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High Catalytic Rates for Hydrogen Production Using Nickel Electrocatalysts with Seven-Membered Diphosphine Ligands Containing One Pendent Amine

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Abstract: A series of Ni-based electrocatalysts, [Ni(7P^{Ph}₂N^{C6H4X})₂](BF₄)₂, featuring sevenmembered cyclic diphosphine ligands incorporating a single amine base, 1-para-X-phenyl-3,6triphenyl-1-aza-3,6-diphosphacycloheptane $(7P^{Ph}_2N^{C6H4X})$ where X = OMe, Me, Br, Cl or CF₃), have been synthesized and characterized. X-ray diffraction studies have established that the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ complexes have a square planar geometry, with bonds to four phosphorus atoms of the two bidentate diphosphine ligands. Each of the complexes is an efficient electrocatalyst for hydrogen production at the potential of the Ni(II/I) couple, with turnover frequencies ranging from 2,400 to 27,000 s⁻¹ with $[(DMF)H]^+$ in acetonitrile. Addition of water (up to 1.0 M) accelerates the catalysis, giving turnover frequencies ranging from 4,100 - 96,000s⁻¹. Computational studies carried out on the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ family indicate the catalytic rates reach a maximum when the electron-donating character of X results in the pK_a of the pendent amine matching that of the acid used for proton delivery. Additionally, the fast catalytic rates for hydrogen production by the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ family relative to the analogous $[Ni(P^{Ph}_{2}N^{C6H4X}_{2})_{2}]^{2+}$ family are attributed to preferred formation of endo protonated isomers with respect to the metal center in the former, which is essential to attain suitable proximity to the reduced metal center to generate H₂. The results of this work highlight the importance of precise pK_a matching with the acid for proton delivery to obtain optimal rates of catalysis.

Introduction

The expanded use of energy from intermittent renewable energy sources such as solar and wind will require the ability to efficiently convert electricity to chemical energy for storage as fuels. Efficient catalysts are necessary for both the production and utilization of hydrogen. Platinum and the hydrogenase enzymes are excellent catalysts for both production and oxidation of hydrogen. Platinum, however, is a precious metal with high cost and low abundance.¹ Hydrogenase enzymes, while remarkably efficient catalysts in nature,²⁻⁴ are expensive to obtain in large amounts and difficult to adapt to large scale commercial applications. These considerations have spawned efforts to design molecular catalysts that employ more abundant metals, such as nickel,⁵ cobalt,⁶⁻¹⁴ iron,¹⁵⁻²⁸ or molybdenum²⁹⁻³¹ as electrocatalysts for the production and oxidation of hydrogen.^{32,33}

Efforts in our laboratory have focused on developing first row metal complexes (Ni,^{5,34,35} Co,^{10,14} Fe³⁶ and Mn³⁷) that contain an amine base in the second coordination sphere, adjacent to a vacant coordination site or a hydride ligand on the metal center. These mononuclear complexes, in which the base facilitates the heterolytic cleavage/formation of the H-H bond and functions as a proton relay,³⁸ mimic an important structural feature proposed for the active site of [FeFe]-hydrogenase enzymes, the presence of an azadithiolate ligand in the dinuclear active site, shown in structure **1**.^{3,4,23} Nickel and cobalt diphosphine complexes that incorporate a positioned base in



 the ligand have been found to be active electrocatalysts for hydrogen production in acidic acetonitrile solutions, and the Fe complexes with similar ligands exhibit evidence for heterolytic cleavage and catalytic oxidation of H_2 .^{5,35,36}

Using a series of $[Ni(P_2^RN_2^R)_2]^{2^+}$ catalysts, where P_2N_2 stands for a 1,3-R'-3,7-R derivative of 1,5-diaza-3,7-diphosphacyclooctane, we have previously examined how the basicity of the proton relay in cooperation with the size and electronic characteristics of the substituent at the phosphorus atoms influence the turnover frequencies for H₂ production.³⁹⁻⁴² Under optimized conditions, $[Ni(P_2^{Ph}N^{C6H4Br}_2)_2]^{2^+}$ (structure **2**, X = Br), containing electron-withdrawing bromo substituents on the aniline rings of the ligand and phenyl groups on the phosphorus atoms, catalyzed the formation of H₂ with turnover frequencies as high as 1040 s⁻¹ and an overpotential of approximately 290 mV.³⁹

The positioned amines in the second coordination sphere play important roles in the catalytic activity of these complexes. Our experimental and theoretical mechanistic studies of $[Ni(P_2^RN_2^R)_2]^{2+}$ catalysts suggest that the transition state for heterolytic H-H bond formation and cleavage has structure **3**.^{38,43-45} Further studies on reduction and protonation of closely related analogs of **2** have shown that intermediates formed during the catalytic cycle potentially include isomeric Ni(0) complexes in which an amine in each ligand is protonated.^{34,46-49} The kinetically formed doubly protonated Ni(0) species has both protons in exo positions relative to the nickel center, "pinched" between the two pendent amines with N-H ••• N bonding. Isomerization to form endo protonated species that would be active in the catalytic cycle has been shown to involve intermolecular deprotonation by a base followed by reprotonated Ni(0) intermediates formed during hydrogen production are in the catalytically active form and that higher catalytic

rates might be achieved if the stabilized exo-protonated structures could be avoided.^{39,47,48} We now present a study of related nickel bis(diphosphine) catalysts that contain ligands that are structurally modified, but which still retain features that allow access to similar transition state structures.⁵⁰ In this paper we report turnover frequencies up to 96,000 s⁻¹ for electrocatalytic hydrogen production with overpotentials ranging from 550 - 640 mV using a modified nickel catalyst containing two 7-membered cyclic diphosphine ligands $7P^{Ph}_2N^{C6H4X}$ (where $7P^{Ph}_2N^{C6H4X}$ is 1-*para*-X-phenyl-3,6-triphenyl-1-aza-3,6-diphosphacycloheptane and X = OMe, Me, Br, Cl or CF₃). Factors that may contribute to the rates are discussed, including the effects of changing from 8-membered to 7-membered cyclic ligands and the impact of reducing the number of amine bases in the ligand backbones.

Results

Synthesis and Characterization of Ligands and Complexes. The synthesis of 1-*para*-X-phenyl-3,6-triphenyl-1-aza-3,6-diphosphacycloheptane ligands $(7P^{Ph}_2N^{C6H4X}, where X = OMe$ (4-OMe), Me (4-Me), Br (4-Br), Cl (4-Cl) and CF₃ (4-CF₃)) was accomplished through the addition of one equivalent of a *p*-substituted aniline to 1,2-bis(hydroxymethylphenyl-phosphino)ethane in CH₃CN and refluxing for 12 hours, as previously reported for 4-H (X = H)⁵¹ and shown in Equation 1. The cyclic ligands containing a 7-membered ring are formed as



approximately 1:1 mixtures of racemic and meso isomers as indicated by ${}^{31}P{}^{1}H$ NMR spectra of the crude reaction mixtures. Recrystallization results in pure ligand, though as a mixture of the *meso-* and *rac*-isomers, which show one singlet each in their ${}^{31}P{}^{1}H$ NMR spectra. ${}^{1}H$ and ${}^{31}P{}^{1}H$ NMR spectral data for each ligand are provided in the Experimental section, and these spectra are consistent with the formulations of these ligands.

The synthesis of the nickel complex of **4-H** was reported previously, and a similar route is followed here.⁵⁰ The addition of two equivalents of **4-OMe**, **4-Me**, **4-Br**, **4-Cl** or **4-CF**₃ to an CH₃CN solution of [Ni(CH₃CN)₆](BF₄)₂ results in formation of [Ni(7P^{Ph}₂N^{C6H4X})₂](BF₄)₂ (where X = OMe, Me, Br, Cl or CF₃, **5-OMe**, **5-Me**, **5-Br**, **5-Cl** or **5-CF**₃), as determined by ³¹P{¹H} NMR spectroscopy and shown in Equation 2. In addition to the homoleptic, mono-



5-OMe	X = OMe	5-Br	X = Br
5-Me	X = Me	5-Cl	X = Cl
5-Н	X = H	5-CF ₃	$X = CF_3$

metallic complexes, the formation of oligomeric metal complexes is suggested by broad resonances in the ${}^{31}P{}^{1}H$ NMR spectra. Since a mixture of *meso-* and *rac-* isomers of **4** was used, the *rac-*isomers may function as bridging ligands between Ni(II) centers to form oligomeric byproducts. The desired monometallic complexes are isolated as orange crystalline products in yields ranging from 26-54% by concentration of the reaction mixture and crystallization by addition of CH₂Cl₂ followed by Et₂O. Each of the products has been fully

characterized by NMR spectroscopy, elemental analyses, and single crystal X-ray crystallography.

X-ray quality crystals of 5-OMe, 5-Me, 5-Br, 5-Cl and 5-CF₃ were grown by slow diffusion of Et₂O into saturated CH₃CN or CH₂Cl₂ solutions of the complexes. The Ni(II) complexes 5-OMe, 5-Me, 5-Br and 5-Cl complexes crystallize with two non-coordinating CH₃CN molecules per unit cell, and no close contacts are observed between the BF₄⁻ anions and any of the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ cations. Complex 5-CF₃ crystallizes with no solvents, and shows the BF₄ ions interacting with the metal center resulting in a pseudo-octahedral structure around the Ni center, with Ni • • • F distances of 3.02 Å. A drawing of each cation is shown in Figure 1. The structures confirm that the ligands coordinate as diphosphine chelates to give a distorted square planar geometry with all four Ni-P bond distances nearly equal, ranging from 2.20-2.23 Å. The P-Ni-P bond angle for each of the diphosphine ligands span a narrow range from 79.7-80.1°. This angle is smaller than the 82-84° typically observed for the P-Ni-P bonds in $[Ni(P_2^RN_2^R)_2]^{2+}$ complexes, ^{39,40} which form two six-membered chelate rings upon binding to the metal. In contrast, for the $[Ni(7P_2^{Ph}N^{C6H4X})_2]^{2+}$ complexes one five-membered and one sixmembered ring formed upon chelation of the ligand. The smaller bite angle of 7P^{Ph}₂N^{C6H4X} compared to the $P^{Ph}_{2}N^{R'_{2}}$ ligands results in a decrease in the steric interactions between the phenyl substituents on adjacent phosphorus atoms of the two ligands³⁹ and a more planar structure than observed in the corresponding $[Ni(P_{2}^{Ph}N_{2}^{R'})_{2}]^{2+}$ cations. For example, in $[Ni(P^{Ph}_{2}N^{C6H4Me}_{2})_{2}]^{2+}$ the dihedral angle between the two planes defined by the Ni atom and the two phosphorus atoms of each diphosphine ligand is 24.16° ,³⁹ whereas it is 0.0° for $[Ni(7P^{Ph}_2N^{C6H4Me})_2]^{2+}$, as in all of the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ structures. Thus the replacement of one six-membered chelate with a five-membered ring has significant structural consequences for



(E) Figure 1. X-ray crystal structure of (A) $[Ni(7P^{Ph}_2N^{C6H4OMe})_2](BF_4)_2 \cdot 2CH_3CN$, 5-OMe (B) $[Ni(7P^{Ph}_2N^{C6H4Me})_2](BF_4)_2 \cdot 2CH_3CN$, 5-Me (C) $[Ni(7P^{Ph}_2N^{C6H4Br})_2](BF_4)_2 \cdot 2CH_3CN$ 5-Br, (D) $[Ni(7P^{Ph}_2N^{C6H4Cl})_2](BF_4)_2 \cdot 2CH_3CN$, 5-Cl and (E) $[Ni(7P^{Ph}_2N^{C6H4CF3})_2](BF_4)_2 \cdot 2CH_3CN$, 5-CF₃. The BF₄⁻ counterions, CH₃CN solvent molecules and H atoms have been omitted for clarity.

Thermal ellipsoids are all shown at the 50% probability level.

complexes. As shown in Figure 1, the two six-membered rings containing the pendent amines are trans to each other across the metal center, and, except for 5-CF₃, adopt boat conformations. The chair conformations of the six-membered rings in observed in 5-CF₃ likely result from the interaction of the BF₄⁻ ions with the metal center in the solid state. The non-bonding Ni•••N distances are 3.17-3.23 Å for 5-OMe, 5-Me, 5-Br and 5-Cl, where the six membered ring is in the boat conformation, and 3.68 Å for 5-CF₃ where the six membered ring is in the chair conformation. Complete crystallographic information along with bond distances and angles for 5-OMe, 5-Me, 5-Me,

The ³¹P{¹H} NMR spectra of **5-OMe**, **5-Me**, **5-Br**, **5-Cl** and **5-CF₃** in CD₂Cl₂ consist of a single peak ranging from 44.6 ppm for **5-OMe** to 41.8 ppm for **5-CF₃**. The ¹H NMR spectra of **5-OMe**, **5-Me**, **5-Br**, **5-Cl**, and **CF₃** in CD₂Cl₂ also show the expected number and intensity of peaks consistent with the four-coordinate X-ray structures. The ³¹P{¹H} NMR spectra of **5-OMe**, **5-Me**, **5-Br**, **5-Cl** and **5-CF₃** in acetonitrile-*d*₃, however, consists of two peaks, a broad singlet (ranging from 51.8 – 48.8 ppm) and a sharp singlet (ranging from 47.2 – 45.2 ppm). In acetonitrile it is believed that the compounds are five-coordinate species with an acetonitrile bound to the nickel center, as previously reported for **5-H**.⁵⁰ As shown in Figure 2, this results in



Figure 2. Proposed isomers of 5 in CH₃CN.

the possibility of three distinct isomers. Low temperature ${}^{31}P{}^{1}H$ and ${}^{1}H$ NMR data in acetonitrile- d_3 indicate isomers **A** and **C** are rapidly interconverting through the dissociation/association of acetonitrile, resulting in the broad downfield singlet observed at room temperature. Isomer **B** has two different ligand environments; however, dissociation/association of the acetonitrile results in a chemically equivalent complex and therefore the sharper upfield chemical shift.

Electrochemical Studies. The cyclic voltammograms of 5-OMe, 5-Me, 5-Br, 5-Cl and 5-CF₃ indicate two overlapping one-electron reversible redox couples, with observed $E_{1/2}$ values (reported as the average of the potentials of the maximum cathodic and anodic current) ranging from -1.05 to -1.14 V vs. the ferrocenium/ferrocene (Cp₂Fe^{+/0}) couple, as summarized in Table 1 (e.g. 5-OMe, Figure 3). A plot of the peak current (i_p) vs. the square root of the scan rate



Figure 3. Cyclic voltammogram of 1.0 mM $[Ni(7P^{Ph}_2N^{C6H4OMe})_2](BF_4)_2$, **5-OMe** in 0.10 M $[Bu_4N][PF_6]/CH_3CN$. Conditions: 1 mm glassy carbon working electrode; scan rate 0.1 V/s at 25 °C.

shows a linear correlation in all cases, implying diffusion-controlled electrochemical events.⁵² The difference in the potential of cathodic and anodic peak potentials (ΔE_p) at a scan rate of 0.1 V/s for these processes is measured to be 120-82 mV (Table 1), where the ΔE_p of Cp₂Fe^{+/0} ranges from 68-71 mV. The observation that the ΔE_p values for the [Ni(7P^{Ph}₂N^{C6H4X})₂]²⁺ family are

neither 70 mV, as observed for the one-electron $Cp_2Fe^{+/0}$ couple, nor close to 30 mV, as predicted for a two-electron process, suggest that **5-OMe**, **5-Me**, **5-Br**, **5-Cl** and **5-CF₃** undergo two,

Table 1.	Selected Electrochemical Data for of [Ni(7P ^{Ph} ₂ N ^{C6H4X}) ₂](BF ₄) ₂ complexes in 0.10 M
[Bu ₄ N][PF	6]/CH ₃ CN.

Complex	Overlapping Ni(II/I , I/0) Observed $E_{1/2}^{a,b}$ (V)	$\Delta E_{\rm p}^{\rm c}$ (mV)		
$[Ni(7P_{2}^{Ph}N^{C6H4OMe})_{2}](BF_{4})_{2}, 5-$	-1 14	120		
OMe	1.1 1	120		
$[Ni(7P^{Ph}_{2}N^{C6H4Me})_{2}](BF_{4})_{2}, 5-Me$	-1.13	120		
$[Ni(7P^{Ph}_{2}N^{Ph})_{2}](BF_{4})_{2}, 5-H$	-1.12	105		
$[Ni(7P^{Ph}_{2}N^{C6H4Br})_{2}](BF_{4})_{2}, $ 5-Br	-1.08	104		
$[Ni(7P^{Ph}_2N^{C6H4Cl})_2](BF_4)_2, $ 5-Cl	-1.08	120		
$[Ni(7P^{Ph}_2N^{C6H4CF3})_2](BF_4)_2, 5-CF_3$	-1.05	82		
^a All potentials are referenced to the $Cp_2Fe^{+/0}$ couple at 0 V. ^b Calculated as the average of the potentials of the maximum cathodic and anodic current. ^c Peak-to-peak separation of cathodic and anodic waves at a scan rate of 0.1 V/s.				

overlapping, one-electron processes as previously observed and simulated for **5-H** (the determination of i_p for the catalytic rate calculations is discussed below).⁵⁰ In the analogous $[Ni(P^{Ph}_2N^{C6H4X}_2)_2]^{2+}$ systems (e.g. **2**) an increase in basicity of the pendent amine results in a negative shift of the redox potential of the complex. The same trend is observed here, with **5-OMe** having the most negative redox potential at -1.14 V and **5-CF**₃ has the most positive redox potential at -1.05 V.³⁹ The observed trend in redox potentials is also in accordance with that predicted by the "electrochemical ligand parameter" (E_L) series developed by Lever which catalogs common substituents by their electron donating/withdrawing ability.^{53,54}

Electrocatalytic Production of Hydrogen. When electrochemical measurements on 5-OMe, 5-Me, 5-Br, 5-Cl and 5-CF₃ are carried out in the presence of acid, a large increase in the cathodic peak current is observed (e.g. 5-Br, Figure 4). Protonated dimethylformamide triflate, [(DMF)H]OTf (p $K_a = 6.1$ in MeCN), a crystalline solid,⁵⁵ was used as the acid.^{56,57} Figure 5 shows that a plot of the catalytic current (i_{cat}) vs. [(DMF)H⁺]^{1/2} gives a linear correlation,



Figure 4. Cyclic voltammograms of $[Ni(7P^{Ph}_2N^{C6H4Br})_2](BF_4)_2$, **5-Br** in 0.10 M $[Bu_4N][PF_6]/CH_3CN$ with subsequent additions of $[(DMF)H]^+$ and H_2O . Conditions: 1 mm glassy carbon working electrode; 25 °C; scan rate 10 V/s.



 Figure 5. Plot of i_{cat} vs. $[[(DMF)H]^+]^{\frac{1}{2}}$ for $[Ni(7P^{Ph}_2N^{C6H4Br})_2](BF_4)_2$, **5-Br**, measured in 0.10 M $[Bu_4N][PF_6]/CH_3CN$ with increasing concentrations of $[(DMF)H]^+$. Conditions: 1 mm glassy carbon working electrode; 25 °C; scan rate 10 V/s. indicating the reaction is first-order with respect to acid concentration (i.e. Equation 3 where *n* is the number of electrons involved in the catalytic reaction, *F* is Faraday's constant, *A* is the area of the electrode, *D* is the diffusion coefficient, *k* is the rate constant, and *x* is the order of the reaction with respect to acid).⁵⁸⁻⁶¹

$$i_{cat} = nFA[\text{cat}]\sqrt{D(k[\text{H}^+]^{\text{x}})} \qquad (3)$$

The observed catalytic current (i_{cat}) in cyclic voltammograms recorded at slower scan rates (ca. < 0.5 V/s) deviated from the plateau shape expected for catalytic waves by displaying a moderate scan rate dependence below scan rates of 1 V/s, as well as peak-shaped diffusioncontrolled wave forms (e.g. **5-OMe**, Figure 6), as previously described for **5-H**.⁵⁰ These wave



Figure 6. Cyclic voltammograms of 1.0 mM $[Ni(7P^{Ph}_2N^{C6H4OMe})_2](BF_4)_2$, **5-OMe** in 0.10 M $[Bu_4N][PF_6]/CH_3CN$ with 0.21 M $[(DMF)H]^+$ at scan rates of 1, 5 and 10 V/s. Conditions: 1 mm glassy carbon working electrode at 25 °C.

shapes have been attributed to significant depletion of acidic substrate at the electrode as expected for very fast catalysts. For each catalyst, detailed studies were conducted to determine the minimum scan rate threshold above which the observed behavior is that expected for a catalytic wave with no significant substrate depletion, as discussed in the Supporting Information.

Cyclic voltammetry studies were carried out on 5-OMe, 5-Me, 5-Br, 5-Cl and 5-CF₃ as a function of acid concentration with sequential additions of $[(DMF)H]^+$ in CH₃CN at scan rates above those that showed i_{cat} independence (i.e. Fig. 6, 5 and 10 V/s scan rates). Due to catalyst decomposition at high acid concentrations, addition was halted once an acid concentration greater than 0.40 M was attained, despite an apparent continuation of catalytic current enhancement. The length of these experiments was restricted to *ca*. 30 min, a period for which minimal (< 5 %) catalyst decomposition was observed under these acidic conditions, as determined by UV-vis spectroscopy for each complex (see Supporting Information). The i_{cat} for each addition of acid was measured at the potential where the current first reaches its plateau (see Supporting Information), and the ratio of i_{cat}/i_p is used in Equation 4 (v = scan rate in V/s).^{52,60-62} Assuming two electrons are passed for each H_2 molecule produced (n = 2), and the acid concentration does not change significantly during the course of the measurement (as indicated by a current plateau), the catalytic rate constant $(k_{obs} = k[H^+]^x)$, or turnover frequency, can be calculated using the simplified Equation 5 (where T = 298 K). Using a constant acid concentration and measuring the i_{cat} as a function of catalyst concentration, the data also show a first-order dependence on catalyst concentration (see Supporting Information).

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RT(k[\mathrm{H}^+]^{\mathrm{x}})}{Fv}} \qquad (4)$$

$$k_{obs} = 1.94 \,\mathrm{V}^{-1} \cdot \upsilon \left(\frac{i_{cat}}{i_p}\right)^2 \qquad (5)$$

Digital simulation of cyclic voltammograms of each Ni complex, in the absence of acid, allowed for the estimation of one-electron corrected i_p values, which differ from experimental i_p values featuring two electrons by a factor largely dependent upon peak overlap (i.e., ΔE_p , discussed further in the Supporting Information). While accounting for dilution, conservative i_p values were used to determine i_{cat}/i_p ratios in order to calculate k_{obs} for each acid addition. With the exception of **5-OMe**, plots of k_{obs} vs. the acid concentration show first-order dependence (e.g. **5-Br**, Figure 7A) on acid concentration up to either 0.43 M [(DMF)H]⁺ or until a 30 minute experiment time, at which point decomposition of the catalyst becomes significant. For **5-OMe** the



Figure 7. Plot of k_{obs} vs. $[(DMF)H]^+$ for $[Ni(7P^{Ph}_2N^{C6H4X})_2](BF_4)_2$, (A) **5-Br** and (B) **5-OMe**, measured in 0.10 M $[Bu_4N][PF_6]/CH_3CN$ with increasing concentrations of $[(DMF)H]^+$. Conditions: 1 mm glassy carbon working electrode; 25 °C; scan rate 10 V/s.

observed rate constant becomes independent of acid concentration above 0.14 M $[(DMF)H]^+$ (Figure 7B). Higher concentrations of acid were not studied due to decomposition of each catalyst, resulting in unreliable measurements. From the plots of k_{obs} vs $[H^+]$ the second-order rate constants (first order in acid and first order in catalyst) were determined in the absence of added water and ranged from 6,300 to 69,000 M⁻¹ s⁻¹ (Table 2). The catalytic production of H₂

Table 2. Electrocatalytic data for hydrogen production.							
Complex	Over- potential ^a	$[(DMF)H]^+$	k_{obs} (s ⁻¹)	$\binom{k}{(M^{-1} s^{-1})}$	$[(DMF)H]^{+},$ $[H_2O]$	k_{obs} (s ⁻¹)	$\binom{k}{(M^{-1} s^{-1})}$
5-OMe	640 mV	0.15 M	7,500	51,000 ^b	0.21 M, 0.52 M	22,000	
5-Me	630 mV	0.39 M	27,000	69,000	0.41 M, 0.74 M	96,000	240,000
5-H°	620 mV	0.43 M	33,000	77,000	0.42 M, 1.2 M	106,000	250,000
5-Br	580 mV	0.40 M	6,100	15,000	0.40 M, 0.74 M	17,000	42,000
5-Cl	580 mV	0.43 M	4,500	10,000	0.43 M, 1.0 M	15,000	34,000
5-CF ₃	550 mV	0.41 M	2,400	6,300	0.40 M 0.81 M	4,100	10,000
^a As determined by the method of Evans for calculating overpotentials. ⁶³ ^b Obtained for the linear region of the k_{obs} vs. [(DMF)H] ⁺ before the acid-independent region. ^c As previously reported. ⁵⁰							

was confirmed by quantitative gas chromatographic analysis of the H_2 produced during a controlled potential electrolysis experiment with **5-Me**. At a potential of -1.4 V and an $[(DMF)H]^+$ concentration of 0.2 M, a current efficiency of 99 ±5% for H_2 production (11 turnovers) was observed.

Based on previous studies in which water was shown to significantly increase catalytic rates for $[Ni(P_2^RN_2^R)_2](BF_4)_2$ complexes, aliquots of purified H₂O were added subsequent to the completion of acid additions, resulting in a further catalytic current enhancement (e.g. **5-Br**, Figure 4).³⁹⁻⁴¹ Water was added until the observed catalytic current enhancement ceased; the data is summarized in Table 2. The second-order rate constants *k* for **5-Me**, **5-Br**, **5-Cl** and **5-CF₃ were found to range from 10,000 to 240,000 M⁻¹s⁻¹ with the addition of water. For catalyst 5-OMe**, at acid concentrations above 0.15 M, the catalytic current and hence the catalytic rate become independent of the acid concentration, with a first-order rate constant (equivalent to the turnover frequency of the catalyst) of 22,000 s⁻¹ in the presence of water (Figure 7B).

Detailed computational studies on 5-OMe, 5-H and 5-CF₃ were carried out to gain further insights into the complex properties and the catalytic process and reported below. All calculations were carried out using the free energies of solvation in acetonitrile, which was also explicitly considered as fifth ligand for all of Ni(II) complexes. The results of these calculations are discussed below.

Discussion

Structural Effects on Catalyst Properties. X-ray diffraction studies of the new complexes **5-OMe**, **5-Me**, **5-Br**, **5-Cl** and **5-CF**₃ have shown that the smaller ring size of the heterocyclic ligand results in significant structural differences in the complexes relative to the $[Ni(P^{R}_{2}N^{R'}_{2})_{2}]^{2+}$ series, and this in turn leads to substantial electronic differences that influence the catalytic activities. An important structural feature in each of the new complexes is the small P-Ni-P bite angle resulting from the $7P^{Ph}_{2}N^{C6H4X}$ ligand (79.7-80.1°). This small bite angle reduces the interligand steric interactions of the phenyl substituents of the phosphorus atoms of the two diphosphine ligands compared to $[Ni(P^{Ph}_{2}N^{C6H4X}_{2})_{2}]^{2+}$ complexes which have somewhat

larger bite angles (82-84°).^{39,40} As a result, all of the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ cations exhibit planar structures with dihedral angles of 0.0° between the two planes defined by the phosphorus atoms of each diphosphine ligand and nickel. In previous studies of $[M(diphosphine)_2]^{2+}$ complexes (where M = Ni, Pd, and Pt), this dihedral angle has been shown to correlate with the potentials of M(II/I) couples.⁶⁴⁻⁶⁶ The potentials of the Ni(II/I) couples shift to more negative values as the complexes become more planar, approaching the potentials of the M(I/0) couples. As a result, the potentials of the Ni(II/I) couples of the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ complexes are more negative by 250-300 mV than those of the corresponding $[Ni(P^{Ph}_2N^{C6H4X})_2]^{2+}$ complexes, which have larger dihedral angles. The resulting redox waves associated with the Ni(II/I) and Ni(I/0) couples overlap for the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ complexes due to the small difference in the Ni(II/I) and Ni(I/0) potentials ($\Delta E_{1/2}$). For example, simulations of cyclic voltammograms of **5-H** indicate a difference in redox potentials of 70 mV.⁵⁰ In contrast, these potentials differ by 190 mV for $[Ni(P^{Ph}_2N^{Ph}_2)_2]^{2+.39}$

An extensive theoretical analysis of the structural, electrochemical and acid/base properties of the 5-OMe, 5-H and $5-CF_3$ derivatives fully supports this interpretation. The calculated reduction potentials of the complexes are reported in Table 3. Overall, the

Table 3. Calculated electrochemical potentials (V) for $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ complexes in CH ₃ CN			
Х	E(II/I)	E(I/0)	
OMe	-1.07	-1.15	
Н	-1.04	-1.18	
CF ₃	-0.98	-1.07	

experimentally measured (overlapping) potential for the Ni(II/I, I/0) processes and the calculated potentials for the Ni(II/I) and Ni(I/0) couples are in good agreement, with the Ni(I/0) couples occurring negative of the Ni(II/I) couples by 0.14 V or less. In particular, calculations semiquantitatively reproduce the shift toward more positive values for the Ni(II/I) couple from **5**-**OMe** to **5**-**CF**₃.

The more negative potentials of the Ni(II/I) couples of the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ derivatives compared to the $[Ni(P^{Ph}_2N^{C6H4X}_2)_2]^{2+}$ analogues also correlates with the hydride donor abilities of their Ni(II) hydrides (Eq. 6). On the basis of previous correlations, the free energy for the

$$[HNi(7P^{Ph}_2N^{Ph})_2]^+ \underbrace{CH_3CN}_{\text{INi}(7P^{Ph}_2N^{Ph})_2]^{2+} + H^- \Delta G^{\circ}_{H^-} = 54.9 \text{ kcal/mol}$$
(6)
5-H

heterolytic cleavage of the Ni-H bond in acetonitrile to form H⁻, $\Delta G^{\circ}_{\text{H}^{-}}$, is estimated to be 54.9 kcal/mol for $[\text{HNi}(7P^{\text{Ph}}_{2}\text{N}^{\text{Ph}})_{2}]^{+}$ (5-H), while that for $[\text{HNi}(P^{\text{Ph}}_{2}\text{N}^{\text{Ph}})_{2}]^{+}$ is 59.0 kcal/mol.^{39,67,68} For the $[\text{HNi}(7P^{\text{Ph}}_{2}\text{N}^{\text{C6H4X}})_{2}]^{+}$ family, the $\Delta G^{\circ}_{\text{H}^{-}}$ values range from 54.5 for 5-OMe to 56.0 kcal/mol for 5-CF₃.

Mechanistic Studies. A likely ECEC mechanism for the formation of H₂ for the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ complexes is proposed in Figure 8. The complexes are first electrochemically reduced (moving clockwise around Figure 8) to the Ni(I) species (<u>ECEC</u>), followed by protonation of a pendent amine (<u>ECEC</u>), and the second electron transfer (EC<u>EC</u>) to form the Ni(0) complex $[Ni(7P^{Ph}_2N^{C6H4X}H)(P^{Ph}_2N^{C6H4X})]^+$. This step is likely followed by a intramolecular proton transfer to form a Ni(II) hydride, $[HNi(7P^{Ph}_2N^{C6H4X})_2]^+$. Finally, the

second protonation step (ECE<u>C</u>) occurs, followed by H-H bond formation, hydrogen elimination and regeneration of the original catalyst.

Computational and experimental data support electron transfer followed by protonation of the Ni(I) species as the first steps in the catalytic process (Fig. 8, steps 1-2). The calculated redox potentials for singly protonated Ni(II) complexes, $[Ni(7P^{Ph}_2N^{C6H4X}H)(P^{Ph}_2N^{C6H4X})]^{3+}$,



Figure 8. Proposed mechanism for catalytic H₂ formation.

resulting from protonation of **5-OMe**, **5-H** and **5-CF**₃, are significantly more positive than those of the non-protonated species (Table 4). For instance, the potential was calculated to be at -0.41 V for the Ni(II/I) couple of the singly endo-protonated complex derived from **5-H** (Table 4). When using $[(DMF)H]^+$ as the proton source (p $K_a = 6.1$ in CH₃CN),⁵⁷ the experimental data

show catalysis occurring near the Ni(II/I)/(I/0) overlapping potentials (i.e. -1.1 V), supporting electron transfer as the first step in the mechanism. Additionally, the computationally derived pK_a values of singly protonated Ni(II) complexes (Table 4) are greater than 6 pK_a units more acidic than

Table 4. Calculated electrochemical potentials (V) and pK_a values in CH ₃ CN for mono-protonated Ni(II) complexes, $[Ni(7P^{Ph}_2N^{C6H4X}H)(7P^{Ph}_2N^{C6H4X})]^{3+}$.			
X	E(II/I)	E(I/0)	pK _a
OMe	-0.42	-0.49	-1.8
Н	-0.41	-0.43	-3.0
CF ₃	-0.30	-0.35	-5.3

[(DMF)H]⁺, indicating protonation at nitrogen prior to reduction of Ni(II) to Ni(I) is unlikely under catalytic conditions.

We calculated the relative free energies and pK_a values of species that can form by reduction followed by protonation. The pK_a values for the lowest free-energy isomers of the singly protonated Ni(I) isomers, $[Ni(7P^{Ph}_2N^{C6H4X}H)(P^{Ph}_2N^{C6H4X})]^{2+}$, are reported in Table 5.

Table 5. Calculated pK_a values in CH ₃ CN for endo and exo isomers of $[Ni(7P^{Ph}_2N^{C6H4X}H)(7P^{Ph}_2N^{C6H4X})]^{2+}$ and endo isomer of $[HNi(7P^{Ph}_2N^{C6H4X}H)(7P^{Ph}_2N^{C6H4X})]^{2+}$ (e/NiH)			
X	e(I)	x(I)	e/NiH
OMe	7.7	4.0	10.3
Н	5.9	1.4	8.9
CF ₃	3.7	-0.2	6.8

Protonation on the nitrogen atoms can occur endo to form $\mathbf{e}(\mathbf{I})$ (\mathbf{e} indicating endo, \mathbf{I} indicating the oxidation state of the metal, Fig. 8, step 2_{endo}) or exo to form $\mathbf{x}(\mathbf{I})$ (\mathbf{x} indicating exo protonation, Fig. 8, step 2_{exo}), with respect to the metal center, resulting in the possibility of branching away from the main catalytic pathway. Calculations show that singly protonated Ni(I) exo isomers, $\mathbf{x}(\mathbf{I})$, are systematically more acidic than the endo isomers $\mathbf{e}(\mathbf{I})$ by $3.7 - 4.5 \text{ pK}_{a}$ units (Table 5). Consequently, $\mathbf{e}(\mathbf{I})$ isomers are more stable than $\mathbf{x}(\mathbf{I})$ isomers (e.g. 5-H, Fig. 9A). This relative energy contrasts with the $[\text{Ni}(\text{P}^{\text{Ph}}_2\text{N}^{\text{C6H4X}}_2)_2]^{2+}$ catalysts, where the $\mathbf{x}(\mathbf{I})$ protonated species is stabilized by a NH•••N hydrogen bond from the second pendent amine in the ligand,⁶⁹ resulting in stabilization of the $\mathbf{x}(\mathbf{I})$ species relative to the $\mathbf{e}(\mathbf{I})$ species (e.g. X = H, Fig. 9B). As such, the



(A) (B) **Figure 9.** Ranking of the lowest-free energy isomers of the singly protonated Ni(I) complexes of (A) $[Ni(7P^{Ph}_2N^{Ph}H)(7P^{Ph}_2N^{Ph})]^{2+}$ and (B) $[Ni(P^{Ph}_2N^{Ph}_2H)(P^{Ph}_2N^{Ph}_2)]^{2+}$.

relative pK_a values of the protonated pendent amines with respect to the pK_a of the proton source (i.e. the exogenous acid, protonated DMF in our studies) will play an important role in determining which protonation pathway is dominant in both cases (Fig. 8, step 2_{endo} or step 2_{exo}). In the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ family, free energy calculations indicate protonation in the **e(1)** position will be favored in the case of **5-CF**₃ and **5-H** (Fig. 8, step 2_{endo}), as the pK_a of **x(1)** position lies 4-5 pK_a units more acidic than that of the proton source, $[(DMF)H]^+$. As the basicity of the pendent amine increases, however, exo protonation may start to play a role in the catalytic pathway. For example, in the case of **5-OMe** the calculated pK_a values of both the **e(1)** and **x(1)** complexes are only 1-2 pK_a units different than that of $[(DMF)H]^+$, so protonation to form the **x(1)** species is thermodynamically favorable (Fig. 8, step 2_{exo}). The resulting effect may be an observed decrease in the catalytic rate of **5-OMe**, as protonation to generate **x(1)** becomes competitive and removes active catalyst from the cycle. As previously reported for the $[Ni(P^R_2N^{R'}_2)_2]^{2+}$ catalysts, exo protonation is thought to result in slower rates of catalytic hydrogen production, and that also appears to be the case for **5-OMe**.⁴⁸

After protonation to form the Ni(I) species, $[Ni(7P^{Ph}_2N^{C6H4X}H)(7P^{Ph}_2N^{C6H4X})]^{2+}$, rapid reduction to Ni(0) likely occurs. As shown in Table 4, the calculated Ni(I/0) redox potentials for the mono endo-protonated $[Ni(7P^{Ph}_2N^{C6H4X}H)(7P^{Ph}_2N^{C6H4X})]^{2+}$ species occur between -0.49 and -0.35 V (Fig. 8, step 3_{endo}), and is -0.71 V when protonated on exo site (Figure 8, step 3_{exo}), well positive of the Ni(II/I) redox couple for $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ complexes where catalysis occurs. As such, reduction and protonation to form the [Ni(7P^{Ph}₂N^{C6H4X}H)(7P^{Ph}₂N^{C6H4X})]²⁺ species is expected to be rapidly followed by a second reduction to form $[Ni(7P^{Ph}_2N^{C6H4X}H)(7P^{Ph}_2N^{C6H4X})]^+$, which are Ni(0) complexes that are either endo **e(0)** or exo

x(0) protonated at the pendant amine. Previous experimental and computational studies on $[Ni(P_2^RN_2^R)_2]^{2+}$ have shown that endo protonated Ni(0) species rapidly isomerize to form Ni(II) hydride species.^{47,70} Similarly, once reduction to form the N-protonated Ni(0) species, $[Ni(7P_2^{Ph}2N^{C6H4X}H)(7P_2^{Ph}2N^{C6H4X})]^+$, occurs rapid intramolecular proton transfer likely follows (Fig. 8, step 4), forming the Ni(II) hydride species $[HNi(7P_2^{Ph}2N^{C6H4X})_2]^+$ (**NiH**). No such intramolecular isomerization is available for the **x(0)** species.

Protonation of the Ni(II) hydride species (NiH) can generate either an endo-protonated hydride (e/NiH, Fig 8, step 5) or an exo-protonated hydride (\mathbf{x} /NiH) (see Figure 10).^{38,47,48} Protonation of $\mathbf{x}(\mathbf{0})$ can occur in an endo position, relative to the nickel, yielding an $\mathbf{e}/\mathbf{x}(0)$ species (which would undergo a rapid intramolecular isomerization to the exo protonated Ni(II) hydride, \mathbf{x} /NiH, Fig. 10) or exo, forming $\mathbf{x}/\mathbf{x}(\mathbf{0})$ (Fig. 10), a doubly protonated Ni(0) species. All of the doubly-protonated species with exo positioned protons (\mathbf{x} /NiH or $\mathbf{x}/\mathbf{x}(\mathbf{0})$), however, are calculated to be systematically higher in free energy than their endo counterpart (\mathbf{e} /NiH). As shown in Figure 10, the energy differences between endo and exo species are even more pronounced for the second protonation than the first (Figure 9). Given that the calculated p K_a



Figure 10. Ranking of the lowest-free energy isomers of the doubly protonated complexes of (A) $[HNi(7P^{Ph}_2N^{C6H4X}H)(7P^{Ph}_2N^{C6H4X})]^{2+}/[Ni(7P^{Ph}_2N^{Ph}H)_2]^{2+}$ and (B) $[HNi(P^{Ph}_2N^{Ph}_2H)(P^{Ph}_2N^{Ph}_2)]^{2+}/[Ni(P^{Ph}_2N^{Ph}_2H)_2]^{2+}$.

values of the lowest energy intermediate (e/NiH) for 5-CF₃, 5-H, and 5-OMe (Table 5) are greater than that of $[(DMF)H]^+$, whereas the calculated p K_a values of the e(I) intermediates are comparable to that of $[(DMF)H]^+$, it is postulated that the first protonation step, Ni(I) + $[(DMF)H]^+ \rightarrow e(I) + DMF$, is the rate-determining step rather than the second protonation step, NiH + $[(DMF)H]^+ \rightarrow e/NiH + DMF$.

In stark contrast to the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^+$ family, protonation studies of the $[Ni(P^R_2N^{R'}_2)_2]^{2+}$ family of compounds, complemented by extensive theoretical modeling, indicate that the energy difference between endo and exo protonation is much smaller, and all isomers are likely populated under ambient conditions (Figure 9).^{38,46-48} Indeed, the presence of the second pendent amine on each phosphine ligand allows the formation of exo hydrogenbonded structures where the proton is "pinched" between two pendent amines, NH•••N. In the case of $[Ni(P^{Ph}_2N^{Ph}_2)_2]^{2+}$ this hydrogen bond stabilizes the x/x(0) and x/NiH species, making

their relative energies comparable (Figure 10).³⁸ The stability of the exo protonated species in the $[Ni(P^{Ph}_2N^{Ph}_2)_2]^{2+}$ family is thought to be a key factor in limiting their rate of catalysis, and one that the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^+$ family has overcome.

The evolution of hydrogen from the e/NiH species (Fig. 8, step 6) is thought to proceed in a heterolytic fashion through a transient dihydrogen Ni(II) complex, $[Ni(P^{Ph}_2N^{Ph}_2)_2(H_2)]^{2+.38}$ As shown Figure 11, computational studies carried out on **5-CF**₃, **5-H**, and **5-OMe** show formation of the Ni(II) dihydrogen complex through a heterolytic transition state from the e/NiHintermediate. The activation barriers calculated for this transition state range from 6.0-7.4 kcal/mol, far smaller than the barrier (> 10 kcal/mol) inferred from the observed turnover frequency, further supporting the proposal that protonation of the Ni(I) species is the ratedetermining step. The barrier for the subsequent H₂ elimination is believed to be low (smaller than those reported above), resulting in facile regeneration of the original Ni(II) catalysts.³⁸



Reaction Progress

Figure 11. Lowest free energy H₂ elimination pathway for 5-OMe, 5-H and 5-CF₃.

Interestingly, the overall free energy for H₂ elimination from the e/NiH intermediate (- ΔG°_{H2}) obtained from our quantum chemical calculations is more favorable for $[Ni(7P^{Ph}_2N^{Ph})_2]^+$ (5-H, - ΔG°_{H2} = -10 kcal/mol) than for $[Ni(P^{Ph}_2N^{Ph}_2)_2]^{2+}$ (- ΔG°_{H2} = -7.5 kcal/mol). As discussed previously,⁷¹ ΔG°_{H2} is the result of a fine balance between the free energy for hydride transfer, ΔG°_{H} -, and the pK_a of the protonated pendent amine of e/NiH. This is evident from the thermodynamic cycle shown in Fig. 12 (e.g. 5-H). The more favorable

$$[\text{Ni}(7P^{\text{Ph}}_{2}\text{N}^{\text{Ph}})_{2}]^{2+} + \text{H}^{-} = [\text{HNi}(7P^{\text{Ph}}_{2}\text{N}^{\text{Ph}})_{2}]^{+} -\Delta G^{\circ}_{\text{H}^{-}}$$

$$[\text{HNi}(7P^{\text{Ph}}_{2}\text{N}^{\text{Ph}})_{2}]^{+} + \text{H}^{+} = [\text{HNi}(7P^{\text{Ph}}_{2}\text{N}^{\text{Ph}})(7P^{\text{Ph}}_{2}\text{N}^{\text{Ph}})]^{2+} -\Delta G^{\circ} = -1.37(\text{p}K_{a})$$

$$H_{2} = H^{-} + H^{+} - \Delta G^{\circ} = 76 \text{ kcal/mol (in CH_{3}CN)}$$

$$[\text{Ni}(7P^{\text{Ph}}_{2}\text{N}^{\text{Ph}})_{2}]^{2+} + H_{2} = [\text{HNi}(7P^{\text{Ph}}_{2}\text{N}^{\text{Ph}})(7P^{\text{Ph}}_{2}\text{N}^{\text{Ph}})]^{2+} -\Delta G^{\circ}_{\text{H}^{2}}$$

Figure 12. Themochemical cycle for the determination of the driving force for hydrogen addition, ΔG°_{H2} .

 $-\Delta G^{0}_{H2}$ for the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^+$ complexes is a consequence of the greater hydride donor ability of $[HNi(7P^{Ph}_2N^{C6H4X})_2]^+$ discussed above, which dominates over the increased basicity of the pendent amine.

Of particular note from the kinetic studies of the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ catalysts is the observation that they all show a first-order dependence on the concentration of acid. This indicates that although two protonation steps must occur during the catalytic cycle, only one protonation step appears to be rate-determining for these catalysts. Evidence that the first protonation event may be rate-determining comes from analysis of the second-order rate constants derived from the observed rate constants for $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ catalysts (column 5 of Table 2) and the pK_a values of proposed intermediates. The calculated pK_a values of the

e/**NiH** intermediates for **5-CF**₃, **5-H**, and **5-OMe** (Table 5) are greater than the pK_a of the $[(DMF)H]^+$ proton source (6.1), whereas the calculated pK_a values of the **e**(**I**) intermediates are comparable to or less than that of $[(DMF)H]^+$. As a result, it is reasonable to assume that the first protonation step, Ni(I) + $[(DMF)H]^+ \rightarrow e(I) + DMF$ (Fig. 8, step 2), is the rate-determining step rather than the second protonation step, NiH + $[(DMF)H]^+ \rightarrow e/NiH + DMF$ (Fig. 8, step 5).

A plot of the second-order rate constants observed for the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ catalysts vs. the pK_a values of the protonated amine of e(I), $([Ni(7P^{Ph}_2N^{C6H4X}H)(7P^{Ph}_2N^{C6H4X})]^{2+})$, shows the maximum rate constant occurring with the pendent amine that best matches the pK_a of the $[(DMF)H]^+$ proton source (Figure 13). The pK_a values of e(I) species derived from more acidic pendent amines than 5-H (5-CF₃, 5-Cl and 5-Br) are below that of [(DMF)H]⁺, resulting in slow (or incomplete) protonation. In complexes where the pendent amine substituents have a greater electron donating ability than the H atom in 5-H, the pendent amine is basic enough to give rise to competitive exo protonation (Fig. 8, step 2_{exo}), and the competitive formation of x(I) becomes likely. This competition is particularly pronounced in the case of the catalytic rate for 5-OMe, which shows acid independence beyond 0.14 M [(DMF)H]⁺, indicating the equilibrium between e(I) protonation/deprotonation plays a key role in limiting the overall catalytic process. Figure 13 illustrates the importance of pK_a matching between the pendent base and the exogenous base for relaying protons from the substrate to the metal via the pendent amines. Additionally, Figure 13 supports the proposed ECEC mechanism. An EECC mechanism would proceed through doubly protonated Ni(0) species that rapidly interconverts to the protonated Ni(II) hydride (Fig. 8, e/NiH). Table 5 shows the pK_a values for the $[HNi(7P^{Ph}_2N^{C6H4X}H)(7P^{Ph}_2N^{C6H4X})]^{2+}$ (e/NiH) species are all greater than that of [(DMF)H]⁺. Hence, if an EECC mechanism were occurring, the expected trend in Figure 13 would not be observed.



Figure 13. Graph of calculated pK_a values of the endo protonated, **e(I)** $[Ni(7P^{Ph}_2N^{C6H4X}H)(7P^{Ph}_2N^{C6H4X})]^{2+}$ complexes vs. their second-order rate constants for hydrogen production. Black line between data points was added to illustrate the trend.

Effect of Water on Catalytic Rates. Addition of water (0.52 - 1.2 M) to reaction mixtures containing $[\text{Ni}(7\text{P}^{\text{Ph}}_{2}\text{N}^{\text{C6H4X}})_{2}]^{2+}$ complexes and $[(\text{DMF})\text{H}]^{+}$ results in significant catalytic rate enhancements, as previously observed for the $[\text{Ni}(\text{P}^{R}_{2}\text{N}^{R'}_{2})_{2}]^{2+}$ family of complexes.^{39.41} Computational and experimental studies on the doubly protonated $[\text{Ni}(\text{P}^{\text{Cy}}_{2}\text{N}^{\text{Bn}}_{2}\text{H})_{2}]^{2+}$ compounds suggest the rates of protonation and deprotonation of the pendent amines are hindered through steric interaction between phosphine substituents and the approaching substrate.⁴⁸ Indeed, the use of smaller substrates for proton delivery ($[(\text{DMF})\text{H}]^{+}$ vs. 2,5-dichloroanilinium) in the $[\text{Ni}(\text{P}^{\text{Ph}}_{2}\text{N}^{\text{C6H4X}}_{2})_{2}]^{2+}$ family of catalysts resulted in higher rates. Additionally, in the family of $[\text{Ni}(\text{P}^{R}_{2}\text{N}^{\text{Ph}}_{2})_{2}]^{2+}$ catalysts that contain bulky substituents at the phosphorus atoms, large increases in the rate of hydrogen production upon addition of water are attributed to more facile proton delivery through water acting as an intermolecular proton relay between the acid substrate and the pendent amine.⁴⁰ In the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ complexes, water is proposed to function in a similar fashion, increasing the rate of protonation through the ease of access of small water molecules to the pendent amines, therefore shuttling protons from the $[(DMF)H]^+$. Experimental and computation work to elucidate the exact role of water in these systems is ongoing in our laboratories.

Conclusions

The observation of high rates for H₂ formation with **5-OMe**, **5-Me**, **5-Br**, **5-Cl** and **5-CF**₃ clearly demonstrates that positioned proton relays in these catalysts play critical roles in all of the individual catalytic steps involving proton transfer and heterolytic formation of H₂. Comparisons of the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ and $[Ni(P^{Ph}_2N^{C6H4X})_2]^{2+}$ catalysts indicate that the increased planarity of the $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ complexes results in greater hydride donor abilities of $[HNi(7P^{Ph}_2N^{C6H4X})_2]^{+}$. The faster catalytic rates for H₂ production by $[Ni(7P^{Ph}_2N^{C6H4X})_2]^{2+}$ complexes is attributed to increased stability of endo vs. exo protonation of the Ni(I) species due to the absence of the stabilizing NH•••N "pinch" interaction that occurs in complexes with $P^{Ph}_2N^{C6H4X}_2$ ligands. The $[Ni(7P^{Ph}_2N^{C6H4X})_2]^+$ family of catalysts also clearly illustrates the importance pK_a matching of the proton relay to the proton source in supporting rapid catalysis. Continuing studies currently underway in our laboratories are aimed at reducing the overpotential required to drive the electrocatalysis, while maintaining high turnover frequencies that are essential for producing an economically viable substitute for platinum.

Experimental Section

General Experimental Procedures. All manipulations with free phosphine ligands and metal reagents were carried out under N_2 using standard vacuum line, Schlenk, and inert atmosphere glovebox techniques. Solvents were purified by passage through neutral alumina using an

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Innovative Technology, Inc., PureSolvTM solvent purification system. The 1.2bis(phenylphosphino)ethane was purchased from Strem and used as received. Ferrocene was purchased from Aldrich and sublimed under vacuum before use. Tetrabutylammonium hexafluorophosphate, [NBu₄][PF₆], was purchased from the Tokyo Chemical Industry (TCI) and recrystallized three times from absolute ethanol. H₂O was purified using a Millipore Milli-Q purifier. and was sparged with nitrogen before use. The meso/rac-1,2bis/hydroxymethylphenylphosphino)ethane⁵¹, $[(DMF)H]^{+55}$ and $[Ni(CH_3CN)_6](BF_4)_2^{72}$ were prepared according to literature procedures.

Instrumentation. NMR spectra were recorded on a Varian Inova spectrometer (500 MHz for ¹H) at 25 °C unless otherwise noted. All ¹H chemical shifts have been internally calibrated using the monoprotio impurity of the deuterated solvent. The ${}^{31}P{}^{1}H$ NMR spectra were referenced to external phosphoric acid at 0 ppm.

All experimental procedures were conducted at ambient temperature, 25 °C, under nitrogen using either standard Schlenk conditions or a Vacuum Atmospheres drybox. A standard three-electrode configuration was employed in conjunction with a CH Instruments 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 (Cypress Systems EE040). The working electrode was treated between scans by a sequence of polishing with diamond paste (Buehler) of decreasing sizes (3 to 0.25 μ m) interspersed by washings with purified H₂O. 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 to room temperature before use. Ferrocene was used as an internal standard, and all potentials reported within this

work are referenced to the ferrocenium/ferrocene couple at 0 V. Acids were measured and transferred to electrochemical solutions via Eppendorf automatic micropipet.

*meso/rac-*7P^{Ph}₂N^{C6H4X} (4-X): To 1,2-bis(hydroxymethylphenylphosphino)ethane (1.5 g, 5.0 mmol) in 15 mL of CH₃CN at 75 °C, the aniline reagent (5.0 mmol) was added as a 1.0 M CH₃CN solution, or by using a solid addition funnel, and the mixture was stirred at 75 °C for 12 h. Solvents were removed, leaving a white powder that was washed with diethyl ether (2×2) mL), dried under vacuum and isolated as nearly a 50/50 mixture of the meso- and rac-isomers. 4-**OMe**: Yield 1.61 g, 82%. ${}^{31}P{}^{1}H{}$ NMR (CD₃CN, ppm): -27.9 (s) and -29.4 (s). ${}^{1}H$ NMR (CD₃CN, ppm): 7.59-6.88 (multiple peaks, 14H, P-C₆ H_5 and N-C₆ H_4 -OCH₃), 4.31-3.63 (multiple peaks, 4H, PCH₂N), 3.79 and 3.74 (s, 3H, N-C₆H₄-OCH₃) 2.52-2.23 (mult., 4H, PCH₂CH₂P). **4-Me**: Yield 1.23 g, 65%. ${}^{31}P{}^{1}H{}$ NMR (CD₂Cl₂, ppm): -26.9 (s) and -27.3 (s). ¹H NMR (CD₂Cl₂, ppm): 7.63-6.78 (multiple peaks, 14H, P-C₆H₅ and N-C₆H₄-CH₃), 4.28-3.43 (multiple peaks, 4H, PCH₂N), 4.69 and 4.64 (s, 3H, N-C₆H₄-CH₃) 2.62-2.31 (mult., 4H, PCH₂CH₂P). **4-Br**: Yield 1.88 g, 85%. ${}^{31}P{}^{1}H{}$ NMR (CD₃CN, ppm): -26.6 (s) and -27.0 (s). ¹H NMR (CD₃CN, ppm): 7.57-6.61 (multiple peaks, 14H, P-C₆H₅ and N-C₆H₄-Br), 4.31-3.61 (multiple peaks, 4H, PCH₂N), 2.49-2.18 (mult., 4H, PCH₂CH₂P). 4-CI: Yield 1.17 g, 59%. ³¹P{¹H} NMR (CD₂Cl₂, ppm): -24.1 (s) and -24.4 (s). ¹H NMR (CD₂Cl₂, ppm): 7.48-7.09 (multiple peaks, 14H, $P-C_6H_5$, $N-C_6H_4-Cl$), 4.22-3.73 (multiple peaks, 4H, PCH_2N), 2.76-2.56 (mult., 4H, PCH₂CH₂P). **4-CF₃**: Yield 2.62 g, 74%. ³¹P{¹H} NMR (CD₃CN, ppm): -25.5 (s) and -26.7 (s). ¹H NMR (CD₃CN, ppm): 7.46-6.64 (multiple peaks, 14H, P-C₆H₅ and N-C₆H₄-CF₃), 4.23-3.61 (multiple peaks, 14H, PCH₂N), 2.36-2.19 (mult., 4H, PCH₂CH₂P).

 $[Ni(7P^{Ph}_2N^{C6H4X})_2](BF_4)_2$ (5-X): A mixture of the *meso/rac*- $7P^{Ph}_2N^{C6H4X}$ ligand, 4-X, (2.00 mmol) was combined with $[Ni(CH_3CN)_6](BF_4)_2$ (1.0 mmol) in 8 mL of CH₃CN forming a dark

red solution that was stirred at room temperature for 1 h. Solvents were removed from the reaction solution, 2 mL of CH₂Cl₂ was added, followed by 5 mL of Et₂O upon which the product precipitated as orange crystalline needles. The product was isolated by filtration and washed with 2×2 mL of Et₂O. **5-OMe**: Yield 306 mg, 30%. Anal. Calc for C₄₆H₅₀B₂F₈N₂NiO₂P₄·CH₃CN: C, 54.38; H, 5.04; N, 3.96. Found: C, 54.34; H, 5.01; N, 3.74. ${}^{31}P{}^{1}H{}$ NMR (CD₂Cl₂, ppm): 44.6 (s). ¹H NMR (CD₂Cl₂, ppm): 7.14-6.83 (multiple peaks, 28H, C₆H₅ and C₆H₄OCH₃), 4.67-4.65 (mult., 4H, PCH₂N), 3.55-3.52 (mult., 4H, PCH₂N), 3.15-3.13 (mult., 4H, PCH₂CH₂P), 2.40-2.38 (mult., 4H, PCH₂CH₂P), 3.72 (s, 6H, C₆H₄OCH₃). 5-Me: Yield 267 mg, 27%. ${}^{31}P{}^{1}H{}$ NMR (CD₂Cl₂, ppm): 44.3 (s). ${}^{1}H$ NMR (CD₂Cl₂, ppm): 7.83-6.94 (multiple peaks, 28H, C₆H₅ and C₆H₄CH₃), 4.71-4.68 (mult., 4H, PCH₂N), 3.79-3.76 (mult., 4H, PCH₂N), 3.06-3.03 (mult., 4H, PCH₂CH₂P), 2.34-2.32 (mult., 4H, PCH₂CH₂P), 2.25 (s, 6H, $C_6H_4CH_3$). **5-Br:** Yield 290 mg, 26%. Anal. Calc for $C_{44}H_{44}B_2Br_2F_8N_2NiP_4$ ·CH₃CN: C, 47.72; H, 4.09; N, 3.63. Found: C, 47.59; H, 3.98; N, 3.59. ³¹P{¹H} NMR (CD₂Cl₂, ppm): 43.5 (s). ¹H NMR (CD₂Cl₂, ppm): 7.23-6.96 (multiple peaks, 28H, C_6H_5 and C_6H_4Br), 4.71-4.68 (mult., 4H, PCH₂N), 3.85-3.80 (mult., 4H, PCH₂N), 3.18-3.16 (mult., 4H, PCH₂CH₂P), 2.40-2.37 (mult., 4H, PCH₂CH₂P). **5-Cl**: Yield 360 mg, 35%. ${}^{31}P{}^{1}H{}$ NMR (CD₂Cl₂, ppm): 43.1 (s). ${}^{1}H{}$ NMR (CD₂Cl₂, ppm): 7.20-6.97 (multiple peaks, 28H, C_6H_5 and C_6H_4Cl), 4.75-4.71 (mult., 4H, PCH₂N), 3.81-3.78 (mult., 4H, PCH₂N), 3.20-3.17 (mult., 4H, PCH₂CH₂P), 2.41-2.39 (mult., 4H, PCH_2CH_2P). 5-CF₃ (X = CF₃): Yield 300 mg, 54%. Anal. Calc. for C₄₆H₄₄B₂F₁₄N₂NiP₄: C, 50.45; H, 4.05; N, 2.56. Found C, 49.96; H, 4.37; N, 2.99. ³¹P{¹H} NMR (CD₂Cl₂, ppm): 41.8 (s); ¹H NMR (CD₂Cl₂, ppm): 7.52-6.97 (multiple peaks, 28H, C₆H₅ and C₆H₄CF₃), 4.89-4.86 (mult., 4H, PCH₂N), 4.17-4.14 (mult., 4H, PCH₂N), 3.23-3.21 (mult., 4H, PCH₂CH₂P), 2.23-2.21 (mult., 4H, (PCH₂CH₂P); ¹⁹F NMR (CD₂Cl₂, ppm, ref. to C₆F₆): -58.57 and -144.64.

Computational Studies. Computational studies on 5-OMe, 5-H and 5-CF₃ were carried out to gain further insights into the complex properties and the catalytic process. Molecular structures were optimized at the DFT level of theory with the hybrid B3P86^{73,74} exchange and correlation functional. The Stuttgart-Dresden relativistic ECP and associated basis set⁷⁵ basis set were used for Ni, and Pople's 6-31G* was used for all nonmetal atoms. An additional polarization p function on hydride hydrogen atoms were included. Harmonic vibrational frequencies were calculated at the optimized geometries using the same level of theory to estimate the zero-point energy (ZPE) and the thermal contributions (298 K and 1 atm) to the gas-phase free energy. Free energies of solvation in acetonitrile (which include the change of thermodynamic conditions of P = 1 atm in the gas phase to 1 M solution) were then computed using a self-consistent reaction field (SCRF) model at the same level of theory as for the other steps. The conductor-like polarizable continuum model (CPCM)^{76,77} was used with Bondi radii.⁷⁸ All geometries were optimized without any symmetry constraint and were verified by vibrational analyses at the same level of theory to ensure that they are minima on the potential energy surface. For some complexes, several conformations were considered, and the lowest energy conformer was chosen for the calculation of the thermodynamic properties. Acetonitrile was explicitly considered as fifth ligand for all of Ni(II) complexes. The pK_a values and redox potential were calculated according to the isodesmic scheme discussed by Chen *et al.*⁷⁹ The $[Ni(P^{Cy}_2N^{Bn}_2)_2]^{2+}$ system is used as reference for the pK_a calculations, and $[Ni(P^{Ph}_2N^{Ph}_2)_2]^{2+}$ for the redox potential. All of the calculations were carried out with Gaussian 09.80

The selection of hybrid B3P86 functional and basis set was shown to yield redox potentials, hydride donor strengths, and pK_a values with good accuracy for a set of complexes with various metals and ligands⁷⁹ and activation barriers for proton transfer and heterolytic H-H

bond formation that compare favorably with CCSD(T) calculations level of theory.⁴³ However, the computational error due to the exchange and correlation functional and the continuum solvation model adopted is error can be as large as 2-3 kcal/mol.^{38,43,81} Therefore isomers separated by small free energy differences, such as the doubly protonated e/NiH, x/NiH, and x/x isomers of the Ni($P^{Ph}_{2}N^{Ph}_{2}$)₂]²⁺ complex (see Figure 10B) cannot be reliably ranked in free energy. Nevertheless differences between the Ni($7P^{Ph}_{2}N^{Ph}_{2}$)₂]²⁺ and [Ni($P^{Ph}_{2}N^{Ph}_{2}$)₂]²⁺ are meaningful, as they are larger than expected error.

Supporting Information

Experimental details for **5-OMe**, **5-Me**, **5-Br**, **5-Cl** and **5-CF**₃ including: electrochemical analysis; catalyst decomposition studies; catalytic scan-rate independence studies; catalytic production of hydrogen rates; reaction order with respect to catalyst; example calculation of k_{obs} ; reaction order with respect to [(DMF)H]⁺; determination of second order rate constants; X-ray crystal data. This information is available free of charge via the internet at http://pubs.acs.org.

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