entire series of catalysts studied here are summarized in Table 4. This table also includes data that shows how turnover frequencies for H₂ production, and this has been attributed to the different basicities of the two pendant amines. To explore the role of the basicity of the pendant amines in more detail, we have measured the catalytic rates of H₂ production for the complexes described in this paper using the following acids: [(DMF)H]+ OTf− (pK$_\text{a}$ MeCN= 6.1)$^{26,27}$ and a 1:1 mol mixture of DMF and [(DMF)H]+ OTf− (1:1 DMF-[(DMF)H]+ OTf−), 4-cyanoanilinium tetrafluoroborate (pK$_\text{a}$ MeCN= 7.0)$^{26,28}$ and 2,6-dichloroanilinium triflate (pK$_\text{a}$ MeCN = 5.0)$^{21}$.

Effect of Substituents X on Catalytic Rates. As discussed in the Introduction, the previously studied $[\text{Ni}(\text{PPh}_2\text{NPh}_2\text{CH}_2\text{P(O)}\text{OEt})_2]\text{(BF}_4\text{)}_2$ and $[\text{Ni}(\text{PPh}_2\text{NPh}_2\text{CH}_2\text{P(O)}\text{OEt})_2]\text{(BF}_4\text{)}_2$ complexes exhibit significantly different rates for H₂ production, and this has been attributed to the different basicities of the two pendant amines. To explore the role of the basicity of the pendant amines in more detail, we have measured the catalytic rates of H₂ production for the complexes described in the preceding paragraph for the $[\text{Ni}(\text{PPh}_2\text{NPh}_2\text{CH}_2\text{P(O)}\text{OEt})_2]\text{(BF}_4\text{)}_2$ series of complexes. By varying the para substituent (X) of the pendant aniline base, it should be possible to probe the effect of changing the basicity at the N atom without significantly altering the steric properties of the catalyst. When [(DMF)H]+ OTf− was used as the acid, the $[\text{Ni}(\text{PPh}_2\text{NPh}_2\text{CH}_2\text{P(O)}\text{OEt})_2]\text{(BF}_4\text{)}_2$ complexes showed activities increasing from 310 to 740 s$^{-1}$ as the electron-withdrawing ability of X increased from OMe to Br, as shown in the first column of Table 4. A lower rate was observed for the CF₃ complex. Plots of the turnover frequency vs the pK$_\text{a}$ values of the corresponding p-XC₆H₄NH₃ acids and of the turnover frequency vs the potentials of the Ni(II/ I) couples are shown in Figure 4. The plots indicate a general increase in the rates as the pK$_\text{a}$ values of the protonated aniline bases decrease and as the redox potentials of the catalysts become more positive. These trends are elaborated in the Discussion.

Effect of Water on Catalytic Rates. The addition of water (0.02–0.5 M) to reaction mixtures containing 0.20–0.45 M [(DMF)H]+ OTf− increased the catalytic rates by 30–60%. Figure 5 shows a representative example. The addition of larger concentrations of water (up to 2.4 M) to solutions containing the anilinium acids resulted in more significant rate increases (200–1400%), see Tables 4 and S1 and S2.
Information). After the maximum current enhancement was reached in each case, the addition of further aliquots of water resulted in a decrease in catalytic activity. The largest proportional gain was realized for the phosphonate complex, \( \text{X} = \text{CH}_2\text{P(O)(OEt)}_2 \) and either 2,6-dichloroanilinium or 4-cyanoanilinium as the acid, and the largest turnover frequency, 1850 s \(^{-1} \), was observed for the phosphonate complex using \([\text{DMF}]+\text{OTf}^-\) as the acid (350 mM) with added water (550 mM). Our initial reported turnover frequency of 350 s \(^{-1} \) for \([\text{Ni}(\text{PPh}_2\text{N}^\text{C}_6\text{H}_4\text{X}_2)\text{BF}_4]_2\) titrated with 1:1 DMF:\([\text{DMF}]+\text{OTf}^-\) red traces) is bracketed by the values reported here for catalysis in the absence of water (270 s \(^{-1} \)) and in its presence (480 s \(^{-1} \)), suggesting the presence of trace quantities of adventitious water in prior experiments.12

The catalytic current was monitored as a function of water concentration to obtain kinetic data on the rate increases observed upon addition of water. Figure 6 shows plots of the observed catalytic rate as a function of water concentration along with fits to the experimental data according to a first-order and a second-order dependence on water concentration. In these kinetic studies, the concentration range over which water produces a measurable effect is small (0.05–2.4 M), and the resulting correlation coefficients for a linear fit (\( R^2 = 0.9916 \)) and a square fit (\( R^2 = 0.9900 \)) are similar, so a reaction order in [water] for the catalytic reaction has not been assigned.

Table 4. Turnover Frequencies (TOF, s \(^{-1} \)) and Overpotentials (OP, mV, in Parentheses) for Electrocatalytic Hydrogen Production by \([\text{Ni}(\text{PPh}_2\text{N}^\text{C}_6\text{H}_4\text{X}_2)\text{BF}_4]_2\) Complexes using Various Acids

<table>
<thead>
<tr>
<th>( \text{X} )</th>
<th>([\text{DMF}]+\text{OTf}^-)</th>
<th>( p_{K_{\text{MeCN}}} = 6.1 )</th>
<th>1:1 DMF:([\text{DMF}]+\text{OTf}^-)</th>
<th>( p_{K_{\text{MeCN}}} = 6.1 )</th>
<th>2,6-Cl(_2)C(_6)H(_4)NH(_3^+)</th>
<th>( p_{K_{\text{MeCN}}} = 5.0 )</th>
<th>4-NCC(_6)H(_4)NH(_3^+)</th>
<th>( p_{K_{\text{MeCN}}} = 7.0 )</th>
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<tbody>
<tr>
<td>( \text{OMe} )</td>
<td>310</td>
<td>(310)</td>
<td>150</td>
<td>(330)</td>
<td>16</td>
<td>(330)</td>
<td>25</td>
<td>(270)</td>
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<tr>
<td>( \text{Me} )</td>
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<td>(330)</td>
<td>280</td>
<td>(350)</td>
<td>51</td>
<td>(360)</td>
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<tr>
<td>( \text{H} )</td>
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<td>290</td>
<td>(310)</td>
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<td>(320)</td>
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<td>(290)</td>
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<td>( \text{Br} )</td>
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<td>(360)</td>
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<td>(320)</td>
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<td>(370)</td>
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<td>(350)</td>
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<tr>
<td>( \text{CF}_3 )</td>
<td>950</td>
<td>(320)</td>
<td>290</td>
<td>(340)</td>
<td>31</td>
<td>(320)</td>
<td>16</td>
<td>(290)</td>
</tr>
</tbody>
</table>

Average of multiple runs. Values obtained after water was added are given in italics. Water concentrations giving maximum turnover frequencies ranged from 0.02 to 2.4 M. More complete information is available in the Supporting Information.

Figure 4. Turnover frequency (s \(^{-1} \); obtained with \([\text{DMF}]+\text{OTf}^-\) as acid and with no added water) for electrocatalytic hydrogen production by \([\text{Ni}(\text{PPh}_2\text{N}^\text{C}_6\text{H}_4\text{X}_2)\text{BF}_4]_2\) complexes: (A) as a function of the protonated form of the para-substituted aniline \( p^{-}\text{X-C}_6\text{H}_4\text{NH}_2 \) from which the \( \text{PPh}_2\text{N}^\text{C}_6\text{H}_4\text{X}_2 \) ligand is derived, and (B) as a function of the potential of the Ni(II/I) couple.

Figure 5. Cyclic voltammograms of \([\text{Ni}(\text{PPh}_2\text{N}^\text{C}_6\text{H}_4\text{CH}_2\text{P(O)(OEt)}_2 \text{BF}_4]_2\) (0.7 mM) in the absence of acid (black trace), with varying [acid] (acid = 1:1 DMF:\([\text{DMF}]+\text{OTf}^-\); red traces) and with varying [water] (blue traces, [acid] = 0.26 M), in acetonitrile (0.2 M Et\(_4\)N\(^+\)BF\(_4^-\)). Scan rate \( v = 50 \text{ mV/s} \). The acid concentration chosen for water addition was sufficient for acid independence in the absence of water.
In some cases where water has been found to act as a cocatalyst, replacement of water with an alcohol has also been found to promote the catalytic reaction of interest. When ethanol (0.23 M) was added to an electrolyte solution containing \([\text{Ni}(\text{Ph})_2]^2+\) and \([\text{DMF}]^+\cdot\text{OTf}^-\) as acid in acetonitrile (0.2 M Et₄N BF₄⁻), no current enhancement was observed. However, with 2,6-dichloroanilinium triflate as the acid, a 6-fold increase in the catalytic rate was observed with added ethanol (1.4 M). Under the same conditions, addition of water increased the turnover frequency by a factor of 14.

**Effect of Dimethylformamide (DMF).** \(^{31}P\) NMR spectra and cyclic voltammograms of complexes \([\text{Ni}(\text{Ph})_2^2+\)(C₆H₄CF₃)\] and \([\text{Ni}(\text{Ph})_2^2+\)(C₆H₄Br)\] in acetonitrile solutions showed that these complexes undergo ligand displacement in the presence of DMF. Dissolving \([\text{Ni}(\text{Ph})_2^2+\)(C₆H₄CF₃)\] in pure DMF solutions resulted in the precipitation of a pale-green crystalline material attributed to \([\text{Ni}(\text{DMF})_2]^2+\)(BF₄⁻). In acetonitrile solutions with lower concentrations of DMF, both \([\text{Ni}(\text{Ph})_2^2+\)(C₆H₄CF₃)\] and the free ligand were observed by \(^{31}P\) NMR. This equilibrium process may contribute to the low catalytic rate observed for this complex with 1:1 DMF: solution. Theoretical studies of the reverse reaction, H₂ elimination, by this class of catalysts suggested structure 4 as the transition state. This structure suggests that hydrogen elimination should be favored by decreasing the basicity of the pendant amines (making the N–H more acidic) and increasing the hydride donor ability of the Ni(II) hydride.

**Dependence of the Catalytic Rates for H₂ Production on X.**

In the current study we sought to explore the effect of changing the basicity of the pendant amines in \([\text{Ni}(\text{Ph})_2^2+\)(C₆H₄X)\] by changing para substituents on the aniline ring, while maintaining the hydride donor ability as constant as possible by using only the phenyl substituent on phosphorus. To this end, a series of \([\text{Ni}(\text{Ph})_2^2+\)(C₆H₄X)\] complexes with a wide range of electron-donor abilities for X have been synthesized and characterized. It can be seen from Figure 4B that the catalytic rates increase as the potentials of the catalysts become more positive. This is both unusual and beneficial. Positive shifts in catalyst potentials resulting from inductive effects typically lead to decreases in catalytic rates for reductive processes such as H₂ production, \(^{31}P\) CO₂ reduction, \(^{32}\) or O₂ reduction. \(^{33}\) The origin of the different behavior observed for the \([\text{Ni}(\text{Ph})_2^2+\)(C₆H₄X)\] catalysts described here is their bifunctional nature, in which both hydride and proton donors are incorporated in the same molecule. More positive potentials for the Ni(II/I) couples resulting from inductive effects will lead to a decrease in the hydride donor ability of the catalyst. This can be seen in Figure 4B that the catalytic rates increase as the potentials of the catalysts become more positive. This is both unusual and beneficial. Positive shifts in catalyst potentials resulting from inductive effects typically lead to decreases in catalytic rates for reductive processes such as H₂ production, \(^{31}P\) CO₂ reduction, \(^{32}\) or O₂ reduction. \(^{33}\) The origin of the different behavior observed for the \([\text{Ni}(\text{Ph})_2^2+\)(C₆H₄X)\] catalysts described here is their bifunctional nature, in which both hydride and proton donors are incorporated in the same molecule. More positive potentials for the Ni(II/I) couples resulting from inductive effects will lead to a decrease in the hydride donor ability of the transition state, but this is offset by an even larger increase in the acidity of the protonated pendant amine. It is the \textit{total} intramolecular driving force for H₂ elimination that affects the catalytic rate, and this does not necessarily parallel the reduction potential of the catalyst.

In acetonitrile, the difference in pKₐ values between free anilinium ions (p-XC₆H₄H⁺) with the most electron-donating group, OMe (11.8)\(^{31}\), and the most electron-withdrawing group, CF₃ (8.0)\(^{21}\), is 3.8 pKₐ units. A similar difference in pKₐ values would be expected for the protonated pendant bases of the corresponding \([\text{Ni}(\text{Ph})_2^2+\)(C₆H₄X)\] complexes, and this should provide an added driving force for H₂ elimination of 5.2 kcal/mol as X is varied from OMe to CF₃. Figure 4A shows a plot of the turnover frequency for H₂ production versus the pKₐ of the corresponding anilinium acid, and it can be seen that the catalytic rates generally increase with the expected increase in the acidity of the protonated pendant amine.

This increase in acidity is partially offset by a decrease in the hydride donor ability. Because the potentials of the Ni(II/I) couples for the X = OMe and CF₃ derivatives differ by 0.14 V, the hydride donor ability of \([\text{HNi}(\text{Ph})_2^2+\)(C₆H₄X)\](BF₄⁻) should decrease by 2.7 kcal/mol relative to X = OMe, based on a
previously published linear free energy relationship between the Ni(II/1) potentials and the hydride donor abilities ($\Delta G^\ddagger_{\mathrm{H}} = 19.2$ $E_{1/2}(\mathrm{I/I}) + 77.3$ kcal/mol). As a result, the decrease in hydride donor ability attenuates the increase in driving force for H$_2$ elimination expected from differences in the acidities of the protonated pendant amines alone. However H$_2$ elimination is still expected to become more favorable by 2.5 kcal/mol (5.2–2.7 kcal/mol) as X is varied from OMe to CF$_3$. The catalytic rates should increase, and the potentials should shift more positive, reducing the overpotential. With the exception of the CF$_3$ complex (discussed further in the next section, Dependence of Catalytic Rates on Acid Strength), the results shown in Figure 4 and Table 4 agree with the expected trend. It is the acidity of the protonated pendant amine that dominates the driving force for H$_2$ elimination and determines the trend in catalytic rates for this series of complexes. This leads to the unusual increase in the catalytic rates for these complexes as the overpotentials decrease.

Dependence of Catalytic Rates on Acid Strength. The effect of acid strength on maximum turnover frequency has been tested by comparing anilinium salts of different acidities as substrates with the expectation that in the acid-independent region, the turnover frequency for a given catalyst will be independent of the pK$_a$ of the acid. This is the case for X = OMe, Me, H, CH$_2$P(O)(OEt)$_2$, and Br. Within a factor of 2, the turnover frequencies are the same regardless of whether 2,6-dichloroanilinium triflate (2,6-Cl$_2$AnH$^+$OTf$^-$, pK$_{\text{MeCN}}$ = 5.1)$^{21}$ or 4-cyanoanilinium tetrafluoroborate (pK$_{\text{MeCN}}$ = 7.0)$^{28}$ is the substrate. However, for the catalyst with X = CF$_3$, the rate is similar to that observed for X = Br when the stronger acid 2,6-dichloroanilinium is used but is considerably slower with 4-cyanoanilinium as the acid. The less acidic 4-cyanoanilinium substrate does not effectively protonate the pendant bases of the intermediate complexes [Ni(P$_{\text{Ph}}$N$_{\text{Cy}}$(CH$_2$)$_2$)$_2$]$^{2+}$ or [HNi(P$_{\text{Ph}}$N$_{\text{Cy}}$((CH$_2$)$_2$)$_2$)]$^+$ under the conditions studied.

A more quantitative estimate of the basicity of the pendant amines in these complexes is instructive. The pK$_a$ values of the protonated anilinium centers in the series of complexes studied here can be estimated by assuming a constant dihedral angle, a reasonable assumption based on experimental data for related systems. The pK$_a$ values for the free anilinium salts, p-XC$_6$H$_4$NH$_3^+$, are 6.8 (OMe); 6.2 (Me); 5.7 (CH$_2$P(O)(OEt)$_2$); 5.6 (H); 4.4 (Br); and 3.0 (CF$_3$). Although these values are estimates, they indicate that formation of [Ni(P$_{\text{Ph}}$N$_{\text{Cy}}$(CH$_2$)$_2$)$_2$]$^{2+}$ intermediates would require relatively strong acids. Under catalytic conditions, acid concentrations as high as 100–200 times that of the catalyst are frequently employed, suggesting that acids weaker than those indicated by the estimated pK$_a$ values of the corresponding [Ni(P$_{\text{Ph}}$N$_{\text{Cy}}$(CH$_2$)$_2$)$_2$]$^{2+}$ intermediates could be used. However, 4-cyanoanilinium, with a pK$_{\text{MeCN}}$ value of 7.0, would likely be ineffective as a proton donor for catalysis by the CF$_3$ complex, i.e., independence of the rate on acid concentration is not likely to be achieved under experimentally relevant conditions. Even [([DMF]H$^+$)$^+$OTf$^-$, with a pK$_{\text{MeCN}}$ of 6.1, would not be expected to fully protonate this catalyst, even at relatively high concentrations. The low basicity, together with the weak coordinating ability of the CF$_3$-containing ligand and its tendency to be displaced by DMF, account for the low turnover frequencies observed for the catalyst with X = CF$_3$ under a variety of conditions.

Dependence of Catalytic Rates on the Nature of the Acid, Water, and Ethanol. Acetonitrile solutions of [(DMF)H$^+$]$^+$OTf$^-$ (pK$_{\text{MeCN}}$ = 6.1)$^{26}$ or 1:1 DMF:[(DMF)H$^+$]$^+$OTf$^-$ gave maximum turnover frequencies far exceeding those obtained with the anilinium acids, even though the pK$_a$ value of [(DMF)H$^+$]$^+$ lies between those of 2,6-dichloroanilinium and cyanoanilinium. With 1:1 DMF:[(DMF)H$^+$]$^+$OTf$^-$, activities were up to 14 times greater than with the anilinium salts, and with [(DMF)H$^+$]$^+$OTf$^-$, activities were between 10 and 50 times greater. These results clearly indicate that the structure of the acid has a substantial impact on catalytic rates even at high acid concentrations where the catalytic rates are independent of acid. In this concentration range the rate-determining step is thought to be the elimination of H$_2$ from a diprotonated Ni(0) intermediate (eq 4).

$$\text{Ni}^{2+} + \text{H}_2 \rightarrow \text{Ni}^0 + 2\text{H}^+$$

For systems that catalyze H$_2$ production, diprotonated Ni(0) intermediates are unstable with respect to H$_2$ elimination (e.g., by an estimated 9 kcal/mol for [Ni(P$_{\text{Ph}}$N$_{\text{Cy}}$(CH$_2$)$_2$)$_2$]$^{2+}$), as a result they have not been detected spectroscopically. However, analogous intermediates have been characterized for related H$_2$ oxidation catalysts by experimental$^{12,14}$ and computational results.$^{14,30}$ Upon addition of H$_2$ to [Ni(P$_{\text{Cy}}$N$_{\text{Bz}}$(CH$_2$)$_2$)$_2$]$^{2+}$ (Cy = cyclohexyl, Bz = benzyl), three isomeric forms of the first observable intermediate, the diprotonated Ni(0) complex [Ni(P$_{\text{Cy}}$N$_{\text{Bz}}$(CH$_2$)$_2$)$_2$]$^{2+}$, shown by structures 3, 7, and 8 (eq 5; Cy and Bz substituents not shown), have been characterized by multinuclear NMR studies. These isomers differ in the sites of protonation and in the conformations of the protonated six-membered chelate rings.

![Diagram](image-url)

Similar isomers are likely to be formed upon protonation of Ni(0) intermediates in the H$_2$ production cycle, but only isomer 3 can continue to evolve as shown in eq 4 to form the proposed nickel hydride/protonated amine ([HNi–NH$_2$])$^{2+}$) transition state, 4, followed by H$_2$ evolution. A similar pathway is not available for isomers 7 and 8. The formation of the catalytically relevant isomer 3 requires two sequential protonations at N atoms in positions that are endo with respect to Ni. Protonation in the endo position is much less likely for sterically bulky acids, as can be appreciated from the structures shown in Figure 1 for [Ni(P$_{\text{Ph}}$N$_{\text{Cy}}$(CH$_2$)$_2$)$_2$]$^{2+}$ and [Ni(P$_{\text{Ph}}$N$_{\text{Cy}}$(CH$_2$)$_2$)$_2$]$^{2+}$. As a result, it is expected that smaller acids would generate isomer 3 more rapidly or in greater amounts than bulkier acids, and this would lead to faster catalytic rates for [(DMF)H$^+$]$^+$ compared to the more sterically demanding acids 2,6-dichloroanilinium and 4-cyanoanilinium.

For all of the acids, the addition of water results in a further increase in the rates of H$_2$ formation catalyzed by the [Ni(P$_{\text{Ph}}$N$_{\text{Cy}}$(CH$_2$)$_2$)$_2$]$^{2+}$ complexes. This is consistent with the hydronium ion formed by protonation of water gaining greater access to the interior of the molecule, enhancing the formation of isomer 3. It seems unlikely that added water increases the turnover frequency by changing either the dielectric of the solvent or the acidity of the solution, since addition of water produces very large catalytic enhancements even at low concentrations.
concentrations where neither dielectric or acidity should change significantly. The highest water concentration at which optimal catalytic rates were obtained was 2.4 M (Table S3 of the Supporting Information), or ~4.3% v/v for the [Ni(PPh2NC6H4X)2]2+ complex having X = CH3P(O)(OEt)2, titrated with 4-cyanoanilinium tetrafluoroborate, with addition of water leading to a 1300% increase in turnover frequency. At 20 °C, a water—acetonitrile mixture having this composition is predicted to have ε = 38.56, a 5% increase compared to neat acetonitrile (ε = 36.67).35 In addition, the different catalysts studied here respond differently to added water, suggesting that specific interactions between water and the catalyst are important, rather than medium effects such as changes to pH or dielectric constants.

It is also possible that the effect of water is related to its ability to serve as a proton relay and/or because of stabilizing effects of hydrogen bonding. Such mechanistic proposals for H—H bond formation or cleavage have been advanced for other systems containing intramolecular bases, and such interactions may be important for the [Ni(Pn3NC6H4X)2]2+ complexes as well. In fact, the addition of ethanol enhances the catalytic rate as does water, albeit to a lesser degree. This effect is seen with 2,6-dichloroanilinium as substrate but not with [(DMF)H]+, again supporting the idea that substrate size is critical in determining catalytic rate. The higher catalytic rates observed for smaller acids and the increased catalytic rates observed in the presence of water are consistent with formation of species such as 3 and 4. The formation of these species requires that both protonation reactions of the doubly reduced [Ni(Pn3NC6H4X)2]2+ complexes occur in the endo positions with respect to Ni. If this interpretation is true, then only a small fraction of the catalyst may participate in the production of H2. This suggests that further design refinements to increase endo protonation and prevent exo protonation could produce significantly more active catalysts than the best catalyst reported here, which has a turnover frequency of 1850 s⁻¹ for H₂ production and is in the 700—9000 s⁻¹ range reported for [NiFe] and [FeFe] hydrogenases.7

Dependence of Catalytic Rates on the Outer Coordination Sphere. The largest turnover frequencies were obtained with [(DMF)H]+OTf⁻ as substrate and with water added to the reaction mixtures. Under these conditions, [Ni(Pn3NC6H4X)(OEt)2]BF4 has a rate of 1850 s⁻¹, the highest reported thus far for this class of catalysts. On the basis of inductive effects, the phosphonate derivative, [Ni(Pn3NC6H4X)(OEt)2]BF4, would be expected to have a turnover frequency slightly lower than that of [Ni(Pn3NC6H4X)2]BF4. This is true when protonated dimethylformamide is used as the acid (see Figure 4 and Table 4). However, in the presence of both acid and water, [Ni(Pn3NC6H4X)(OEt)2]BF4 is more than twice as fast as [Ni(Pn3NC6H4X)2]BF4. This result indicates that groups such as phosphonate, located in the outer coordination sphere of these molecules, can exert a significant influence on the catalytic rate even though they are far from the catalytic site. This also suggests that further modification of the outer coordination sphere to control the delivery of protons to endo positions may be a fruitful avenue for further improvement of these catalysts.

### SUMMARY AND CONCLUSIONS

Previous studies of nickel and cobalt catalysts containing diphosphine ligands with and without pendant amines have demonstrated the importance of the pendant amines in improving catalyst performance in terms of overpotentials and rates. In addition, positioned pendant amines improve catalytic rates significantly compared to catalysts with nonpositioned pendant amines. To study the effect of the acidity of the pendant amine on catalytic activity, a series of complexes of the formula [Ni(Pn3NC6H4X)2]2+, where the para-aniline substituent X = OMe, Me, H, CH3P(O)(OEt)2, Br and CF3 were synthesized and characterized. The turnover frequencies for this series of catalysts are increased by electron-withdrawing para substituents, which favor the release of H2 in the catalytic cycle. Increasing the electron-withdrawing nature of the para substituents of the pendant base also results in more positive potentials for the Ni(II/1) couple at which catalysis occurs. Consequently, the favorable but unusual behavior is observed in which the turnover frequency increases as the overpotential decreases. This behavior is expected to be more common for bifunctional catalysts for H2 production that have both hydride and proton donors incorporated in the same molecule.

In this work it is also demonstrated that the size of the acid as well as the presence of water has a significant influence on turnover frequencies. The dependence on size and water are attributed to the preference of smaller acids to protonate at the catalytically active endo positions of the catalyst. This suggests that controlling the delivery of protons to endo sites should further increase the rates of these catalysts; such studies are currently in progress.

Finally, in the presence of [(DMF)H]+OTf⁻ and water, [Ni(Pn3NC6H4X)(OEt)2]2+ has a turnover frequency of 1850 s⁻¹, more than twice as fast as for the electronically comparable [Ni(Pn3NC6H4X)2]2+ catalyst and in the 700—9000 s⁻¹ range reported for [NiFe] and [FeFe] hydrogenases.7 These rates are the highest reported thus far for this class of catalysts, and they suggest that, in addition to the first and second coordination spheres, the outer coordination sphere can also be used to enhance catalyst performance.

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### EXPERIMENTAL SECTION

Materials and Methods. All manipulations were carried out using standard Schlenk or inert-atmosphere glovebox techniques using oven-dried glassware, unless otherwise indicated. THF (Alfa-Aesar, anhydrous, nonstabilized), acetonitrile (Alfa-Aesar, anhydrous, amine-free), and ether (Burdick & Jackson) were purified by sparging with N₂ and passage through neutral alumina, and ethanol (Pharmco-Aaper absolute anhydrous) was purified by sparging with N₂ and passage through calcium sulfate, using a solvent purification system (PureSolv, Innovative Technologies, Inc.). Dimethylformamide (Burdick & Jackson) was dried over activated 4 Å molecular sieves. Ethyl acetate (Aldrich) was used as received and handled under nitrogen. Dimethylformamide-dichloroanilinium (Alfa-Aesar) was recrystallized from hot ethanol and dried under vacuum. Trifluoromethanesulfonic acid (Aldrich, 99%) was used as received and handled under nitrogen. Dimethylformamide-trifluoromethanesulfonic acid, [(DMF)H]+OTf⁻, was prepared by the method of Favier and Duñach.53 Water was dispensed from a Millipore Milli-Q purifier and sparged with nitrogen. Ferrocene (Aldrich) was sublimed under vacuum before use. Phenylphosphine (Strem, 99%) paraformaldehyde (Aldrich, 95%), diethyl para-amino-phenylphosphonate (Acros, 98%), and para-trifluoromethylaniline (Aldrich, 99%) were used as received; para-anisidine (Aldrich 99%) was sublimed before use.

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Ar
methylsilane. The 31P NMR spectra were referenced to external
product was collected by filtration and dried in vacuo (2.54 g, 4.94 mmol, solvent volume reduced on a vacuum line to 20 mL, and the white solid
60
over a period of 30 min. The resulting white suspension was heated for 2 h at
suspension was immersed in a hot oil bath (65
with phenylphosphine (1.87 g, 17.0 mmol), paraformaldehyde (1.10 g, 33.0 mmol), and 25 mL of ethanol. The resulting suspension was held at 65 °C and stirred for 12 h, forming a clear solution. A solution of para-trifluoromethylaniline (2.62 g, 16.3 mmol) in 10 mL of ethanol was added dropwise to the hot solution over a period of 30 min. Completion of the addition resulted in a white suspension that was heated for 2 h at 45 °C. The mixture was cooled to room temperature, the solvent volume reduced on a vacuum line to 20 mL, and the white solid product was collected by filtration and dried in vacuo (3.74 g, 6.33 mmol, 78%).

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Syntheses. \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \). A 250 mL Schlenk flask was charged with phenylphosphine (1.87 g, 17.0 mmol), paraformaldehyde (1.10 g, 33.0 mmol), and 25 mL of degassed absolute ethanol. The resulting suspension was immersed in a hot oil bath (65 °C) and stirred for 12 h resulting in a clear solution. A degassed solution of para-anisidine (2.09 g, 17.0 mmol) in 10 mL ethanol was added dropwise to the hot solution over a period of 30 min. The resulting white suspension was heated for 2 h at 60 °C. The reaction mixture was cooled to room temperature, the solvent volume reduced on a vacuum line to 20 mL, and the white solid product was collected by filtration and dried in vacuo (2.54 g, 4.94 mmol, 58%). \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \). A 250 mL Schlenk flask was charged with phenylphosphine (1.87 g, 17.0 mmol), paraformaldehyde (1.10 g, 33.0 mmol) and 25 mL of degassed absolute ethanol. The resulting suspension was immersed in a hot oil bath (65 °C) and stirred for 12 h resulting in a clear solution. A degassed solution of para-anisidine (2.09 g, 17.0 mmol) in 10 mL ethanol was added dropwise to the hot solution over a period of 30 min. The resulting white suspension was heated for 2 h at 60 °C. The reaction mixture was cooled to room temperature, the solvent volume reduced on a vacuum line to 20 mL, and the white solid product was collected by filtration and dried in vacuo (2.54 g, 4.94 mmol, 58%).}

Phenylphosphine (2.22 g, 20.2 mmol) and paraformaldehyde (1.256 g, 45.95 mmol) were combined in 10 mL of ethanol and heated with stirring to 60–65 °C for 2 h at which point the mixture had become almost clear. The mixture was then warmed to 85 °C for 4 h and held at 70 °C for 12 h to ensure complete reaction before cannula transferring a 25 mL ethanol solution of diethyl para-aminobenzylphosphonate (4.907 g, 20.17 mmol) to the reaction mixture. The reaction mixture was held at 70 °C for 2 h before removing the solvent, and the residue was transferred to a glovebox for the remaining workup. The residue was stirred with 40 mL of THF forming a white solid and a yellow solution. The solid was collected on a frit, rinsed with ether, and dried in vacuo (5.773 g, 6.75 mmol, 75%). Addition of 60 mL of ether to the filtrate solution resulted in the formation of a light-yellow solid (0.549 g, 0.73 mmol, 7.2%). The combined solids were purified by crystallization from a mixture of acetonitrile and ether. \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \). A 250 mL Schlenk flask was charged with phenylphosphine (1.79 g, 16.2 mmol), paraformaldehyde (0.990 g, 33.0 mmol), and 25 mL of ethanol. The resulting suspension was held at 65 °C and stirred for 12 h, forming a clear solution. A solution of para-trifluoromethylaniline (2.62 g, 16.3 mmol) in 10 mL of ethanol was added dropwise to the hot solution over a period of 30 min. Completion of the addition resulted in a white suspension that was heated for 2 h at 45 °C. The mixture was cooled to room temperature, the solvent volume reduced on a vacuum line to 20 mL, and the white solid product was collected by filtration and dried in vacuo (3.74 g, 6.33 mmol, 78%).

\[ \text{Ph}_2\text{P}^{\text{SMe}} \text{SiMe}_3 \] and \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \). A 250 mL Schlenk flask was charged with phenylphosphine (1.79 g, 16.2 mmol), paraformaldehyde (0.990 g, 33.0 mmol), and 25 mL of ethanol. The resulting suspension was held at 65 °C and stirred for 12 h, forming a clear solution. A solution of para-trifluoromethylaniline (2.62 g, 16.3 mmol) in 10 mL of ethanol was added dropwise to the hot solution over a period of 30 min. Completion of the addition resulted in a white suspension that was heated for 2 h at 45 °C. The mixture was cooled to room temperature, the solvent volume reduced on a vacuum line to 20 mL, and the white solid product was collected by filtration and dried in vacuo (3.74 g, 6.33 mmol, 78%).

\[ \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \text{Ni}(\text{MeCN})_6\text{BF}_4 \]. Two equivalents of \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \) (1000 mg, 1.694 mmol) were added to a solution of \( \text{Ni}(\text{MeCN})_6\text{BF}_4 \) (422 mg, 0.845 mmol) in acetonitrile (15 mL). After stirring overnight, the resultant red solution was filtered through a plug of Celite. The solvent was removed from the filtrate under vacuum. The red powder was washed with ether and dried in vacuo (1.15 g, 0.814 mmol, 66%). \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \text{Ni}(\text{MeCN})_6\text{BF}_4 \). Two equivalents of \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \) (1000 mg, 1.694 mmol) were added to a solution of \( \text{Ni}(\text{MeCN})_6\text{BF}_4 \) (422 mg, 0.845 mmol) in acetonitrile (15 mL). After stirring overnight, the resultant red solution was filtered through a plug of Celite. The solvent was removed from the filtrate under vacuum. The red powder was washed with ether and dried in vacuo (1.15 g, 0.814 mmol, 66%). \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \text{Ni}(\text{MeCN})_6\text{BF}_4 \). Two equivalents of \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \) (1000 mg, 1.694 mmol) were added to a solution of \( \text{Ni}(\text{MeCN})_6\text{BF}_4 \) (422 mg, 0.845 mmol) in acetonitrile (15 mL). After stirring overnight, the resultant red solution was filtered through a plug of Celite. The solvent was removed from the filtrate under vacuum. The red powder was washed with ether and dried in vacuo (1.15 g, 0.814 mmol, 66%). \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \text{Ni}(\text{MeCN})_6\text{BF}_4 \). Two equivalents of \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \) (1000 mg, 1.694 mmol) were added to a solution of \( \text{Ni}(\text{MeCN})_6\text{BF}_4 \) (422 mg, 0.845 mmol) in acetonitrile (15 mL). After stirring overnight, the resultant red solution was filtered through a plug of Celite. The solvent was removed from the filtrate under vacuum. The red powder was washed with ether and dried in vacuo (1.15 g, 0.814 mmol, 66%). \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \text{Ni}(\text{MeCN})_6\text{BF}_4 \). Two equivalents of \( \text{PPh}_2\text{N}^{\text{GHCF3}} \text{NiCl}_2 \) (1000 mg, 1.694 mmol) were added to a solution of \( \text{Ni}(\text{MeCN})_6\text{BF}_4 \) (422 mg, 0.845 mmol) in acetonitrile (15 mL). After stirring overnight, the resultant red solution was filtered through a plug of Celite. The solvent was removed from the filtrate under vacuum. The red powder was washed with ether and dried in vacuo (1.15 g, 0.814 mmol, 66%).
suspended solid that was collected on a filter, washed with 20 mL of ether, and dried in vacuo to obtain (0.104 g, 0.060 mmol, 14%) of additional product. [31P(NH3)]1H NMR (CD3CN): δ 5.0 (CH2PPh2CH2); 27.6 (P(O)(OEt)); H NMR (CD3CN): δ 7.40 (t, J = 7 Hz, 4H, Ph); 7.35 – 7.25 (m, 16H, Ph); 4.19 (d, J = 14 Hz, 8H, PCH2N); 3.97 (d of q, J = 8, 7 Hz, 16H, OCH2CH2); 3.13 (d, J = 21 Hz, 8H, PhCH2P); 1.18 (t, J = 7 Hz, 24H, OCH2CH2). ESI-MS: Observed [(P2N2)2Ni(BF4)2] m/z 1653.4564, predicted 1653.4621.

**Determination of pKa** MeCN for Diethyl 4-Aminobenzylphosphonate. Anilinium tetrafluoroborate was isolated as an oil by reacting aniline (0.122 g, 0.502 mmol) with tetrafluoroboric acid ethere (0.1 mL, ~0.57 mmol). Then CD3CN (1.0 mL) was added to a mixture of aniliniumtetrafluoroborate (0.006 g, 0.02 mmol) and anilinium tetrafluoroborate (0.004 g, 0.02 mmol). Rapid interconversion was observed between anilinium and aniline (PhNH3+) and PhNH3) and between 4-(diethyl phosphonomethyl)phenylammonium and 4-aminobenzylphosphonate (NH3C6H4CH2P(O)(OEt)2) and NH2C6H4CH2P(O)(OEt)2) by 1H NMR, and the relative abundances at equilibrium were determined by comparing the observed ortho and meta arylic shifts with those of the pure free bases and their respective conjugate acids: NH3C6H4CH2P(O)(OEt)2: δ 6.97, 6.57; NH3C6H4CH2P(O)(OEt)2: δ 7.32, 7.21; PhNH3+; δ 7.08, 6.63; PhNH3: δ 7.53, 7.39. The observed exchange-averaged chemical shifts for NH3C6H4CH2P(O)(OEt)2/ NH3C6H4CH2P(O)(OEt)2: δ 7.08, 6.76, correspond to a mole ratio of 0.69. Similarly the average chemical shifts observed for PhNH3/PhNH3: δ 7.19, 6.81, correspond to a mole ratio of 0.76. From this data, the equilibrium constant Kc = [PhNH3]/[NH3C6H4CH2P(O)(OEt)2]/[NH3C6H4CH2P(O)(OEt)2] was calculated to be 1.4. The experiment was repeated twice more using 0.012 g (0.049 mmol) of NH3C6H4CH2P(O)(OEt)2 and 0.006 g (0.03 mmol) PhNH3BF4 as well as 0.004 g (0.02 mmol) of NH3C6H4CH2P(O)(OEt)2 and 0.002 g (0.01 mmol) of PhNH3BF4 to obtain a Kc value of 1.4 in both cases. The pKc MeCN of NH3C6H4CH2P(O)(OEt)2 is 10.62. The sum of the pKc MeCN of PhNH3 is 10.62 and log Ka.

**Catalytic Hydrogen Production.** Determination of Rate and Overpotential. All catalytic experiments were carried out at ambient temperature, 22 °C. Solutions of electrolyte (0.2 M Et4N BF4 or “Bu4N OTf” in acetonitrile), analyte (~5 mM catalyst in electrolyte solution), and titrant (~1.7 M acid in acetonitrile) were prepared in the glovebox. Absence of moisture from a sample electrolyte solution (<1 ppm water) was established using a Karl Fischer coulometric titrator. Internal reference ferricenium/ferrocene was used to track electrolyte dilution due to titrant addition. A scan rate of 50 mV/s was used for all runs. Overpotentials were taken as the difference between E1/2 and the thermodynamic potential E° for the reduction of acid to free base plus one-half equivalent H2 gas. The potentials at which jmax values were measured were located by finding the most positive potential for each catalytic wave beyond the E1/2 of the Ni(II/1) couple for which the second derivative of the i – E trace is approximately zero. These potentials were 100 – 150 mV negative of E1/2. A representative experiment is given in the following section.

Using [Ni(PPh3)2(N2H4Me)]BF4 as Catalyst and 1:1 DMF/-DMF” OTF as Acid. In a glovebox, [Ni(PPh3)2(N2H4Me)]BF4 (1.1 mg, 0.92 μmol) was weighed into a 4 mL glass vial and dissolved in 2.0 mL acetonitrile (0.2 M tetraethylammonium tetrafluoroborate), then 5 μL of acetonitrile (0.054 μL ferrocene) was added as internal reference. In a separate vial, [DMF]H+OTF− (190 mg, 0.851 mmol) was weighed and dissolved in 0.50 mL acetonitrile. To this solution was added 60 μL (0.77 mmol) DMF. These vials were capped and removed from the box. The analyte solution vial was fitted with electrodes under a stream of acetonitrile-saturated nitrogen, and a baseline voltammogram was recorded. Titrant was transferred via microsyringe in 20–100 μL increments. Aliquot volumes were adjusted as required to obtain acid concentrations for which the catalytic current became constant within 15 additions, to minimize bias due to different catalyst stabilities. After each addition of titrant, the electrode was polished, and a voltammogram was recorded. Scans showing unusual line shape features, or catalytic half-peak potentials or current enhancements at significantly more negative values than prior runs, were repeated after thorough polishing of the electrode. Titration was continued until three successive additions resulted in no further increase in catalytic current enhancement. Once acid- independence was established, degassed water was admitted in 1 μL increments until the catalytic current stopped increasing. A similar procedure was used for other acids and catalysts studied.

Order with Respect to Water. To assess the reaction order of the catalyst enhancement with respect to added water, the peak current of solutions containing catalyst and acid were measured by cyclic voltammetry. Once the system had reached zero-order conditions in acid, a small volume (10 μL) of a 9:1 acetonitrile–water solution was added followed by manual stirring of the solution. The peak current of the system was then measured. This process was repeated until the peak current began to decrease.

**Controlled Potential Coulometry.** A three-necked flask having a total volume of 150 mL was used as the bulk electrolysis vessel and was assembled under a flow of nitrogen with each neck accepting an electrode fed through a pierced rubber septum. The working electrode consisted of a copper wire attached to a reticulated vitreous carbon cylinder; the reference and counter electrodes were a Ag wire and graphite rod, respectively, placed into 5 mm glass tubes terminating in Vycor frikted disks and filled with acetonitrile (0.1 M Et4N BF4) electrolyte solution. A solution of [Ni(PPh3)2(N2H4Me)]BF4 (12 mg, 9.5 μmol), ferrocene, and Et4N BF4 (990 mg, 4.6 mmol) in 10 mL acetonitrile and a solution of [(DMF)H]+OTF− (742 mg, 3.3 mmol) in 5 mL acetonitrile were prepared in the glovebox. The catalyst/ferrocene solution was then transferred to the reaction vessel via syringe, and a cyclic voltammogram was obtained. The acid solution was then added, and controlled potential coulometry was performed at −0.90 V versus the ferrocenium/ferrocene internal reference. After 29.3 C of charge was passed, a 200 μL sample of the headspace gas was removed via gastight syringe and analyzed by gas chromatography. Using the moles of H2 produced (0.29 mmol) and the charge passed (29.3 C), a current efficiency of 94 ± 5% was calculated for H2 production.

**X-Ray Diffraction Studies.** Crystals of appropriate size were mounted on a nylon fiber using NVH immersion oil, transferred to a Bruker-AXS Kappa APEX II CCD diffractometer (Mo Kα radiation R = 0.71073 Å; graphite monochromator), and cooled to the data collection temperature of 100(2) K. Unit cell parameters were obtained from 90 raw data frames, 0.95 Ψ, from three different sections of the Ewald sphere. The raw data were integrated, and the unit cell parameters refined using SAINT. Data analysis was performed using XPREP. The data sets were treated with SADABS absorption corrections based on redundant multicrystal data (Sheldrick, G. Bruker-AXS, 2001). Structure solutions and refinements were performed using SHELXTL-97 (Sheldrick, 2008). All nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Crystal data for [Ni(PPh3)2(N2H4Me)]3+[BF4]2 and [Ni(PPh3)2(N2H4Me)]2+[BF4]3 are shown in Table S3, Supporting Information. Crystals of [Ni(PPh3)2(N2H4Me)]2+[BF4]3 suitable for X-ray diffraction studies were grown from a THF/ether solution at room temperature. Preliminary data indicated a primitive monoclinic cell, and systematic absences were consistent with the space group P21/n. The asymmetric unit contains one [Ni(PPh3)2(N2H4Me)]2+[BF4]3 cation, two BF4– anions, and two molecules of THF solvent located on general positions, yielding Z = 4 and Z′ = 1. One of the BF4– anions is disordered over two positions. These positions were located from the difference map and restrained to be equivalent using SADi and EADP commands to stabilize.
the refinement. One of the molecules of THF is also disordered, but this disorder is minor and does not affect the overall identity of the structure, so it was ignored. This accounts for the 1.45 intensity Q-peak remaining in the list. The C44 methyl carbon has a larger than average ellipsoid compared to the rest of the structure. This atom is not incorrectly assigned, as the bond distances are comparable to the three other tolyl methyl bonds in the structure, and the protons for this methyl can be assigned, as bond distances are comparable to the rest of the structure. This atom is not incorrectly disordered.

**BF4**


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