Hydrogenation of CO₂ in Water Using a Bis(diphosphine) Ni−H Complex

Samantha A. Burgess, † Alexander J. Kendall, ‡ David R. Tyler, † John C. Linehan,*,‡† and Aaron M. Appel,*‡†

+Catalysis Science Group, Pacific Northwest National Laboratory, Richland, Washington 99352, United States
‡Department of Chemistry and Biochemistry, University of Oregon, Eugene, Oregon 97403, United States

Supporting Information

ABSTRACT: The water-soluble Ni bis(diphosphine) complex [NiL₂](BF₄)₂ (L = 1,2-[bis(dimethoxypropyl)phosphino]ethane and the corresponding hydride, [HNiL₂]BF₄, were synthesized and characterized. These complexes were specifically designed for CO₂ hydrogenation. For HNiL₂, the hydricity (ΔG°₂H⁻) was determined to be 23.2(3) kcal/mol in aqueous solution. On the basis of the hydricity of formate, 24.1 kcal/mol, the transfer of a hydride from HNiL₂⁺ to CO₂ to produce formate is favorable by 1 kcal/mol. Starting from either NiL₂²⁻ or HNiL₂⁺ in water, catalytic hydrogenation of CO₂ was observed with NaHCO₃ (0.8 M) as the only additive. A maximum turnover frequency of [4.0(5)]×10⁻¹ h⁻¹ was observed at 80 °C and 34 atm of a 1:1 mixture of CO₂ and H₂. This report demonstrates the use of a homogeneous first-row transition-metal catalyst for CO₂ hydrogenation in water using NaHCO₃ as an inexpensive, readily available base.

KEYWORDS: CO₂ hydrogenation, hydricity, homogeneous catalysis, nickel, aqueous bicarbonate

INTRODUCTION

Carbon dioxide, a potent greenhouse gas, is byproduct generated from the combustion of fossil fuels. The concentration of CO₂ in the atmosphere has been rising from 280 ppm at the start of the Industrial Revolution to the current level of ca. 405 ppm.1 Carbon-neutral energy sources such as solar and wind can be used to decrease CO₂ emissions, but these sources are intermittent and therefore require a means of storing chemical energy.2−6 The hydrogenation of CO₂ could provide a way to store energy in chemical bonds, and the potential products formic acid and methanol are particularly attractive because both have high volumetric energy densities and are easily transportable, unlike hydrogen.7 Additionally, methanol could be used directly as an alternative to gasoline for transportation. Therefore, significant research efforts have focused on the utilization of CO₂ as a C1 feedstock for the production of fuels.8−11

A number of transition-metal catalysts have been reported for the hydrogenation of CO₂ to formate. Many of these systems have utilized complexes of late transition metals, such as ruthenium, iridium, and rhodium.10−25 Prior to 2010, only a limited number of catalysts based on less expensive, first-row transition metals had been reported.26−29 In recent years, the number of first-row transition-metal catalysts for CO₂ hydrogenation has been increasing. Specifically, catalysis has been reported using complexes of iron,30−39 cobalt,40−45 nickel,46−49 and copper.50−52 Beller and co-workers have reported both Fe and Co tetraphosphine catalysts for CO₂ hydrogenation.38,40 In 2015, Hazari, Bernskoetter, and co-workers reported CO₂ hydrogenation in the presence of a Bronsted base using a series of Fe hydride catalysts supported by PNP ligands containing secondary and tertiary amines.36 The activity was observed to increase when a Lewis acid cocatalyst was utilized. Recently, an Fe(II) hydrido carbonyl complex, [Fe(PNP)(H)(CO)] (PNP = 2,6-diaminopyridylbis(diisopropylphosphine)), was reported to be an active catalyst for the hydrogenation of CO₂ and NaHCO₃ to formate.37 The authors reported that a protic solvent was needed for catalysis to occur. Under optimal conditions in ethanol with added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 25 °C and 80 bar total pressure a turnover number (TON) of 1032 for formate was obtained. [Fe(PNP)-(H)(CO)] is also active in 4/1 H₂O/THF with NaOH as the base.

Recently, we have reported catalysts based on complexes of first-row transition metals: specifically, complexes of cobalt and copper.42,43,50−52 The cobalt complex Co(dmpe)H (dmpe = 1,2-bis(dimethylphosphino)ethane) is an active catalyst for CO₂ hydrogenation.42,43 In the presence of Verkade’s base (2,8,9-trisopropyl-2,5,8,9-tetraaza-1-phosphobiclyclo [3.3.3]-undecane), Co(dmpe)H catalyzes hydrogenation of CO₂ with a TOF (turnover frequency) of 3400 h⁻¹ at room temperature using 1 atm of a 1/1 mixture of H₂ and CO₂.42,43 In 2015, the first catalysts based on copper for the hydrogenation of CO₂ were reported.50−52 The Cu(I) complex of the branched triphos ligand hydrogenates CO₂ to formate in...
basic solutions with a TOF of 48 h\(^{-1}\) at 140 °C (40 atm of a 1/1 mixture of H\(_2\) and CO\(_2\), 25 mM DBU).\(^{51,52}\)

The majority of the reported catalysts for the reduction of CO\(_2\) operate in aprotic organic solvents, which makes the need for a protic solvent for the hydrogenation of CO\(_2\) using [Fe(PNP)(H\(_2\))(CO)] noteworthy.\(^{53}\) However, there are several examples of noble-metal catalysts for CO\(_2\) hydrogenation in aqueous media.\(^{53-61}\) For example, Ir(III) complexes of the type [Cp\(^*\)Ir(L\(_{NN}\))(OH\(_2\))]\(^{21}\) (L\(_{NN}\) = bpy, bisimidazoline, bipyrimidine, azole-pyrimidine) have been well studied for CO\(_2\) hydrogenation in aqueous solutions.\(^{59,62}\)

Additionally, a Ru(II) complex, [RuCl\(_2\)(PTA)]\(_4\) (PTA = 1,3,5-triaza-7-phosphaadamantane), has been reported to catalyze CO\(_2\) hydrogenation in water with added bicarbonate.\(^{56}\)

The pH of the reaction solution was found to affect the TOF, with the highest activity near a pH of 6. The pH dependence for catalytic hydrogenation of CO\(_2\) is expected to be affected by the favorability of the conversion of CO\(_2\) to formate as well as the favorability of regeneration of the active hydride.\(^{53}\) These factors need to be balanced to ensure catalyst longevity and activity.

Hydricity (\(\Delta G^0_{\text{HH}}\)) is defined as the Gibbs free energy for cleavage of an M–H bond to give a hydride (H\(^-\)), as illustrated in eq 1.\(^{54,66}\) The hydricity of a transition-metal hydride complex determines whether or not a hydride can be transferred from the complex to a hydride acceptor, such as CO\(_2\). The free energy for the loss of a hydride from formate to generate CO\(_2\) (g) can be described as the hydricity (\(\Delta G^0_{\text{HH}}\)) of formate, which has been estimated to be 44 kcal/mol in acetonitrile and 24 kcal/mol in H\(_2\)O.\(^{60-68}\) Transition-metal hydrides that are more hydridic than formate (have \(\Delta G^0_{\text{HH}}\) less than 44 kcal/mol in acetonitrile) are capable of transferring a hydride to CO\(_2\). Only a limited number of hydricity determinations for transition-metal hydrides in water have been reported.\(^{46,69-73}\)

\[
M\text{–H(solv)} = M^+\text{(solv)} + H^-\text{(solv)}
\]

Our continued research efforts have focused on the development of first-row transition-metal catalysts for the hydrogenation of CO\(_2\). While a nickel phosphine was one of the first compounds identified to catalytically convert CO\(_2\) and H\(_2\) into formate, there have been few systematic studies of nickel and those that have been performed were entirely in nonaqueous solvents.\(^{26,27,46-49,66,74,75}\) Our experience with cobalt phosphines has demonstrated that, while the hydricity of the cobalt phosphine hydrides is sufficient for transfer of a hydride to CO\(_2\) (Scheme 1, step A), the low acidities of bis(diphosphine) cobalt dihydride complexes results in the need for an excessively strong base. This requirement for an excessively strong base results in unnecessary driving force to achieve a high catalytic rate, analogous to an overpotential for an electrocatalyst.

In water, the challenges of completing a catalytic cycle for the hydrogenation of CO\(_2\) are increased, as the operable pH range is insufficiently basic under CO\(_2\) pressure to deprotonate the cobalt dihydride. Bis(diphosphine) complexes of nickel hydrides do not have sufficient hydricity (low enough \(\Delta G^0_{\text{HH}}\)) to add a hydride to CO\(_2\) in organic solvent; however, we have overcome this limitation by moving to water, in which [HNi(dmpe)]\(^+\) is hydridic enough to transfer a hydride to CO\(_2\) to generate formate.\(^{63}\) In this case the solution basicity needed (pH of 13.3 or higher) to regenerate [HNi(dmpe)]\(^+\) is too high to be accessible in an aqueous solvent under CO\(_2\) pressure.\(^{63}\) Since the required pH needed to regenerate a metal hydride is inversely proportional to \(\Delta G^0_{\text{HH}}\), we have sought a complex that is a weaker hydride donor (higher \(\Delta G^0_{\text{HH}}\)) to enable regeneration of the hydride complex in the presence of CO\(_2\). For this reason we synthesized [NiL\(_2\)][BF\(_4\)] (L = 1,2-[bis(dimethoxymethyl)phosphino]ethane; see Chart 1). The alkyl arms of the water-soluble phosphine L should decrease the hydricity of the metal monohydride relative to [HNi(dmpe)]\(^+\). Here we report that [HNiL\(_2\)]\(^+\) is an active catalyst for CO\(_2\) hydrogenation in water.

**RESULTS**

The diphosphine ligand L was synthesized according to the literature procedure.\(^{76}\) The Ni complex [NiL\(_2\)][BF\(_4\)] was prepared as shown in Scheme 2. A THF suspension of NiBr\(_2\)-3H\(_2\)O was added dropwise to a solution of L in THF. The

\[
\text{Scheme 2. Synthesis of NiL}_2^{2+}
\]
resulting mixture was stirred at room temperature for 16 h. Pure [NiL2]([Br]2) was obtained as a red oil after addition of cold ether. A salt metathesis reaction between [NiL2]([Br]2) and AgBF4 gave [NiL2]([BF4]2). The 31P{1H} NMR spectrum of [NiL2]([BF4]2) in CDCl3 contains a single resonance at 55.96 ppm for the phosphine complex.

The addition of cesium formate to an acetoniol solution of NiL2+ gave HNiL2+ after 45 min at room temperature. A characteristic hydride resonance is observed at -14.12 ppm in the 1H NMR spectrum of HNiL2+. The 31P{1H} NMR resonance for HNiL2+ is shifted 17 ppm upfield of that for NiL2+ to 43.30 ppm. The 13C{1H} NMR spectrum showed the presence of CO2.

The hyridicity (ΔG°H) of HNiL2+ was determined by heterolysis of H2 using two different sets of measurements.65,67 In the first method an aqueous solution of NiL2+ in 0.8 M NaHCO3 (aq) was charged with 1 atm of H2 and heated at 80 °C for 3 h. After the mixture was cooled to room temperature, the concentration of HNiL2+ relative to the starting NiL2+ was determined by integration of the corresponding resonances in the 31P{1H} NMR spectrum. The pH of the reaction solution was determined from the measured equilibrium between NiL2+ and HNiL2+, the pressure of H2, the solution pH, and the free energy for heterolysis of H2 using two different sets of measurements.65,67

<table>
<thead>
<tr>
<th>temp (°C)</th>
<th>TOF (h⁻¹)</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>[2.2(2)] × 10⁻²</td>
<td>[6.2(7)] × 10⁻⁸</td>
</tr>
<tr>
<td>60</td>
<td>[8.3(1)] × 10⁻²</td>
<td>[2.3(8)] × 10⁻⁸</td>
</tr>
<tr>
<td>80</td>
<td>[4.0(5)] × 10⁻⁴</td>
<td>[1.1(1)] × 10⁻⁴</td>
</tr>
<tr>
<td>100</td>
<td>[6.4(1)] × 10⁻¹</td>
<td>[2.1(1)] × 10⁻¹</td>
</tr>
</tbody>
</table>

“Average TOF for formate production using NiL2+ (0.029 M) using a 1/1 mixture of H2 and CO2 (34 atm) in H2O buffered with 0.8 M of sodium bicarbonate to pH 9.0 at various temperatures.

Figure 1. Eyring plot for CO2 hydrogenation using NiL2+ using a 1/1 mixture of CO2 and H2 (34 atm) in H2O buffered with 0.8 M of sodium bicarbonate to pH 9.0 (R² = 0.98123).

To determine the effect of CO2 and H2 on the catalytic CO2 hydridization using NiL2+, the reaction was carried out at several different mixtures of H2 and CO2 as shown in Table S1 of the Supporting Information. Very similar TOFs of [4.0(5)] × 10⁻⁴ and [3.4(3)] × 10⁻¹ h⁻¹ were obtained using 1/1 and 3/1 mixtures of H2 and CO2 respectively. Slower TOFs were observed but not quantitatively reproduced with a 15/85 mixture of H2:CO2, suggesting that the reaction is inhibited by either CO2 or the solution acidification resulting therefrom. Lowering the total gas pressure of a 1/1 mixture of H2 and CO2 from 34 to 17 atm
resulted in an ~9-fold decrease in rate. No increase in rate was observed when the total pressure of a 1:1 mixture of H2 and CO2 was increased from 34 to 51 atm. The observed decrease in rate with decreased H2 pressure suggests that H2 addition is rate limiting. The lack of rate enhancement upon increasing the fraction of H2 from 1/1 to 3/1 or increasing the total pressure from 34 to 51 atm with a 1/1 mixture of H2 and CO2 could be a result of saturation kinetics for the rate dependence on the pressure of H2. Similarly, Ogo and co-workers have reported saturation behavior in H2 for CO2 hydrogenation with [Cp*Rh(L)(H)]2+ (Cp*=η^5-C5Me5, L = 2,2’-bipyridine, 4,4’-dimethoxy-2,2’-bipyridine). No CO was detected in the headspace for the catalytic reactions by GC analysis.

To investigate the potential conversion of bicarbonate, an experiment was conducted without an applied pressure of CO2. Addition of only H2 (34 atm) to a solution of NiL22+ in H2O buffered with 0.8 M of sodium bicarbonate gave 3 turnovers of CO2 for 1 equiv of Ni(dmpe)2+. The observed decrease in pH would therefore change the basicity of the starting solution. The results suggest that the pH decrease in pH might be a result of a decreasing pH because of the reaction (ΔG°Hφ, a pH >13.3 would be required for catalysis with HNi(dmpe)2+ to be favorable.

To facilitate regeneration at lower pH, we sought to decrease the hydricity of the nickel complex and thereby obtain an active catalyst. In acetonitrile, moving from HNi(dmpe)2+ to an analogue with ethyl groups in terminal positions, HNi(depe)2+ results in a metal hydride that is a 5 kcal/mol weaker hydride donor (55.3 kcal/mol for HNi(depe)2+ versus 49.9 kcal/mol for HNi(dmpe)2+). Assuming that a similar difference in hydricity for dmpe versus depe would be observed in water, we predicted that exchanging the methyl groups of dmpe for longer substituents could generate an active nickel catalyst. This change would result in a complex that is still hydricid enough to transfer a hydride to CO2 (ΔG°Hφ < 24 kcal/mol in H2O) but would not require as high of a pH to regenerate the metal monohydride from the metal dihydride. The water-soluble diphosphine ligand 1,2-[bis(dimethoxypropyl)phosphino]-ethane L was chosen as a suitably modified ligand to replace dmpe in our targeted Ni catalyst. The hydricity of HNi(dmpe)2+ in water has been determined to be 16 kcal/mol. The hydricity of HNiL22+ in water has now been determined to be 23.2 kcal/mol, corresponding to a 7 kcal/mol difference in hydricity in comparison to HNi(dmpe)2+. This result suggests that HNiL22+ might be a result of a decreasing pH because of the reaction shown in eq 2.

\[
\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) = \text{H}^+ + \text{HCO}_2^-
\]

**DISCUSSION**

There are three factors that determine whether or not a transition-metal complex will serve as a CO2 hydrogenation catalyst: (1) the complex has to be able to activate dihydrogen, (2) the acidity of the H2 addition product must be in a range that will allow formation of the hydride complex, and (3) the resulting hydride complex needs to be capable of donating a hydride to CO2. For Co(dmpe)2+, the acidity of the H2 addition product was critical, because a very strong base (Verkade’s base, pKb of the conjugate acid in acetonitrile is 33.6) was needed to deprotonate H2Co(dmpe)2+. For bis(diphosphine) complexes of Ni, the acidity of the H2 addition product is less of a concern, because they are difficult to observe as a result of high acidity. However, our previous attempt to generate a catalytic system using HNi(dmpe)2+ demonstrated that while the transfer of a hydride from HNi(dmpe)2+ to CO2 is favorable, this complex is not catalytic for the hydrogenation of CO2 because the hydride could not be regenerated, even at pH 11.8. Essentially, stronger hydride donors require higher basicity to regenerate the hydride through heterolysis of H2. On the basis of the hydricity (ΔG°Hφ), a pH >13.3 would be required for catalysis with HNi(dmpe)2+ to be favorable.

An induction period (~2 h at 80 °C) was observed for catalytic CO2 hydrogenation to formate using NiL22+ (0.029 M) in H2O with added NaHCO3 (0.8 M) and a 1/1 mixture of H2 and CO2 (34 atm total pressure). When the temperature was lowered to 40 °C, the induction period was observed to increase to ~4 h. Conversely, no induction period was observed with a 1/1 mixture of H2 and CO2 (34 atm total pressure). The precise cause of the induction period is unknown. It is not likely to result from the formation of Ni nanoparticles, because the reaction solution after catalysis is a clear yellow solution and no free phosphine is observed by 31P NMR spectroscopy. One possible explanation for the observed induction period is that the initial formation of HNiL2+ is limiting. The latter does not form until the reaction mixture is heated, and the rate of formation is accelerated with increasing temperatures. At 80 °C, the induction period was observed using a 1/1 mixture of H2 and CO2 (34 atm total pressure), but this induction period was not observed when a 3/1 mixture of H2 and CO2 was used (34 atm total pressure). This result supports the hypothesis that a certain amount of HNiL2+ may need to be formed before catalysis is observed because the increased pressure of H2 leads to faster formation of Ni−H. Interestingly, a still unexplained induction period ranging from 15 min to >2 h was observed for catalytic CO2 hydrogenation using Co(dmpe)2+ in the presence of DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene).

The induction period observed for CO2 hydrogenation with NiL22+ is still observed when Na2CO3 (0.12 M) is added to 0.8 M NaHCO3 (aq). Addition of Na2CO3 would increase the basicity of the starting solution. The results suggest that the pH...
KOH was not a suitable base for this reaction, as a solid was by balancing the hydride donor ability of \( \text{HNi}^{2+} \) to generate paramagnetic, NMR-silent species such as \( \text{HNi}^{2+}(\text{solvent})_2 \). The length of the induction period was observed to decrease with increasing temperatures and H2 pressures. These features are consistent with the induction period resulting from the formation of \( \text{HNi}^{2+} \).

The pH of the solution decreased as the CO2 hydrogenation reaction progressed. Water buffered with either a carbonate or phosphate buffer is still acidified upon addition of CO2, inherently leading to a solution with a pH near 8. Due to acidification with CO2, the simplest choice of a base is bicarbonate, which leads to a solution buffered by the CO2/\( \text{HCO}_3^- \) acid/base pair. For a solution with 1 M bicarbonate and under 1 atm of CO2, the resulting solution pH should be \( \sim 7.8 \), on the basis of the solubility and acidity of CO2. For the catalytic studies, three concentrations of NaHCO3 were screened (0.2, 0.4, and 0.8 M) at 80 °C and 17 atm of a 1/1 mixture of H2 and CO2. The TOF for formate production was observed to increase with increasing base concentration, with 0.8 M NaHCO3 generating the most formate (see the Supporting Information). Higher concentrations of NaHCO3 in water led to precipitation of NiL22+. Other bases (NEt3, NHEt2, and DBU) were also investigated; however, NaHCO3 gave superior results. Specifically, minimal formate (≤2 turnovers) was obtained with NEt3, NHEt2, and DBU. KOH was not a suitable base for this reaction, as a solid was formed upon addition of KOH to a solution of NiL22+ in water. The system is very sensitive to a change in pH. Unfortunately, we were unable to determine the pH using operando \( ^{31}P\{^1H\} \) NMR spectroscopy as in our previous study,6 because the use of phosphate inhibited catalysis.

On the basis of the above data, NiL22+ appears to operate under the same mechanism as shown in Scheme 1. More specifically, the proposed catalytic cycle for CO2 hydrogenation to formate in aqueous NaHCO3 involves the addition of H2 to NiL22+ to give unobserved \( \text{H}_2\text{NiL}^{2+} \), which is quickly deprotonated by base to form the Ni–H complex HNiL2+. Hydride transfer from HNiL2+ to CO2 gives formate and regenerates the starting material. NiL22+ and HNiL2+ are the only two species observed by NMR spectroscopy during catalysis. Despite the slow rates of catalysis, NiL22+ and HNiL2+ appear to be stable under the reaction conditions for long periods of time (≈50 h).

**SUMMARY AND CONCLUSIONS**

The bis(diphosphine) complex of nickel NiL22+ is an active catalyst for CO2 hydrogenation in water, with NaHCO3 as the only added base. Catalytic turnover of this complex was enabled by balancing the hydride donor ability of HNiL2+ with the ability to regenerate the hydride at a near-neutral pH. The driving force for hydride transfer from HNiL2+ to CO2 is small (1 kcal/mol), which enables catalysis to occur, at slow catalytic rates.

NiL22+ is the first homogeneous nickel catalyst for the hydrogenation of CO2 in water. The use of water as a green reaction solvent is an area of increasing interest, and it provides an opportunity to utilize the stabilization of reaction intermediates that can be provided by this polar, hydrogen-bonding solvent. Future work in our laboratory will focus on the development of other water-soluble first-row transition-metal catalysts for CO2 hydrogenation.

**EXPERIMENTAL SECTION**

General Considerations. Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen. Purified water (18 MΩ) was obtained from a Millipore Water Direct-Q UV3 apparatus. The purified water was deoxygenated before use by sparging with N2 for 2 h. Diethyl ether (Et2O) and tetrahydrofuran (THF) were dried using a PureSolv system using CuO and molecular sieves under N2. All other reaction solvents were purified and dried according to the literature.80 H2 and CO2 gas mixtures were purchased from Oxarc and Matheson as the highest quality available and used as received. All commercially obtained reagents were used as received unless otherwise specified. The ligand \( L \) was synthesized as previously reported.76 NMR spectra were recorded on a 300 or 500 MHz Varian spectrometer (1H 300.09 or 500.02 MHz, respectively) and are referenced using the deuterated solvent signals or an internal standard. Data for \( ^{31}P\{^1H\} \) NMR spectra are reported as follows: chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and relative integration. \( ^{31}P\{^1H\} \) NMR spectra are reported relative to the external standard of 0.1% H3PO4 in D2O or neat H3PO4 (δ 0 ppm). The temperature of the NMR probe was calibrated using a PEEK NMR tube filled with ethylene glycol and the equation \( T(K) = (4.218 – Δ)/0.009132 \), where Δ is the shift difference (ppm) between the CH2 and OH resonances of ethylene glycol. Measurements of pH were performed using a Thermo Scientific Orion Dual Star pH/SE Bench Top with a Mettler Toledo Inpro 6030 pH combination electrode. The electrode was calibrated with pH 7 and 10 buffers.

**Synthesis of [NiL22+][Br2]**. To a blue-brown suspension of NiBr2·3H2O (542 mg, 1.99 mmol, in 3.0 mL of THF, ca. 600 mM) was added a solution of \( L \) (1.603 g, 4.191 mmol, in 13.0 mL of THF, ca. 300 mM) dropwise. The mixture slowly became a solution and turned dark brown-red. The solution was stirred for 16 h at room temperature. The red-brown solution was purified by dropwise addition of the crude solution into cold Et2O, causing separation of a red oil. The Et2O layer was decanted off and the red oil was collected as the pure complex (1.747 g, 85.6%). \( ^1H \) NMR (300 MHz, CDCl3): \( δ \) 3.44 (t, \( J = 5.7 \) Hz, 16H), 3.32 (s, 24H), 2.30–2.02 (m, 22H), 1.94–1.72 (m, 18H). \( ^{11}B \) NMR (121 MHz, CDCl3): \( δ \) 52.02. HRMS (ES+-TOF) m/z: [\( \text{M}^+ \)] calcd for \([\text{C}_{2}\text{H}_{10}\text{BrNiO}_{6}\text{P}_{4}]^{+}\) 901.3341; found 901.3334.

**Synthesis of [NiL22+][BF4]**. To a solution of NiL22+ (0.883 g, 0.898 mmol) in 50 mL of THF was added a solution of AgBF4 (0.375 g, 1.93 mmol, in 10 mL of THF, ca. 200 mM) dropwise at room temperature. The red solution turned turbid yellow upon addition. The mixture was stirred at room temperature for 5 h. The mixture was then filtered. The resulting filtrate was reduced to an oil under vacuum and taken up into a minimal amount of THF (5.0 mL) and added dropwise into cold Et2O, causing separation of an orange oil. The Et2O layer was decanted off, and the orange oil was collected as the pure complex (535 mg, 59.6%). \( ^1H \) NMR (500 MHz, CDCl3): \( δ \) 3.57–3.40 (m, 16H), 3.34 (s, 24H), 2.44–1.96 (m, 22H), 1.96–1.66 (m, 18H). \( ^{11}B \) NMR (160 MHz, CDCl3): \( δ \) –0.77. \( ^{31}C\{^1H\} \) NMR (126 MHz, CD3CN): \( δ \) 72.75, 58.85, 25.38, 23.53, 22.25. \( ^{31}P\{^1H\} \) NMR (202 MHz, CDCl3): \( δ \) 55.96. HRMS (ES+-TOF) m/z: [\( \text{M}^+ \)] calcd for \([\text{C}_{6}\text{H}_{12}\text{O}_{2}\text{BrNiO}_{6}\text{P}_{4}]^{+}\) 1011.2779; found 1011.2783. Anal. Calcd
for C_{24}H_{40}B_5F_{10}O_5P_7Ni: C, 43.36; H, 8.09. Found: C, 42.83; H, 8.06.

Synthesis of [HNIl_2]BF_4 from Cesium Formate. [HNIl_2] (BF_4) (0.030 g, 0.030 mmol) was dissolved in acetonitrile (~5 mL) in a J. Young tube. Cesium formate (0.022 g, 0.11 mmol) was added. The tube was sonicated for 1 h, during which time the color changed from red-orange to yellow. The product was analyzed by NMR spectroscopy but not isolated. Typically this complex is formed in situ during PEEK NMR cell experiments.

1H NMR (499 MHz, D_2O): δ 3.86 (m, 16H), 3.53 (s, 24H, CH_3), 2.23–2.06 (m, 14H), 1.91–1.81 (m, 26H), −13.92 (s, 1H, Ni−H). 12C(1H) NMR (126 MHz, D_2O): δ 71.74, 70.96, 56.85, 24.08, 23.27, 21.12. 13C(1H) NMR (126 MHz, CD_3CN): δ −125.77, 73.46, 58.77, 26.50, 26.40, 25 0.70. 31P(1H) NMR (202 MHz, D_2O): δ 43.00 (s). 19F NMR (470 MHz, CD_3CN): δ −151.43.

High-Pressure Reactions in PEEK NMR Tubes. Hydrogenation reactions at 17–51 atm and temperatures between 40 and 100 °C were run in PEEK high-pressure NMR spectroscopy tubes designed and built at Pacific Northwest National Laboratory, as reported previously. Operators of high-pressure equipment such as that required for these experiments should take proper precautions to minimize the risk of personal injury.

In a typical experiment, 0.8 M NaHCO_3 was prepared in a volumetric flask. A 350 μL portion of this solution was used to dissolve [HNIl_2](BF_4)_2. The resulting solution was added to a PEEK cell containing a capillary with C_9D_8 as an internal standard. The cell was sealed and connected to a high-pressure line equipped with a vacuum pump and an ISCO syringe pump. The line was purged with gas three times. Opening the PEEK cell to static vacuum (3 × 30 s) degassed the headspace above the sample. Gas was delivered to the cell from an ISCO syringe pump running constantly at 34 atm. The contents of the PEEK NMR spectroscopy cell were mixed using a vortex mixer until the pressure stabilized. After stabilization, the cell was inserted into the NMR spectrometer, which had been preheated to the desired temperature. The sample was heated in the spectrometer for the remainder of the experiment. The time for the catalysis experiments started upon insertion of the NMR cell into the heated NMR probe. This time neglects the typical 2.5–3 min between pressurizing and inserting the sample into the spectrometer. 1H NMR spectra were acquired, with 16 scans for each spectrum. The delay time was set to 60 s, the acquisition time was set to 5 s, the pulse width was set to 2 μs, and the gain was set to 2. Each spectrum required 17 min 20 s to complete. The concentration of the formate was determined by integration of the formate resonance relative to the residual C_9D_8 resonance in the C_9D_8 internal standard.

Determining Concentration Dependences Using PEEK NMR Spectroscopy Cells. To determine the dependence of the catalytic rate on the concentration of NaHCO_3, the general procedure described above for NMR spectroscopy using PEEK cells was used. The only modification to the procedure was that 0.2 or 0.4 M NaHCO_3(aq) was used instead of 0.8 M. The results are shown in Figure S11 in the Supporting Information.

Hydricity Determination Method 1. TAPS sodium salt (0.023 g, 0.086 mmol) was added to a solution of [HNIl_2](BF_4)_2 (0.009 g, 9 × 10^{-3} mmol) in water (500 μL) in a J. Young tube. The tube was charged with 1 atm of H_2. Hydride formation was detected by 31P(1H) NMR spectroscopy after 26 h. The reaction was periodically monitored by 31P(1H) NMR spectroscopy until an equilibrium between the starting material and Ni–H had been established (18 days). The pH of the solution was measured (pH 7.82), and TAPS (0.045 g, 0.19 mmol, 20 equiv) was added. The tube was charged with H_2, and the reaction was periodically monitored by 31P(1H) NMR spectroscopy for 19 days until equilibrium had been reached (pH 9.13). The resulting hydricity value of 23.5 kcal/mol was obtained from the reaction run in both the forward and reverse directions using the equations shown in Scheme 3.

Hydricity Determination Method 2. [HNIl_2](BF_4)_2 (0.009 g, 9 × 10^{-3} mmol) was dissolved in 0.8 M NaHCO_3(aq) (500 μL) in a J. Young tube. The tube was charged with 1 atm of H_2 and heated in a temperature-controlled oil bath at 80 °C for 6 h. After the mixture was cooled to room temperature, the ratio of starting material to HNIl_2 was measured by 31P(1H) NMR spectroscopy. The pH of the solution was measured, and the ΔG°_H value was calculated using the equations shown in Scheme 3. The procedure was repeated two additional times.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b00350.

Experimental details, NMR data, representative kinetic plots, and tables of catalytic performance (PDF)

AUTHOR INFORMATION

Corresponding Authors
E-mail for J.C.L.: john.linehan@pnnl.gov.
E-mail for A.M.A.: aaron.appel@pnnl.gov.

ORCID
John C. Linehan: 0000-0001-8942-7163
Aaron M. Appel: 0000-0002-5604-1253

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
S.A.B., J.C.L., and A.M.A. were supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy. D.R.T. and A.J.K. acknowledge the National Science Foundation under award number CHE-1503550 for partial support of this research and the donors of the American Chemical Society Petroleum Research Fund (ACS PRF 53962-ND3).