Thermochemical Studies of Nickel Hydride Complexes with Cationic Ligands in Aqueous and Organic Solvents

Andrew D. Cypcar*, Tyler A. Kerr*, Jenny Y. Yang*ab*

*Department of Chemistry, University of California, Irvine, California, 92697, United States
abPhysical Sciences Division, Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington 99354, United States
*j.yang@uci.edu

ABSTRACT: Transition metal hydride complexes are key intermediates in a variety of catalytic processes. Transfer of a hydride, hydrogen atom, and proton are defined by the thermochemical parameters of hydricity, bond dissociation free energy (BDFE), and pKα, respectively. These values have been studied primarily in organic solvents to predict or understand reactivity. Despite growing interest in the development of aqueous metal hydride catalysis, BDFE measurements of transition metal hydrides in water are rare. Herein, we report two nickel hydride complexes with one or two cationic ligands that enable the measurement of BDFE values in both aqueous and organic solvents using their reduction potential and pKα values. The Ni(I/0) reduction potentials increase anodically as more charged groups are introduced into the ligand framework and are among the most positive values measured for Ni complexes. The complex with two cationic ligands, 2-Ni(II)-H, displays exceptional stability in water with no evidence of decomposition at pH 1 for at least 2 weeks. The BDFE of the nickel hydride bond in 2-Ni(II)-H was measured to be 53.8 kcal/mol in water, and between 50.9-56.2 kcal/mol in acetonitrile, consistent with prior work that indicates minimal solvent dependence for BDFEs of O-H and N-H bonds. These results indicate transition metal hydride BDFEs do not change drastically in water and inform future studies on highly cationic transition metal hydride complexes.

INTRODUCTION

Transition metal hydride complexes are common intermediates in catalytic reactions and can react as hydride, H-atom, or proton donors.1 For example, in one of the simplest reductions, the hydrogen evolution reaction (HER), electrocatalysts are known to form H-H bonds through either a heterolytic mechanism through protonation of a metal hydride2 or through homolytic bond formation, where H-atoms from two M-H complexes combine to form H2 and two reduced metal centers.3 Additionally, metal hydrides are implicated in CO2 reduction reactions2,4,5 and organic transformations, such as hydrogenation6,7 and radical hydrofunctionalization8,9 reactions.

The thermodynamic parameters of a metal hydride — hydricity, BDFE (bond dissociation free energy), and pKα — define the free energies for hydride transfer, proton transfer, and hydrogen atom transfer (HAT), respectively. These values are interrelated through square schemes (Figure 1a).4 For metal hydrides, these values have been most commonly studied in organic solvents, particularly acetonitrile (MeCN).4,10,11 In water, pKα values of approximately 20 transition metal hydrides have been documented,11 and there has been more recent interest in evaluating aqueous hydricity values.3,12-15 However, there is a notable dearth of transition metal hydride BDFEs that have been measured in water.16 Most prominent is the work of Wayland and coworkers, where equilibrium measurements were used to obtain estimates of BDFEs in metal porphyrin complexes.16,17

Measuring BDFEs of metal hydrides in water presents unique challenges (Figure 1b). Protonation of a metal hydride by protons in water to form H2 and the corresponding oxidized metal is often favorable.2 To obtain a BDFE value using a square scheme, an accurate pKα value and one electron reduction potential are needed. However, the narrow pH range of water limits the range of measurable pKα values, and most transition metal complexes exhibit irreversible redox events in water. The BDFE value could also be measured by equilibrium

Figure 1. (a) Square scheme depicting relationship between thermodynamic parameters of a metal hydride. (b) Challenges contributing to the difficulty of measuring BDFEs of transition metal hydrides in water.
measurements with H-atom donors/acceptors with known BDFE values, but few of these have been reported in water.\textsuperscript{18}

\textbf{Scheme 1. Synthesis of cationic Ni bis(disphosphine) complexes.}

In order to elucidate a more complete understanding of aqueous metal hydride thermochemistry and how it relates to values in organic solvents, we investigated a metal complex soluble in both MeCN and water. The desired solubility properties were achieved by adding charged functional groups,\textsuperscript{19} which are commonly used to engender water solubility to organometallic complexes, although they can change other thermochemical properties.\textsuperscript{20} Specifically, nickel complexes with two disphosphine ligands containing an amine in the backbone were singly or doubly methylated (Scheme 1). These highly charged nickel complexes enabled the study of nickel hydride BDFEs in aqueous and organic solvents.

\textbf{RESULTS}

\textbf{Synthesis and characterization.} We synthesized charged, water-soluble derivatives of the previously reported nickel(bisdiphosphine) complex, Ni(PNP)\textsubscript{2}\textsuperscript{21} (0-Ni) (PNP = Et\textsubscript{2}PCH\textsubscript{2}NMeCH\textsubscript{2}PET\textsubscript{2}), through methylation of the backbone amines (Scheme 1). Attempts to methylate the free PNP ligand resulted in a complex mixture of products, none of which could be assigned as the desired cationic ligand by \textsuperscript{1}H and \textsuperscript{31}P{[\textsuperscript{1}H]} NMR spectroscopy. However, direct methylation of the ligand bound to a metal is preceded in related metal phosphine complexes.\textsuperscript{22-25}

Upon methylation with one or two equivalents of methyl triflate (MeOTf), the Ni(0) complexes 1-Ni and 2-Ni were prepared and characterized by \textsuperscript{1}H and \textsuperscript{31}P{[\textsuperscript{1}H]} NMR spectroscopy (where 1 and 2 refers to the nickel complex with one and two cationic ligands, respectively). 2-Ni was further studied by single crystal X-ray crystallography and is a rare example of a structurally characterized dicationic Ni(0) complex (Figure 2). For comparison, we also obtained a solid-state structure of Ni(depp)\textsubscript{2} (depp = Et\textsubscript{3}PCH\textsubscript{2}CH\textsubscript{2}PET\textsubscript{2}, Figure S1).\textsuperscript{26} The average Ni-P bond lengths (2.160(4) Å) of 2-Ni are significantly longer than in Ni(depp)\textsubscript{2} (2.148(5) Å) indicating weaker Ni-P interactions with the cationic ligands. We also attempted methylation of the Ni(II) species, 2-Ni(II). However, treatment of 0-Ni(II) with 2 equivalents of MeOTf resulted in a complex mixture of species, as determined by \textsuperscript{31}P{[\textsuperscript{1}H]} NMR spectroscopy. Attempts to isolate the 2-Ni(I) and 2-Ni(II) complexes through chemical oxidation and electrochemical oxidation of 2-Ni were also unsuccessful (see Supporting Information).

\textbf{Electrochemical Studies.} 1-Ni and 2-Ni were further characterized electrochemically. All electrochemical potentials in acetonitrile (MeCN) are referenced to the Fe(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}Fe\textsuperscript{2+} reduction potential. Cyclic voltammetry (CV) of 2-Ni in MeCN exhibits a quasireversible Ni(I/0) redox event with an \textit{E}_{\text{1/2}} = -0.49 V followed by an irreversible oxidation at -0.11 V that we assign as oxidation to Ni(II) (Figure 3a, Figure S2). We suspect that after oxidation to the Ni(II), the cationic ligand(s) dissociate from the nickel center, followed by oxidation of a free phosphine ligand at approximately 1.1 V.\textsuperscript{27,28} Free ligand was observed when chemical oxidation was attempted (see SI). CV of 1-Ni in MeCN shows a reversible Ni(I/0) event at -0.82 V followed by an irreversible feature at -0.31 V assigned as the Ni(II/I) couple (Figure S3). The redox potentials of 1-Ni and 2-Ni follow a trend with 0-Ni, where increasing the number of cationic ligands corresponds to more anodic reduction potentials, and loss of reversibility for the Ni(II/I) couple (Table 1). The Ni(I/0) reduction potentials of 1-Ni and 2-Ni are among the most positive recorded for Ni complexes.\textsuperscript{29}

Cyclic voltammetry of 2-Ni in pH 7 buffered water shows a reversible Ni(I/0) couple at -0.11 V vs. NHE, as evidenced by the linear correlation of the square root of the scan rate with the current, and \(\Delta E_{\text{p}} = 70 \text{ mV} \) which is near the ideal 59 mV of a one electron couple (Figure 3, Figure S4). This result is in contrast to the Ni(II/IV) couple in MeCN, which is quasireversible. Similar to its behavior in MeCN, the Ni(II/I) couple is irreversible. 1-Ni at pH 7 also has a reversible Ni(I/0) event followed by an irreversible event assigned to the Ni(II/I) couple (Figure S5). Insolubility of the non-methylated compound 0-Ni and instability of 0-Ni(II) in water precludes determination of the potentials for the neutral analogue for comparison.

\textbf{Figure 2.} Solid-state structure of 2-Ni. Thermal ellipsoids are shown at 80% level of probability. Hydrogens and outer-sphere triflate anions have been omitted for clarity.
Protonation Studies. Protonation studies were performed in both MeCN and water (Scheme 1, above). Protonation of 2-Ni with four equivalents of [DMF(H)]OTf (DMF = dimethylformamide, pKₐ = 6.1) in MeCN forms 2-Ni(II)–H, which was characterized by ¹H NMR and ³¹P{¹H} NMR spectroscopic analysis. A hydride resonance was observed in the ¹H NMR spectrum at -15.84 ppm. The expected quintet splitting of the hydride resonance with phosphorus was not observed, despite being observed in 0-Ni(II)-H.²¹ The putative hydride is unstable; it decomposes over the course of several hours, resulting in free ligand and a paramagnetic species observable by electron paramagnetic resonance (EPR) spectroscopy (Figure S6). The EPR spectrum of this species indicates the decomposition forms an S = ½ nickel-based complex. The anisotropic g factor of the paramagnetic species greater than the g factor of a free electron (2.0023) suggesting the signal arises from a species with more than a half full d orbital set.¹¹

Due to the instability of the hydride 2-Ni(II)-H in MeCN, a precise pKₐ could not be obtained. Bounds for the pKₐ were determined using acids of different pKₐ and varying concentrations as needed. Addition of 10 equivalents of 4-trifluoromethylanilinium tetrafluoroborate (pKₐ = 8.03) to 2-Ni completely consumes nearly all of the Ni(0) species, forming 2-Ni(II)-H and the decomposition product. When one equivalent of this acid was used, incomplete reaction of 2-Ni was observed. Addition of 10 equivalents of the weaker acid 4-methoxylanilinium tetrafluoroborate (pKₐ = 11.86) to 2-Ni forms <5% of 2-Ni(II)-H and the decomposition product after 16 hours. From these studies we estimate the pKₐ is between 7.0 and 10.9 for 2-Ni(II)-H in MeCN (Figure S7).

Near quantitative protonation of 2-Ni in water was achieved by dissolving the complex in a pH 1 solution, forming 2-Ni(II)-H. In H₂O a characteristic hydride resonance is present at -15.69 ppm which is not present when D₂O is used. Remarkably, this hydride complex is stable in pH 1 water for over two weeks, and minimal decomposition is observed over ~3 months (Figure S8 and S9). The pKₐ of this complex in water was measured to be 2.6 by monitoring the relative concentration of 2-Ni and 2-Ni(II)-H in pH 2.5 or pH 4 buffered water with ³¹P{¹H} NMR spectroscopy. The sample was monitored for 24 hours to ensure equilibrium was achieved (Figure S10).

The protonation reactivity of 1-Ni is complicated due to two possible sites of protonation—at the metal or backbone amine—and the tendency of the compound to decompose into the homoletic complexes 0-Ni and 2-Ni in solution. Upon treatment of 1-Ni with acid in MeCN, multiple hydride species are observed, and can be assigned as 0-Ni(II)-H, 2-Ni(II)-H and presumably 1-Ni(II)-H. Due to this ligand exchange, the pKₐ could not be accurately determined in MeCN. Protonation of 1-Ni in water was also difficult to study due to pH dependent solubility. The aqueous pKₐ value of 0-Ni in water could not be determined because of it is not soluble.

BDFE determination. With both redox potential and pKₐ data in hand, the BDDE of the Ni-H bond of 2-Ni(II)-H was calculated using equation 1, where E² is the E½ of the Ni(I/0)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ni(I/0) vs. Fe(C₆H₅)₂⁺⁺⁺ (V) MeCN</th>
<th>Ni(II/I) vs. Fe(C₆H₅)₂⁺⁺⁺ (V) MeCN</th>
<th>Ni(I/0) vs. NHE (V) H₂O, pH 7</th>
<th>Ni(II/I) vs. NHE (V) H₂O, pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-Ni</td>
<td>-1.24 (rev)²¹</td>
<td>-0.64 (rev)²¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Ni</td>
<td>-0.82 (rev)</td>
<td>-0.31 (irrev)</td>
<td>-0.27 (rev)</td>
<td>0.05 (irrev)</td>
</tr>
<tr>
<td>2-Ni</td>
<td>-0.49 (quasi)</td>
<td>-0.11 (irrev)</td>
<td>-0.11 (rev)</td>
<td>0.55 (irrev)</td>
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*Irreversible potentials were recorded from Eox, the potential at the maximum oxidative current. *Best assignment for this feature.
The stability of 2-Ni(II)—H in water allowed for the measurement of its aqueous BDFE, which is a very rare example of a transition metal hydride BDFE measured in water. This BDFE of 53.8 kcal/mol is in the range of most measured transition metal hydrides in organic solvents (typically between 50-60 kcal/mol). Due to the necessity of using a pKₐ bracket, only a BDFE range of 50.9-56.2 kcal/mol could be obtained in MeCN. The measured BDFEs of 53.8 kcal/mol and 50.9-56.2 kcal/mol in water and MeCN, respectively, are very similar. This result is consistent with BDFEs of O-H and N-H bonds measured in multiple solvents; there is very little solvent dependence. Since the BDFE is within the typical range for transition metal hydrides, there appears to be little or no perturbation of the bond strength from either the water solvent or from the proximally located charges.

The hydricity values for 1-Ni and 2-Ni could not be rigorously determined in aqueous or organic solvent because reversible or quasi-reversible Ni(II/II) couples could not be obtained. Further, the inaccessibility of the Ni(II) analogues of 1-Ni and 2-Ni obviated the use of H₂ equilibrium to determine hydricity, as this method requires stable Ni(II) complexes. A lower bound of hydricity for 2-Ni(II)—H could be estimated at 35 kcal/mol, because no H₂ evolution was observed in pH 1 water after 2 weeks. Alternatively, the potential pKₐ method can be used to estimate a hydricity of 48 kcal/mol. However, the irreversible Ni(II/II) couple limits the accuracy of this value.

CONCLUSIONS

New monocationic and dicaticion nickel(0) bis(diphosphine) complexes 1-Ni and 2-Ni were synthesized and characterized by NMR spectroscopy and cyclic voltammetry. 2-Ni was further characterized by single crystal X-ray crystallography. Electrochemical studies reveal the Ni(I/I) couples of the cationic species are significantly anodically shifted relative to the neutral analog, and are among the most positive values measured for nickel complexes. Protonation studies were used to obtain the pKₐ values of the 2-Ni(II)—H species in both water and acetonitrile. The nickel hydride bond dissociation free energies for 2-Ni(II)—H was measured in water and MeCN. The BDFE value in MeCN is very similar to the value obtained in water, which is consistent with previous studies that demonstrate solvent invariance for BDFEs of O-H and N-H bonds. This work more broadly suggests that the bond strengths of transition metal hydrides are not perturbed in water, and measured BDFE values of transition metal hydrides in organic solvents would likely be similar to the BDFE of these metal hydride bonds in water. This conclusion informs the development of transition metal hydride catalysis in aqueous conditions.

EXPERIMENTAL SECTION

General Experimental Details. All manipulations were performed under an atmosphere of N₂ in a glovebox or through the use of a Schlenk line. Chemicals were obtained from commercial sources without further purification, unless otherwise noted. HPLC grade water degassed under active vacuum was used for aqueous studies. Nondeuterated organic solvents were degassed by sparging with argon and then dried by passage through an alumina column under argon pressure on a Solvent Drying System (JC Meyer Solvent Systems) and stored over activated 3 angstrom molecular sieves under a N₂ atmosphere. Deuterated solvents were purchased from Cambridge Isotope Laboratories and degassed by freeze-pump-thaw methods then dried over activated molecular sieves prior to use, with the exception of D₂O, which was stored without molecular sieves. Tetraethylammonium hexafluorophosphate (TBAFP⁺) was recrystallized from ethanol three times. PNP, \(^{24}\)}

\[ \Delta G^\circ_{\text{HR}} = 1.37(pK_a) + 23.06(E°) + \Delta G^\circ_c \]  

(1)

**DISCUSSION**

We prepared new highly-charged complexes 1-Ni and 2-Ni through a post-metalation methylation procedure, which selectively methylated the backbone amines of the ligand. Cationic phosphine ligands are relatively rare in the literature, and in most cases impart significantly different properties on the complex compared to their neutral analogs.\(^{35,36}\) The same is true for the cationic PNP ligands prepared in this work, which result in very electron-poor metal centers, making them weaker hydride donors. Unfortunately, the highly positive nature of these ligands makes it difficult to form the more electron deficient Ni(I) and Ni(II) complexes of 1-Ni and 2-Ni. The ligands also seem to be susceptible to dissociation, as protonation experiments in MeCN show the appearance of free ligand, which is also evident in chemical oxidation experiments.

The cationic ligands result in significant anodic shifts to the redox potentials of the nickel center relative to the neutral analog. Since there is only a single methylene spacer between the cation and the donor phosphorus atoms, we would expect significant inductive effects reducing the donor strength of the ligand. The Ni(I/I) reduction potential of 2-Ni in MeCN (-0.49 V) is very similar to a calculated reduction potential of a P₂N₂ type Ni(0) bisdiphosphine complex (-0.51 V) with 2 protons attached to the backbone pendant amines.\(^{36}\)

The nickel hydride complex 2-Ni(II)—H was synthesized in situ via protonation of 2-Ni. The anodic shift in potential from the cationic ligands is expected to result in a poorer hydride donor. As a result, protonation to form H₂ is likely unfavorable.\(^{37}\) In contrast, the overall tricationic 2-Ni(II)—H complex is less stable in MeCN, leading to paramagnetic species. We hypothesize that with a higher dielectric constant, water can better stabilize the highly charged 2-Ni(II)—H species than MeCN. The trends observed in the reduction potential and electrochemical reversibility are also consistent with this hypothesis. As more charged ligands are introduced, the reversibility of the Ni(I/I) and Ni(II/I) couples decreased in MeCN, suggesting the chemical events of ligand dissociation become more favorable with more cationic ligands. However, in water, the Ni(I/I) couple remains reversible.

The stability of 2-Ni(II)—H in water allowed for the measurement of its aqueous BDFE, which is a very rare example of a transition metal hydride BDFE measured in water. This BDFE of 53.8 kcal/mol is in the range of most measured transition metal hydrides in organic solvents (typically between 50-60 kcal/mol). Due to the necessity of using a pKₐ bracket, only a BDFE range of 50.9-56.2 kcal/mol could be obtained in MeCN. The measured BDFEs of 53.8 kcal/mol and 50.9-56.2 kcal/mol in water and MeCN, respectively, are very similar. This result is consistent with BDFEs of O-H and N-H bonds measured in multiple solvents; there is very little solvent dependence. Since the BDFE is within the typical range for transition metal hydrides, there appears to be little or no perturbation of the bond strength from either the water solvent or from the proximally located charges.

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Ni(PNP)$_2^{21}$, Ni(depp)$_2^{26}$, (DMF(H))OTf$_2$, 4-methoxyanilinium tetrafluoroborate, and 4-trifluoromethylnilinium tetrafluoroborate were synthesized as previously reported. NMR spectroscopic measurements were obtained on a Bruker AVANCE600 instrument. Phosphorus NMR spectroscopy samples were referenced to internal or external H$_2$PO$_4$ or were referenced to the solvent signal of the proton spectrum. pH 7 buffer was made with monobasic and dibasic sodium phosphate. pH 1 solutions were made from sulfuric acid. pH 2.5 and pH 4 buffered solutions were made with citric acid and sodium citrate. X-ray diffraction studies were carried out at the UCI Department of Chemistry X-ray Crystallography Facility on a Bruker SMART APEX II diffractometer. Data were collected at 133 K using Mo Kα radiation ($\lambda = 0.71073$ Å). The APEX2 program package was used to determine the unit cell parameters and for data collection. The raw frame data was processed using SAINT and SADAB to yield the reflection data file. The structures were solved using XT and the data were refined using XL using SHELXLxle as a graphical user interface. Electrospay Ionization Mass Spectrometry experiments were performed on a Micromass LCT at the University of California, Irvine Mass Spectrometry Facility. Electrochemical measurements were obtained on a Pine WaveDiver 10 bipotentiostat, equipped with AfterMath software. The working electrode was a glassy carbon disc with a 1 mm diameter, the counter electrode was a glassy carbon rod, and a silver wire was used as a pseudo reference in organic solvents, and a saturated calomel reference electrode (SCE) in saturated KCl was used in aqueous solution. Aqueous potentials were converted to SCE using the conversion factor of NHE = 0.244 V vs. SCE. EPR spectra were taken on an X-band Bruker EMX spectrometer, outfitted with an EMX standard resonator and a Bruker PremiumX microwave bridge. EPR simulations were performed with EasySpin. Spectra were taken as frozen solutions. Water pH measurements were performed with a Thermo Scientific Orion Star A216 Benchtop pH/RDo/DO meter.

**Synthesis of 2-Ni.** A thawing solution of MeOTf (81 mg, 0.50 mmol, 2.1 equiv) in benzene (5 mL) was added to a thawing, stirring solution of 0-Ni (125 mg, 0.237 mmol, 1.0 equiv) in benzene (3 mL). The solution immediately turned cloudy and was warmed to room temperature. After 20 minutes, the suspension was filtered, and the resulting white solid was dissolved in MeCN. The solvent was removed in vacuo to yield 2-Ni as a white solid powder (200 mg, 84% yield). The solid was dissolved in minimal MeCN, and ether was layered on top yielding crystals suitable for single crystal X-ray diffraction.

**In situ synthesis of 2-Ni(II)-H in MeCN.** Four equiv of [DMF(H)]OTf were added to an NMR tube charged with CD$_2$CN (0.6 mL) and 2-Ni (10 mg, 1.0 equiv), consuming all of 2-Ni and forming 2-Ni(II)-H (95% conversion). 3P$_1$ [NI] NMR (600 MHz, CD$_2$CN, 23 °C): δ 1.0, (dt, 24H, CH$_2$), 1.6-1.74 (m, 16H, CH$_2$), 3.24 (s, 20H, NCH$_2$P & NCH$_3$). 31P [NI] NMR (600 MHz, D$_2$O, 23 °C): δ 1.05 (dt, 24H, CH$_2$), 1.6-1.80 (m, 16H, CH$_2$), 3.35 (s, 12H, NCH$_3$), 3.39 (s, 8H, NCH$_3$P). 31P [HI] NMR (203 MHz, CD$_2$CN, 23 °C): δ 4.72 (s). 13C NMR (151 MHz, CD$_2$CN, 23 °C): δ 62.4, 56.5, 24.2, 8.1. ESI-MS: m/z calc’d [2-Ni(II)-H]+ 560.3, found m/z 560.2.

**In situ synthesis of 2-Ni(II)-H-Io in H$_2$O.** 0.5 mL of pH 1 water was added to an NMR tube charged with 2-Ni (10 mg, 1.0 equiv) and 2-Ni(II)-H (95% conversion). 3P$_1$ [NI] NMR (600 MHz, H$_2$O, 23 °C): δ 1.11 (q, 24H, CH$_2$), 1.9 (m, 8H, CH$_2$), 3.31 (s, 12H, NCH$_3$). 31P [HI] NMR (203 MHz, CD$_2$CN, 23 °C): δ 5.49.

**Synthesis of 1-Ni.** A thawing solution of MeOTf (12 mg, 0.074 mmol, 1.0 equiv) in benzene was added to a thawing, stirring solution of 0-Ni (39 mg, 0.074 mmol, 1.0 equiv) in benzene (3 mL). The solution immediately turned cloudy and was warmed to room temperature. After 20 minutes, the suspension was filtered, and the recovered solid was dissolved in MeCN. The MeCN solvent was removed in vacuo, and the resultant white solid was washed with minimal ether and hexanes. The remaining solvent was removed in vacuo, yielding a white solid (48 mg, 95% yield). 1H NMR (600 MHz, CD$_2$CN, 23 °C): δ 1.1 (m, 24H, CH$_2$), 1.34-1.63 (m, 16H, CH$_2$), 2.27 (s, 3H, NCH$_3$). 24H, C NMR (4.9, 4H, NCH$_2$P), 3.12 (s, 4H, NCH$_3$P). 31P [NI] NMR (203 MHz, CD$_2$CN, 23 °C): δ 4.4 (t, J$_{pp}$ = 12.1 Hz). 5.05 (t, J$_{pp}$ = 12.1 Hz). 13C NMR (151 MHz, CD$_2$CN, 23 °C): δ 60.3, 60.1, 55.9, 52.6, 21.2, 8.3, 7.8. ESI-MS: m/z calc’d [1-Ni -H$^-$]+ 542.3, found m/z 542.2.

**pK$_a$ measurement of 2-Ni in water.** A 4 mM solution of 2-Ni was buffered to a solution pH of 2.47 or 3.95 was added to an NMR tube, establishing an equilibrium between the 2-Ni and 2-Ni(II)-H species. A 31P [HI] NMR spectrum was acquired and the integrations of 2-Ni and 2-Ni(II)-H were noted. After 48 hours, another 31P [HI] NMR spectrum was taken and the ratio of the signals were unchanged. There is a small impurity of 1-Ni (~2%), but that integration amount is unchanged over 48 hr.

**pK$_a$ bracket measurement of 2-Ni in MeCN.** To 4 mM solutions of 2-Ni in an NMR tube was added 10.0 equiv of 4-methoxyanilinium tetrafluoroborate (pK$_a$ = 11.86$^b$) or 4-trifluoromethylnilinium tetrafluoroborate (pK$_a$ = 8.03$^a$). A 31P [HI] NMR spectrum was taken, showing near complete conversion to 2-Ni(II)-H or no conversion leaving only the 2-Ni species. A bracketing study was performed with one equiv of different acids, but incomplete conversion of the Ni(II) species to the 2-Ni(II)-H prevented use of the 1 equiv bracket.

**ACKNOWLEDGEMENTS**

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**SUPPORITING INFORMATION**

Experimental details, attempted chemical oxidation attempts, electrochemical data, NMR and EPR spectra. CCDC Deposition Numbers: 2181764, 2181765.

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