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Thermodynamic Properties of the Ni−H Bond in Complexes of the Type $[HNi(P_2^RN_2^{R'})_2](BF_4)$ and Evaluation of Factors That Control Catalytic Activity for Hydrogen Oxidation/Production

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Thermodynamic data for hydride complexes of the general formula $[HNi(P_2^RN_2^{R'})_2](BF_4)$, **3**, which have been reported previously to function as effective catalysts for the electrochemical oxidation or production of hydrogen, have been determined. Values of $\Delta G°_{H+}$, $\Delta G°_{H\bullet}$, and $\Delta G°_{H-}$ have been determined for **3a** where R = Cy, R′ = Bz, for **3b** where R = R′ = Ph, and for the new complex **3c**, R = Ph, R′ = Bz. In addition, the ΔG values for the heterolytic addition of hydrogen to the Ni(II) precursor complexes $[Ni(P_2^RN_2^{R'})_2](BF_4)_2$, **1a−c**, have been determined experimentally or calculated. The data are useful for understanding the factors that control the catalytic activities observed for these complexes and for the design of additional catalysts.

Introduction

The development of inexpensive molecular catalysts for hydrogen oxidation may ultimately lead to viable replacements for the costly platinum catalysts currently used in hydrogen fuel cells.[1] The feasibility of developing highly active catalysts for H_2 oxidation and proton reduction based on iron or nickel complexes has been supported by the identification of the structures of hydrogenase enzymes that contain Fe-only and Ni−Fe clusters at their active sites.[2−9] The enzyme characterizations have led to studies on simpler model complexes attempting to mimic the structure and function of these enzymes.[10−20] There has also been significant progress in the development of totally synthetic molecular catalysts for hydrogen production using complexes of non-noble metals such as molybdenum and cobalt.[21−23]

One aspect of effective design of hydrogen oxidation/production catalysts is the control of the thermodynamic properties of the complexes. For example, the heterolytic cleavage of H_2 should be at or near equilibrium to avoid high-energy intermediates. This implies that the hydride acceptor ability of the metal ion and the proton acceptor ability of the base must be energetically matched to provide enough energy to drive the heterolytic cleavage of hydrogen, but this reaction should not be strongly exergonic. Under these conditions, modification of the electron donor properties of ligand substituents can lead to a change in the thermodynamic bias of the catalyst reactivity for either hydrogen oxidation or hydrogen production.

In previous work we have studied the thermodynamic properties of the metal−hydride bond in an extended series of nickel diphosphine complexes[24−28] as well as in a number of other metal hydride derivatives.[29−35] The studies have led to the significant extension of previous tabulations of pK_a values for metal hydrides and to the determinations of $\Delta G°$ values for

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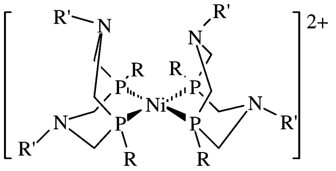
hydrogen atom dissociation. In addition, methods for the determination of Δ*G*° values for the hydride donor/acceptor ability of metal hydrides have been developed on the basis of related thermodynamic parameters, such as the reversible reduction potentials of the complexes[24] and the equilibrium constants for heterolytic hydrogen activation.[27]

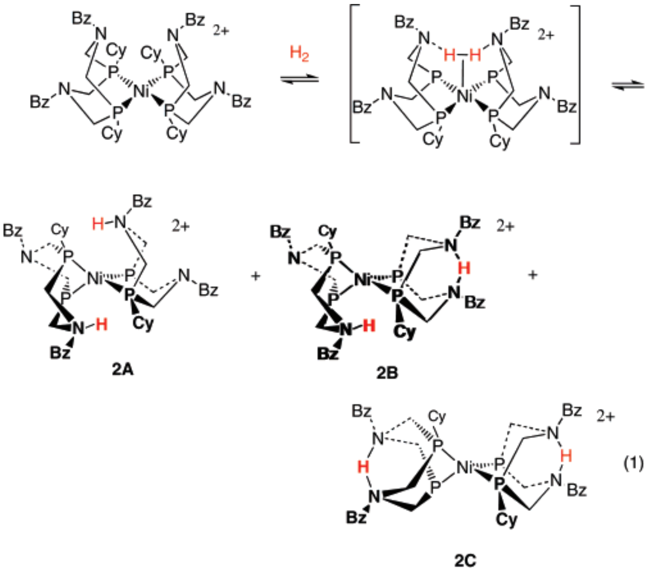
We have recently reported the synthesis of a new series of nickel(II) diphosphine complexes that contain cyclic ligands of the general formula shown in structure **1**. [Ni(P$^{Cy}{}_2$N$^{Bz}{}_2$)$_2$](BF$_4$)$_2$, **1a**, serves as a catalyst for the electrochemical oxidation of hydrogen in acetonitrile solution in the presence of a base.[36] The complex [Ni(P$^{Ph}{}_2$N$^{Ph}{}_2$)$_2$(CH$_3$CN)](BF$_4$)$_2$, **1b**, is a very effective catalyst for the electrochemical reduction of protons.[36,37]



1a: R = cyclohexyl; R’ = benzyl

1b: R = R’ = phenyl

Although thermodynamic considerations were used to guide the design of complexes **1a** and **1b**, a systematic study of the thermodynamics of the corresponding nickel hydride derivatives has not yet been reported. In previous studies, the formation of the hydride derivative [HNi(P$^{Cy}{}_2$N$^{Bz}{}_2$)$_2$]$^+$, **3a**, was found to involve an unusual sequence of steps.[37] Addition of hydrogen to [Ni(P$^{Cy}{}_2$N$^{Bz}{}_2$)$_2$]$^{2+}$ at −78 °C results in the reduction of the complex to a diprotonated tetrahedral Ni(0) product, **2A**, as shown in eq 1. At room temperature additional isomers of the Ni(0) derivatives, **2B** and **2C**, are observed by NMR spectroscopy. The reaction is proposed to proceed by simultaneous protonation of two proximal amine bases by the (undetected) nickel dihydrogen moiety, while the metal center serves as the two-electron acceptor. The relatively fast rates for the catalytic reactions have been attributed to this positioning of two basic sites so that simultaneous interaction of dihydrogen with the metal center and the amines results in a decreased activation barrier for hydrogen addition and elimination. This reversible reaction with H$_2$ has been monitored by visible spectroscopy, and an equilibrium constant for reaction 1 in acetonitrile has been determined to be 190 ± 20 atm^{-1} at 22 °C.[36] This corresponds to a free energy of −3.1 kcal/mol for reaction 1.



The Ni(II) hydride derivative [HNi(P$^{Cy}{}_2$N$^{Bz}{}_2$)$_2$](BF$_4$), **3a**, is rapidly formed when the isomers of **2**, maintained under an atmosphere of H$_2$, are deprotonated with triethylamine in acetonitrile, eq 2.[36] Complex **3a** shows a characteristic pentet

$$2 + \text{base} \Leftrightarrow \underset{\textbf{3a}}{[\text{HNi}(\text{P}^{\text{Cy}}{}_2\text{N}^{\text{Bz}}{}_2)_2](\text{BF}_4)} + [\text{Hbase}](\text{BF}_4) \quad (2)$$

(J_{PH} = 19.4 Hz) in the ^{1}H NMR spectrum at −10.7 ppm, assigned to the hydride ligand, and a singlet in the {^{1}H}^{31}P NMR spectrum at 14.1 ppm. The deprotonation reaction is reversible, and the hydride complex **3a** is converted back to the doubly protonated Ni(0) derivatives, **2A−C**, upon reaction with tetrafluoroboric acid or anisidinium tetrafluoroborate. This reaction represents an unusual pH-dependent intramolecular redox event in which protonation leads to a formal two-electron reduction of the metal, while deprotonation results in a two-electron metal oxidation. The determination of an equilibrium constant for reaction 2 would allow us to determine the pK_a of the pendant amine base in the cyclic ligand of **2**, as well as a number of additional thermodynamic parameters for the hydride derivative **3a**. In this paper we report the complete characterization of the thermodynamic properties of **3a** and of the corresponding hydrides of **1b** and of a closely related new complex **1c**, where R = Ph and R′ = Bz. The relative rates of H$_2$ oxidation and production using these catalysts can be understood in terms of the thermodynamic bias of the complexes.

Results

Thermodynamic Data for [HNi^{II}(P$^{Cy}{}_2$N$^{Bz}{}_2$)$_2$]$^+$, 3a. When anisidine is used as the base instead of triethylamine in eq 2, an equilibrium is observed. Integrations of the ^{31}P NMR spectra were used to determine the ratios of **3a**/**2**, and mass balance was used to determine the ratios of anisidine and anisidinium. From this data, equilibrium constants (where K = [HBase$^+$]**3a**/**2**[Base]) were calculated for **2A**, **2B**, and **2C**, respectively, at 22 ± 2 °C. By adding pK_{eq} to the pK_a of anisidinium in acetonitrile (11.9),[38,39] pK_a values for the protonated amines were obtained for each of the isomers of **2**. These data are given in Table 1.

The equilibrium constants determined for eq 2 using anisidine as the base can be used to derive a number of important thermodynamic properties associated with the Ni−H bond of [HNi^{II}(P$^{Cy}{}_2$N$^{Bz}{}_2$)$_2$]$^+$, **3a**. For example, the pK_a values can be

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Table 1. Equilibrium Constants for Eq 3 and pK_a Values for Protonated Amines in Isomers 2A−C

isomer	K	pK_a
2A	0.032 ± 0.004	13.4 ± 0.2
2B	0.026 ± 0.003	13.5 ± 0.2
2C	0.047 ± 0.003	13.2 ± 0.2

Scheme 1. Thermodynamic Cycle for the Determination of $\Delta G°_{H^-}$ for $[HNi^{II}(P^{Cy}_2N^{Bz}_2)_2]^+$

$$[HNi^{II}(P^{Cy}_2N^{Bz}_2)_2]^+ + H^+ \Leftrightarrow [Ni^0(P^{Cy}_2N^{Bz}HN^{Bz})_2]^{2+} \quad -1.37\times pK_a \qquad -18.4 \quad (3)$$

$$[Ni^0(P^{Cy}_2N^{Bz}HN^{Bz})_2]^{2+} \Leftrightarrow [Ni^{II}P^{Cy}_2N^{Bz}_2)_2]^{2+} + H_2 \quad -RT\ln K_{eq} \qquad +3.1 \quad (4)$$

$$\underline{H_2 \Leftrightarrow H^+ + H^- \qquad 76.0 \quad (5)}$$

$$[HNi^{II}(P^{Cy}_2N^{Bz}_2)_2]^+ \Leftrightarrow [Ni^{II}(P^{Cy}_2N^{Bz}_2)_2]^{2+} + H^- \qquad 60.7 \quad (6)$$

used together with the free energy discussed above for H_2 binding by **1a** to calculate the hydride donor ability, $\Delta G°_{H^-}$, of **3a**, as shown in Scheme 1, eqs 3−6.

Using the average of the pK_a values obtained for the isomers of **2** (13.4), the free energy associated with protonation of **3a** in acetonitrile is −18.4 kcal/mol, reaction 3. On the basis of the experimental determination discussed above, the dissociation of H_2 from $[Ni^0(P^{Cy}_2N^{Bz}HN^{Bz})_2]^{2+}$, **2**, requires 3.1 kcal/mol, reaction 4. The heterolytic cleavage of H_2 in acetonitrile, reaction 5, requires 76 kcal/mol.[27,40] The sum of reactions 3−5 is reaction 6, the loss of hydride from **3a**, which has a free energy of 60.7 ± 0.6 kcal/mol.[41] This hydride donor value and the redox potentials of Ni(II) diphosphine complexes can be used in well-established thermodynamic cycles (Schemes 1S and 2S of the Supporting Information) to calculate a pK_a value of 21.2 ± 1.5 and a homolytic solution bond dissociation free energy of 53.2 ± 2 kcal/mol for the hydride ligand of **3a**.

A more direct determination of the pK_a value of $[HNi^{II}(P^{Cy}_2N^{Bz}_2)_2]^+$ by determining the equilibrium constant for its deprotonation by an appropriate base in acetonitrile was not feasible because of the low solubility of the resulting complex $[Ni^0(P^{Cy}_2N^{Bz}_2)_2]$, **4**, in acetonitrile. However, using benzonitrile as the solvent and tetramethylguanidine (TMG) as the base resulted in an apparent equilibrium for the deprotonation of $[HNi^{II}(P^{Cy}_2N^{Bz}_2)_2]^+$ over short reaction times (<1 h), for which $K = \mathbf{4}[HTMG^+]/\mathbf{3a}[TMG] = (2.2 \pm 0.5) \times 10^2$. At longer reaction times significant product precipitation occurs. The pK_a for protonated tetramethylguanidine is reported to be 23.3 in acetonitrile,[42] and previous studies have shown that relative pK_a values in benzonitrile and acetonitrile solvents are the same within experimental error.[24] Adding the pK_{eq} value determined for **3a** in benzonitrile to the pK_a value of $HTMG^+$ in acetonitrile gives a pK_a value of 21.0 ± 1.0 for **3a**. The number provides a cross-check of the pK_a value of 21.2 determined from equilibrium measurements of **1a** in acetonitrile according to Scheme 1S.

Thermodynamic Data for $[HNi^{II}(P^{Ph}_2N^{Ph}_2)_2]^+$, 3b. As previously reported,[36,37] complex **1b**, $[Ni^{II}(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)]^{2+}$, is a very active catalyst for H_2 production, and the thermodynamic properties of intermediates in this reaction are of interest. Unlike **1a**, complex **1b** does not add H_2 in the absence of an external base. In the presence of anisidine in acetonitrile, the reaction of **1b** with hydrogen can be shown by ^{31}P NMR spectroscopy to form the hydride complex **3b**, eq 7, and the equilibrium constant was found to be 0.30 ± 0.06 atm^{-1}.[36] Using the thermodynamic cycle shown in Scheme 3S,

$$\underset{\mathbf{1b}}{[Ni^{II}(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)]^{2+}} + H_2 + \text{base} \Leftrightarrow \underset{\mathbf{3b}}{[HNi^{II}(P^{Ph}_2N^{Ph}_2)_2]^{2+}} + \text{Hbase}^+ \quad (7)$$

the hydride acceptor ability of $[Ni^{II}(P^{Ph}_2N^{Ph}_2)_2]^{2+}$ was determined to be −59.0 ± 1.0 kcal/mol. This information and the potentials of the Ni(II/I) and Ni(I/0) couples of $[Ni^{II}(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)]^{2+}$ can be used as shown in Scheme 1S to calculate a pK_a value of 16.3 ± 1.5 for the hydride ligand of **3b**. Similarly a homolytic bond dissociation free energy of 52.4 ± 2.0 kcal/mol for **3b** is calculated according to Scheme 2S. The reduction potentials for the Ni(II/I) and Ni(I/0) couples of $[Ni^{II}(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)]^{2+}$ used in these calculations are given in Table 2 in the Discussion.

Synthesis of $[Ni(P^{Ph}_2N^{Bz}_2)_2(CH_3CN)](BF_4)_2$, 1c. The new complex **1c** has been synthesized in order to further study how the ligand substituents influence the thermodynamic properties of the nickel hydride derivative and the catalytic activity for the oxidation or formation of hydrogen. The new cyclic ligand was synthesized from phenylphosphine, paraformaldehyde, and benzylamine, as described for the other ligands,[36,37] and reacted with $[Ni(CH_3CN)_6](BF_4)_2$ to form **1c** in 87% yield. ^{31}P and ^1H NMR spectral data and elemental analysis results are given in the Experimental Section. The cyclic voltammogram of **1c** in acetonitrile shows two reversible one-electron reduction waves with $E_{1/2} = -0.94$ and -1.19 V versus ferrocene$^{0/+}$. Single crystals of **1c** were grown from acetonitrile/diethyl ether, and an X-ray diffraction study was carried out. The structure contains discrete five-coordinate nickel dications, two BF_4 anions, and two acetonitrile molecules per nickel dication. Although disorder in the anions and free solvent molecules was not successfully resolved, the study does establish that the gross structural features of the nickel complex ion are similar to those of $[Ni(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)]^{2+}$, published previously.[36] The complex cation is a trigonal bipyramid with two apical phosphorus atoms, while two phosphorus atoms and an acetonitrile molecule occupy the equatorial positions. One of the six-membered chelate rings of each cyclic ligand is in the boat conformation, while the other chelate ring assumes the chair form.

Electrocatalytic Properties of 1c. The cyclic voltammogram of **1c** was monitored in the presence of hydrogen and an external base, but no catalytic activity for the electrochemical oxidation of hydrogen was observed for this complex on the time scale of cyclic voltammetry. Complex **1c** was observed to catalyze the electrochemical reduction of protons, and this reaction has been investigated in more detail.

Figure 1 shows a series of cyclic voltammograms of **1c** in acetonitrile recorded first in the absence of acid (the bottom scan) and then at increasing concentrations of bromoanilinium tetrafluoroborate. The two reversible one-electron waves shown in the bottom cyclic voltammogram correspond to the Ni(II/I) ($E_{1/2} = -0.94$ V) and Ni(I/0) ($E_{1/2} = -1.19$ V) couples for this

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Table 2. Thermodynamic Properties of 3a–c and Related Complexes

complex (RR′)	$E_{1/2}$(II/I) for **1a–c**	$E_{1/2}$(I/0) for **1a–c**	pK_a Ni–H	$\Delta G°_{H^-}$, kcal/mol	$\Delta G°_{H\bullet}$, kcal/mol	pK_a NH	$\Delta G°_{(H2)}$, kcal/mol
3a (CyBz)	−0.80	−1.28	21.2 (22.6)[a]	60.7 (61.9)[b]	53.2	13.4	−3.1
3b (PhPh)	−0.84	−1.02	16.3 (17.2)	59.0 (61.2)	52.4	(6)[c]	(+9)[c]
3c (PhBz)	−0.94	−1.19	19.4 (20.7)	57.1 (59.2)	52.8	11.8	+2.7
6 (PNP)	−0.64	−1.24	22.2 (21.8)	66.7 (65.0)	53.2	11.2	−6.0
7 (depp)	−0.61	−1.34	23.3 (23.9)	67.2 (65.6)	54.4		

[a] Values in parentheses represent expected values based on linear free energy correlations using pK_a = 20.8$E_{1/2}$(I/0) − 4.0. [b] Values in parentheses represent expected values based on linear free energy correlations using $\Delta G°_{H^-}$ = 19.2$E_{1/2}$(II/I) + 77.3. See ref 47. [c] Values estimated as described in the text.

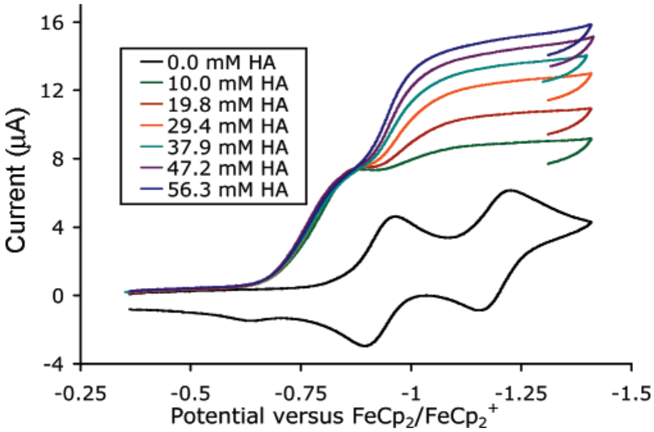

Figure 1. Cyclic voltammograms of **1c** in acetonitrile/0.3 M Bu$_4$NBF$_4$ at a scan rate of 50 mV/s with no acid (bottom scan) and with increasing amounts of *p*-bromoanilinium tetrafluoroborate, as shown in inset.

complex. As acid is added, the reduction waves shift to more positive potentials, and evidence for a catalytic increase in current is observed for the second wave at $E_{1/2} = -0.95$ V. The observed anodic shift in the reduction potential is consistent with protonation of one or more N atoms of **1c** in the presence of *p*-bromoanilinium tetrafluoroborate, resulting in electron withdrawal from the nickel center.

Figure 2a shows the i_c/i_p ratio for **1c** as a function of acid concentration (where i_c is the catalytic current and i_p is the peak current for the catalyst in the absence of acid), and Figure 2b shows the same data, reported previously, for **1b**.[37] As the acid concentration increases, the catalytic current for each complex initially increases and then becomes independent of acid concentration. The acid-independent region indicates saturation with acid and a rate-limiting step such as H_2 elimination or an intramolecular proton transfer. Using the data in this region of each plot, the rate constants, *k*, for hydrogen evolution can be calculated using the relationship shown in eq 8 (where ν = scan rate and *n* = number of electrons transferred, 2).[43–45] The

$$\frac{i_c}{i_p} = \frac{n}{0.4463}\sqrt{\frac{RTk}{F\nu}} \qquad (8)$$

turnover frequency of 5 s^{-1} at 22 °C for **1c** is much smaller than that for **1b** (350 s^{-1}) and indicates that **1c** is a poorer catalyst for H_2 production than **1b** by about 2 orders of magnitude. A comparison of the overpotentials required for the two catalysts is also relevant in their evaluation. Although the potential for proton reduction for **1c** is shifted to a more negative value than the potential of −0.86 V observed for **1b**, **1c** requires a much weaker acid for optimal catalysis than **1b**. Protonated

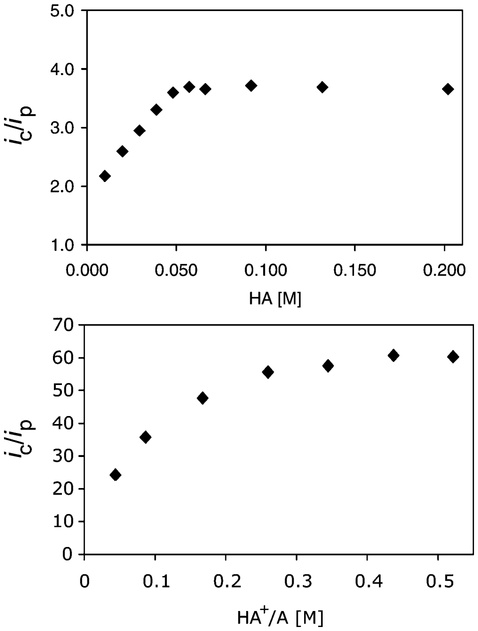

Figure 2. Plots of i_c/i_p (as defined in text) for (a) [Ni($P^{Ph}_2N^{Bz}_2$)$_2$(CH$_3$CN)](BF$_4$)$_2$, **1c**, as *p*-bromoanilinium tetrafluoroborate is added, and (b) [Ni^{II}($P^{Ph}_2N^{Ph}_2$)$_2$(CH$_3$CN)](BF$_4$)$_2$, **1b**, as (HDMF)OTf is added.

DMF with a pK_a value of 6.1 in acetonitrile was used for **1b**, and bromoanilinium with a pK_a value of 9.4 was used for **1c**.[38] Using a value of −0.14 V for the standard potential of the H_2/H^+ couple in acetonitrile[46] and the pK_a values of the acids as an estimate of the pH values in acetonitrile under catalytic conditions, overpotentials for H_2 evolution can be calculated for complexes **1b** and **1c** of −0.3 and −0.2 V, respectively.

Thermodynamic Data for [HNi($P^{Ph}_2N^{Bz}_2$)$_2$]$^+$, 3c. The reaction of **1c** with hydrogen in the presence of an external base was found to form the hydride derivative [HNi^{II}($P^{Ph}_2N^{Bz}_2$)$_2$]$^+$, **3c**. This product was identified by the characteristic pentet (J_{PH} = 29 Hz) for the hydride resonance in the ^{1}H NMR spectrum at −8.1 ppm in acetonitrile and a broad singlet in the ^{31}P NMR spectrum at 10.9 ppm. When the reaction of **1c** with hydrogen was carried out in acetonitrile with an excess of anisidine (6–10 equiv), an equilibrium was observed by ^{31}P NMR spectroscopy, eq 9. An equilibrium constant of (1.3 ± 0.1) × 10^{-2}

$$\underset{\mathbf{1c}}{[\mathrm{Ni^{II}}(\mathrm{P^{Ph}}_2\mathrm{N^{Bz}}_2)_2(\mathrm{CH_3CN})]^{2+}} + \text{base} + \mathrm{H_2} \Leftrightarrow \underset{\mathbf{3c}}{[\mathrm{HNi^{II}}(\mathrm{P^{Ph}}_2\mathrm{N^{Bz}}_2)_2]^+} + \mathrm{Hbase}^+ \qquad (9)$$

was determined for this reaction by integration of the ^{31}P resonances for **1c** and **3c** and by mass balance of the anisidine/anisidinium ratio. This equilibrium constant was used in a thermo-

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(43) Delehay, P.; Stiehl, G. L. *J. Am. Chem. Soc.* **1952**, *74*, 3500–3505.
(44) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

dynamic cycle analogous to that shown in Scheme 3S to determine a $\Delta G°_{H^-}$ value of 57.1 ± 0.3 kcal/mol for $[HNi^{II}(P^{Ph}{}_2N^{Bz}{}_2)_2]^+$. From this value and the potentials of the Ni(II/I) and Ni(I/0) couples in acetonitrile, a pK_a value of 19.4 ± 1.0 and a homolytic bond dissociation energy of 52.8 ± 1.0 kcal/mol were calculated using the thermodynamic cycles shown in Schemes 1S and 2S, respectively.

The addition of 1−2 atm of H_2 to $[Ni(P^{Ph}N^{Bz})_2](BF_4)_2$ (**1c**) in the absence of an external base was monitored by cyclic voltammetry and ^{31}P NMR spectroscopy. The data suggested that products were formed in very low concentrations. Further ^1H and ^{31}P NMR studies of H_2 addition to **1c** were therefore carried out at high pressures (17.7, 52.4, and 68.7 atm) at 25 ± 2 °C. New broad resonances are observed in the ^{31}P NMR spectrum that increase and decrease in intensity as the H_2 pressure is increased and decreased. These are assigned to isomers of $[Ni(P^{Ph}{}_2NH^{Bz}N^{Bz})_2](BF_4)_2$ (**5A**−**C**) with structures analogous to **2A**−**C**. The predominant new species, **5A**, exhibits a broad singlet at 10.2 ppm, and this species is assigned a structure analogous to **2A**. Upon cooling to −40 °C, this resonance becomes an AB quartet centered at 9.6 ppm with a coupling constant of 22 Hz. Two equally intense resonances at 11.1 and −12.3 ppm are assigned to isomer **5B** with a structure analogous to **2B**. The resonance at −12.3 ppm becomes an unresolved AB quartet at −40 °C. Similar behavior was observed previously for isomer **2B**.[37] The singlet at −13.4 ppm is assigned to the isomer **5C** with a structure analogous to **2C**. At 25 °C the ratio of **5A**:**5B**:**5C** is 79:20:1. Two new resonances are also observed in the ^1H NMR spectrum upon addition of H_2 at high pressures. A broad resonance at 13.6 ppm is assigned to the protons interacting with two amines in structures **5B** and **5C**. A second broad resonance appearing at 6.3 ppm is assigned to the protonated amines in isomer **5A**. These assignments are based on analogy to structures **2A**−**C**, which were determined by one- and two-dimensional NMR experiments of ^{15}N- and ^2H-labeled complexes.[37] These high-pressure NMR experiments indicate that the mode of heterolytic activation of H_2 by **1a** and **1c** is similar; both involve the two-electron reduction of Ni(II) to Ni(0) and the protonation of two pendant N atoms of the cyclic diphosphine ligands. Integrations of the ^{31}P NMR spectra as a function of pressure to determine the ratio of Ni species present resulted in the determination of an equilibrium constant of 0.011 ± 0.002 atm^{-1}. This corresponds to a free energy of +2.7 ± 0.2 kcal/mol for the addition of H_2 to **1c**.

Discussion

We are interested in developing a better understanding of the energetics of possible catalytic intermediates in the oxidation and production of hydrogen by complexes such as **1a**−**c** as a basis for understanding the relative catalytic rates. Table 2 summarizes the thermodynamic data for these complexes as well as those for the closely related systems $[Ni(PNP)_2]^{2+}$, **6**, and $[Ni(depp)_2]^{2+}$, **7**[25] (where PNP = $Et_2PCH_2N(Me)CH_2PEt_2$) and depp = bis(diethylphosphino)propane).

Comparisons of Reduction Potentials. Columns 2 and 3 of Table 2 list the potentials of the Ni(II/I) and Ni(I/0) couples versus ferrocene$^{0/1+}$ in acetonitrile. Previous studies have shown that the potentials of the Ni(I/0) couples are determined almost exclusively by the electron-donating ability of substituents on the diphosphine ligand.[25] It is expected that the complex with cyclohexyl substituents, $[Ni(P^{Cy}{}_2N^{Bz}{}_2)_2](BF_4)_2$, **1a**, would have a more negative potential than complexes **1b** and **1c** with phenyl substituents. Of these latter two complexes, $[Ni(P^{Ph}{}_2N^{Ph}{}_2)_2](BF_4)_2$, **1b**, contains the weaker electron donor in the phosphine backbone and therefore displays the more positive potential. The nitrogen atom in the chelate backbone of the diphosphine ligand is expected to withdraw electron density from phosphorus and nickel compared to a methylene group, and the more positive Ni(I/0) potential observed for $[Ni(PNP)_2]^{2+}$, **6**, and **1a** compared to $[Ni(depp)_2]^{2+}$, **7**, is consistent with this reasoning.

The Ni(II/I) couple is affected by both the electron-donating or -withdrawing nature of the substituents on the diphosphine ligand and the natural bite angle (NBA) of the diphosphine ligands.[25,34] Electron-donating substituents of course result in more negative potentials, and smaller bite angles also result in more negative Ni(II/I) potentials. The origin of the influence of a NBA is a tetrahedral distortion from a square-planar geometry in the Ni(II) complexes caused by steric interactions between phosphine substituents. This distortion, which increases with increasing NBAs, results in a reduced antibonding overlap between the σ orbitals of the phosphine ligands and the d_{x2-y2} orbital of nickel. The LUMOs for these Ni(II) complexes have lower energies as this distortion increases and the Ni(II/I) potentials become more positive. Structural studies show that Ni(II) complexes containing diphosphine ligands with propylene backbones and the PNP ligand have P−Ni−P bond angles of 91 ± 2°. The bond angles for Ni complexes containing the cyclic $P^{Cy}{}_2N^{Bz}{}_2$ and $P^{Ph}{}_2N^{Ph}{}_2$ ligands are 82 ± 2°. The more negative Ni(II/I) potentials observed for complexes **1a**−**c** compared to $[Ni(depp)_2]^{2+}$ and $[Ni(PNP)_2]^{2+}$ are attributed to the smaller NBAs of **1a**−**c**. Among the three complexes **1a**−**c**, the complex with the largest phosphine substituent, cyclohexyl for **1a**, should have the largest tetrahedral distortion and the most positive redox potential for the Ni(II/I) couple, as observed. The steric interactions between the phenyl substituents on phosphorus for **1b** and **1c** are expected to be the same, and in this case the increased electron-donating ability of the NBz group compared to the NPh group should lead to a more negative potential of **1c** compared to **1b**.

Comparisons of pK_a and $\Delta G°_{H^-}$ Values. It is important to understand the parameters controlling the potentials of the Ni(II/I) and Ni(I/0) couples, because these potentials show linear correlations with the hydride donor abilities and the pK_a values, respectively, of the corresponding Ni hydrides.[25] The measured pK_a and $\Delta G°_{H^-}$ values of the metal hydrides are shown in Table 2, columns 4 and 5, respectively. The values in parentheses were calculated from the previously determined linear correlations of the Ni(II/I) couple with hydricity and the Ni(I/0) couple with pK_a based on several $[Ni(diphosphine)_2]^{2+}$ complexes.[47] It can be seen that there is relatively good correlation, with the calculated values being within 2 kcal/mol or 1.5 pK_a units of the measured values. These results indicate that the same relationships found previously for other $[Ni(diphosphine)_2]^{2+}$ complexes hold for complexes **1a**−**c** as well and that there are no unusual thermodynamic consequences introduced by incorporation of a pendant base into the backbone of the diphosphine ligand or by using cyclic ligands. In addition, the agreement between the experimentally determined thermodynamic values and those predicted using linear free energy correlations indicates that these correlations can be used to design catalysts with hydride acceptor properties appropriately balanced for H_2 production and oxidation. For the sake of completeness, the

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(45) (a) Saveant, J. M.; Vianello, E. *Electrochim. Acta* **1965**, *10*, 905−920. (b) Saveant, J. M.; Vianello, E. *Electrochim. Acta* **1967**, *12*, 629−646.

(46) Felton, G. A. N.; Glass, R. S.; Lichtenberger, D. L.; Evans, D. H. *Inorg. Chem.* **2006**, *45*, 9181−9184.

(47) The revised value for the pK_a of anisidinium (see ref 38) has led to slightly revised free energy relationships from those published in ref 27.

homolytic bond dissociation free energies are shown in column 6. The values observed are very similar and within the range observed previously for other $[HNi(diphosphine)_2]^+$ derivatives.[24,25]

A comparison of the pK_a values of benzyl- and methylammonium ions indicates that the pK_a decreases by about 1.6 units when methyl is replaced by benzyl in these simple ions.[42] However in the nickel complexes, the pK_a value of 13.4 for the protonated benzylamine unit in **2** is *larger* than that observed previously for $[HNi(PNP)(PNHP)]^{2+}$ (11.2), which has a methyl substituent on nitrogen. This increase in the pK_a values for **2** suggests that the positioning of the nitrogen atom in close proximity to the Ni(0) center or to a second amine results in stabilization of the NH proton by about 3.8 pK_a units (13.4 − expected value of 9.6), or 5 kcal/mol. Recent theoretical studies have suggested similar interactions of ammonium NH protons with the metal in ruthenium complexes.[48] These interactions could also be partly responsible for the large positive shift of the Ni(I/0) potential observed for **2** compared to **1a**.[37]

Calculations and Comparisons of $\Delta G°_{(H2)}$ Values. The free energies for heterolytic H_2 addition to the complexes in Table 2 are tabulated in column 8. To avoid high-energy intermediates during the oxidation or production of H_2 via a heterolytic process, it is important to match the hydride acceptor ability of the metal with the proton acceptor ability of the base so that $\Delta G°$ for this reaction is close to zero. The free energy required to heterolytically cleave H_2 to form H^+ and H^- in acetonitrile, eq 5, is 76 kcal/mol.[27,40] For $[Ni(P^{Cy}_2N^{Bz}_2)_2](BF_4)_2$, **1a**, the hydride donor ability is 60.7 kcal/mol, and this requires an acid with a ΔG_{H+} of 15.3 kcal/mol, or pK_a value of 11.2, for H_2 activation and release to be reversible. The pK_a of the protonated pendant base in **2** was measured to be 13.4 ($\Delta G_{H+} = 18.4$ kcal/mol), and it is the combination of hydride acceptor ability (−60.7 kcal/mol) and proton acceptor ability (−18.4 kcal/mol) of **1a** that results in a driving force of −3.1 kcal/mol for the formation of **2** from **1a** and H_2. Similar calculations have been carried out previously for $[Ni(PNP)_2]^{2+}$, **6**. The hydride acceptor ability is −66.7 kcal/mol and the pK_a value of the protonated NH in $[HNi(PNP)(PN\mathit{H}P)]^{2+}$ is 11.2, corresponding to a free energy of −6.0 kcal/mol for H_2 addition to $[Ni(PNP)_2]^{2+}$.[25]

A $\Delta G°_{H2}$ value of +2.7 kcal/mol was determined for $[Ni(P^{Ph}_2N^{Bz}_2)_2](BF_4)_2$, **1c**, from high-pressure NMR data. This data and the $\Delta G°_{H^-}$ value of $[HNi(P^{Ph}_2N^{Bz}_2)_2](BF_4)$ can be used to calculate a pK_a value of 11.8 for the protonated amines in isomers of **5** using the thermodynamic cycle shown in Scheme S4. Again, this pK_a value is *larger* than that observed previously for $[HNi(PNP)(PNHP)]^{2+}$ (11.2), which has a methyl substituent on nitrogen and ethyl substituents on phosphorus. This unexpectedly large pK_a value for **5** also suggests that the positioning of the nitrogen atom in close proximity to the Ni(0) center or to a second amine results in stabilization of the NH protons.

Because the H_2 addition product of $[Ni(P^{Ph}_2N^{Ph}_2)_2](BF_4)_2$, **1b** (in the absence of base), was not detected spectroscopically, it was not possible to experimentally determine the pK_a value of the product, which is expected to form isomers of nickel(0) derivatives with two protonated amines, analogous to **2A**−**C** and **5A**−**C**. However, this pK_a value can be estimated. For example, for **1b** the presence of a phenyl substituent on nitrogen compared to a benzyl group in **1c** would be expected to decrease the pK_a of the protonated amine by a value comparable to the difference of the pK_a values of benzylammonium (pK_a = 16.8) and anilinium (pK_a = 10.6) in acetonitrile.[41] This leads to the expectation of a pK_a value of about 6 for the H_2 adduct of **1b**.

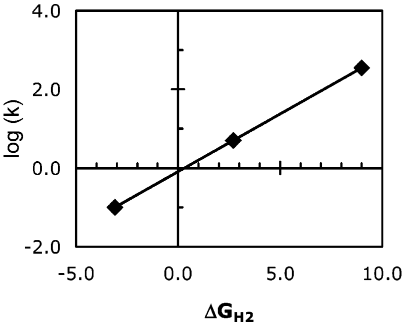

Figure 3. Plot of log of the rate constant for H_2 production/oxidation versus the free energy for H_2 binding for complexes **1a**−**c**.

This estimate, together with the hydride acceptor ability for **1b** of −59.0 kcal/mol, allows us to calculate a free energy for H_2 addition to **1b** of approximately +9 kcal/mol.

It is clear from the free energies for the heterolytic addition of H_2 to complexes **1a**−**c** that complex **1a** is biased by the nature of its ligand substituents toward H_2 uptake. It is expected (and observed) to be the best of the three derivatives in the role of a H_2 oxidation catalyst. Conversely, if this complex were to function as a catalyst for H_2 formation, the product would rapidly inhibit the catalyst unless H_2 could be continuously removed. Complex **1b** is significantly biased toward H_2 loss, consistent with this compound serving as an exceptionally effective H_2 production catalyst. For complex **1c**, the bias for H_2 evolution is small, and the catalytic rate for H_2 production is about 2 orders of magnitude smaller than that observed for **1b**. A graphical representation of this correlation is shown in Figure 3, in which the log of the rate constant for H_2 production/oxidation is plotted versus $\Delta G°_{H2}$. Although the rates of H_2 oxidation and production in these catalytic reactions are controlled by transition state energies, a knowledge of the factors controlling the thermodynamics of the intermediates can greatly assist in understanding their bias toward H_2 production or oxidation.

Summary. This work demonstrates that the thermodynamic properties of $[Ni(P^R_2N^{R'}_2)_2](BF_4)_2$ and $[HNi(P^R_2N^{R'}_2)_2](BF_4)$ derivatives and a knowledge of the factors controlling these properties can be used in the design of electrocatalysts for H_2 oxidation and production. The observation that the potential of the Ni(II/I) couple for $[Ni(P^{Cy}_2N^{Bz}_2)_2](BF_4)_2$ is more positive than the Ni(II/I) couples of $[Ni(P^{Ph}_2N^{Bz}_2)_2](BF_4)_2$ and $[Ni(P^{Ph}_2N^{Ph}_2)_2](BF_4)_2$ can be understood in terms of a larger tetrahedral distortion expected for $[Ni(P^{Cy}_2N^{Bz}_2)_2](BF_4)_2$ arising from increased steric interactions between the cylohexyl substituents on phosphorus. This leads to the interesting situation in which a better electron-donating cyclohexyl substituent results in a more positive Ni(II/I) potential, a better hydride acceptor, and a catalyst that is biased for H_2 oxidation compared to $[Ni(P^{Ph}_2N^{Bz}_2)_2](BF_4)_2$, which has phenyl substituents on phosphorus that are poorer electron donors. These results indicate that the steric bulk of the phosphorus substituents can be used to tune the hydride acceptor ability of these complexes and bias the reactivity toward either H_2 production or H_2 oxidation if the pendant base is kept constant. Similarly, the electron-donating or -withdrawing ability of the amine substituent can be used to control the driving force for H_2 uptake or release as seen by comparing $[Ni(P^{Ph}_2N^{Bz}_2)_2](BF_4)_2$ and $[Ni(P^{Ph}_2N^{Ph}_2)_2](BF_4)_2$. As a result, it is possible to finely tune the thermodynamic properties of these complexes for either H_2 production or oxidation. The free energy associated with H_2 uptake and release has been shown to correlate with the rates of H_2 oxidation/

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(48) Shi, F. *Organometallics* **2006**, *25*, 4034−4037.

production, consistent with this reaction being the rate-determining step of the catalytic cycles.

Experimental Section

General Methods and Materials. All procedures were carried out under an inert atmosphere using standard Schlenk techniques or a glovebox. Solvents were distilled under nitrogen using standard procedures. Complexes **1a** and **1b** were prepared as described previously.[36] Anisidine and tetramethylguanadine (TMG) were purchased from commercial suppliers. Anisidinium tetrafluoroborate was prepared by adding an equivalent of HBF_4-Et_2O to anisidine in ether. The resulting precipitate was filtered and washed with ether. A similar procedure with triflic acid was used to prepare (HTMG)OTf. Equilibrium data were determined at 22 ± 2 °C unless stated otherwise.

Instruments. NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. ^1H chemical shifts are reported relative to tetramethylsilane using residual solvent protons as a secondary reference. ^{31}P chemical shifts are reported relative to external phosphoric acid, and all ^{31}P NMR spectra were proton decoupled. Cyclic voltammetry experiments were carried out on a Cypress Systems computer-aided electrolysis system with glassy carbon working and counter electrodes. A silver wire was used as a pseudoreference electrode. Ferrocene was used as an internal standard, and all potentials are referenced to the ferrocene/ferrocenium couple.

$[Ni(P^{Ph}{}_2N^{Bz}{}_2)_2(CH_3CN)](BF_4)_2$. Phenyl phosphine, $PhPH_2$ (1.31 g, 11.9 mmol), and paraformaldehyde (0.71 g, 23.8 mmol) were combined in 100 mL of EtOH and allowed to stir in an oil bath at 77 °C for 0.5 h. To this solution was added benzylamine (1.28 mL, 11.9 mmol). The solution was refluxed with stirring for 18 h, resulting in a white, flaky precipitate. The solution was filtered and washed three times with 30 mL of EtOH. Yield: 2.02 g, 4.19 mmol, 70%. ^{31}P NMR (CD_2Cl_2): −55.5 (s). The crude ligand (2.02 g, 4.19 mmol) was combined with $[Ni(CH_3CN)_6](BF_4)_2$ (1.05 g, 2.10 mmol) in 30 mL of acetonitrile. This solution was stirred for 2 h, after which the volume was reduced to 10 mL. Diethyl ether (10 mL) was added, and the solution was left overnight, producing a batch of dark pink crystals, which were filtered. The remaining solvent was removed by vacuum, leaving a dark pink solid. Yield: 2.25 g, 1.82 mmol, 87%. Crystals were obtained by recrystallization of the product from acetonitrile (8 mL)/Et_2O (20 mL). Anal. Calcd for $C_{62}H_{67}B_2F_8N_5P_4Ni$: C, 60.13; H, 5.45; N, 5.66. Found: C, 59.90; H, 5.47; N, 5.51. ^1H NMR (CD_3CN): 7.5 to 7.0 (4 m, 40 H, Ar−H); 3.9 (br d, $J = 15$ Hz, 8 H, NCH_2P); 3.4 (d, $J = 8$ Hz, 7.9 H, NCH_2Ph); 3.1 (br d, $J = 44$ Hz, 8 H, NCH_2P). ^{31}P NMR (CD_3CN): 3.62 (br s).

Heterolytic Cleavage of H_2 by $[Ni(P^{Cy}{}_2N^{Bz}{}_2)_2](BF_4)_2$. $[Ni(P^{Cy}{}_2N^{Bz}{}_2)_2](BF_4)_2$, **1a** (25 mg, 0.021 mmol), was weighed into three NMR tubes and dissolved in d_3-acetonitrile (0.54, 0.52, 0.50 mL). After the solutions were purged with hydrogen for 3 min, they were treated with aliquots of a 1.00 M anisidine solution in CD_3CN (0.062, 0.082, 0.103 mL, 0.062−0.103 mmol). The reaction mixtures were shaken and analyzed by ^{31}P NMR within 10 min of mixing to obtain an equilibrium constant based on the relative integrals of the ^{31}P peaks corresponding to the isomers of $[Ni^0(P^{Cy}{}_2N^{Bz}\mathit{H}N^{Bz})_2]^{2+}$, **2**, and $[HNi(P^{Cy}{}_2N^{Bz}{}_2)_2](BF_4)$, **3a**. Four peaks were observed in the ^{31}P NMR spectrum at the following chemical shifts: 19.8 ppm (attributed to **2A**), 17.4 and −6.7 ppm (attributed to **2B**), −9.2 ppm (attributed to **2C**), and 14.1 ppm (attributed to **3a**). The ratios of the four peaks were monitored over the next 4 h, and the same ratios were observed within experimental error for each mixture.

pK_a of $[HNi(P^{Cy}{}_2N^{Bz}{}_2)_2](BF_4)$. A solution of $[NiP_2{}^{Cy}N_2{}^{Bz})_2](BF_4)_2$, **1a** (0.015 g, 0.012 mmol), in 0.60 mL of benzonitrile was prepared in an NMR tube. After the NMR solution was purged with hydrogen for 3 min, 1,1,3,3-tetramethylguanidine (3.l μL, 0.025 mmol) was added. The reaction mixture was shaken and analyzed by ^{31}P NMR spectroscopy within 5 min of mixing to determine the ratio of product and reactant nickel complexes. The ^{31}P NMR spectrum showed a peak corresponding to the product, $[Ni^0(P_2{}^{Cy}N_2{}^{Bz})_2]$, at 9.9 ppm and a peak corresponding to the reactant, $[HNi(P_2{}^{Cy}N_2{}^{Bz})_2](BF_4)$, at 13.6 ppm. The NMR was recorded again 1 h later, and the same ratios were observed within experimental error. The same procedure was repeated with two additional samples.

Heterolytic Cleavage of H_2 by $[Ni(P_2{}^{Ph}N_2{}^{Bz})_2](BF_4)_2$. Solutions of $[Ni(P^{Ph}{}_2N^{Bz}{}_2)_2](BF_4)_2$, **1c** (25 mg, 0.021 mmol), in 0.60 mL of d_3-acetonitrile were prepared in three NMR tubes. After the solutions were purged with hydrogen for 3 min, they were treated with aliquots of a 1.00 M anisidine solution in CD_3CN (0.12, 0.17, 0.21 mL, 0.12−0.21 mmol). The reaction mixture was shaken and analyzed by ^{31}P NMR after 20 min. The resulting spectrum showed a peak corresponding to the starting complex, $[Ni(P^{Ph}{}_2N^{Bz}{}_2)_2](BF_4)_2$, **1c**, at 3.5 ppm and a peak corresponding to the product, $[HNi^{II}(P^{Ph}{}_2N^{Bz}{}_2)_2]^+$, **3c**, at 10.9 ppm The same ratios were observed within experimental error for each mixture over the next 4 h.

Addition of H_2 to $[Ni(P_2{}^{Ph}N_2{}^{Bz})_2](BF_4)_2$. Solutions of $[Ni(P^{Ph}{}_2N^{Bz}{}_2)_2](BF_4)_2$, **1c**, in 0.2 mL of d_3-acetonitrile were added to a high-pressure NMR tube that has been described previously,[49] and the tube was pressurized sequentially to 17.7, 68.7, and 52.4 atm. The solutions were mixed vigorously using a vortex mixer to ensure H_2 mixing, and the ratios of the metal complexes were determined by integration of the ^{31}P NMR spectra at 25 °C. Spectra recorded after 0.5 and 24 h were the same. ^{31}P NMR (CD_3CN, −40 °C, 51.0 atm): isomer **5A**, AB quartet, $\delta_A = 11.7$, $\delta_B = 7.5$, $J_{AB} = 22$ Hz; isomer **5B**, unresolved AB quartet, $\delta_A = -8.7$, $\delta_B = -15.5$, J_{AB} unresolved, singlet at 9.1 (integration ratio of singlet to AB quartet = 1:1); isomer **5C**, singlet at −13.4. ^1H NMR (CD_3CN, −40 °C, 51.0 atm): NH proton of **5A** observed as broad singlet at 6.2 ppm, NH of **5C** observed as broad singlet at 13.6 ppm.

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Supporting Information Available: Thermodynamic Schemes 1S for determining pK_a values of nickel hydride complexes, 2S for determining $\Delta G^\circ_{H\cdot}$ values, 3S for determining $\Delta G^\circ_{H^-}$ values, and 4S for determining pK_a values for protonated pendant amines. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070143V

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