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Hydrogenation of CO_2 in Water Using a Bis(diphosphine) Ni–H Complex

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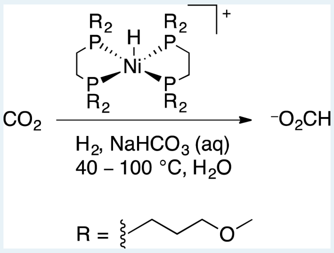
Ⓢ *Supporting Information*

ABSTRACT: The water-soluble Ni bis(diphosphine) complex $[NiL_2](BF_4)_2$ (**L** = 1,2-[bis(dimethoxypropyl)phosphino]ethane and the corresponding hydride, $[HNiL_2]BF_4$, were synthesized and characterized. These complexes were specifically designed for CO_2 hydrogenation. For $HNiL_2^+$, the hydricity ($\Delta G°_{H^-}$) 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 $HNiL_2^+$ to CO_2 to produce formate is favorable by 1 kcal/mol. Starting from either NiL_2^{2+} or $HNiL_2^+$ in water, catalytic hydrogenation of CO_2 was observed with $NaHCO_3$ (0.8 M) as the only additive. A maximum turnover frequency of $[4.0(5)] \times 10^{-1}$ h^{-1} was observed at 80 °C and 34 atm of a 1:1 mixture of CO_2 and H_2. This report demonstrates the use of a homogeneous first-row transition-metal catalyst for CO_2 hydrogenation in water using $NaHCO_3$ as an inexpensive, readily available base.



KEYWORDS: *CO_2 hydrogenation, hydricity, homogeneous catalysis, nickel, aqueous bicarbonate*

INTRODUCTION

Carbon dioxide, a potent greenhouse gas, is a byproduct generated from the combustion of fossil fuels. The concentration of CO_2 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 CO_2 emissions, but these sources are intermittent and therefore require a means of storing chemical energy.[2−6] The hydrogenation of CO_2 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 CO_2 as a C1 feedstock for the production of fuels.[8−11]

A number of transition-metal catalysts have been reported for the hydrogenation of CO_2 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 CO_2 hydrogenation has been increasing. Specifically, catalysis has been reported using complexes of iron,[30−39] cobalt,[40−45] nickel,[26,46−49] and copper.[50−52]

Beller and co-workers have reported both Fe and Co tetraphosphine catalysts for CO_2 hydrogenation.[38,40] In 2015, Hazari, Bernskoetter, and co-workers reported CO_2 hydrogenation in the presence of a Brønsted 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, $[Fe(PNP)(H)_2(CO)]$ (PNP = 2,6-diaminopyridylbis(diisopropylphosphine)), was reported to be an active catalyst for the hydrogenation of CO_2 and $NaHCO_3$ to formate.[33] 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. $[Fe(PNP)(H)_2(CO)]$ is also active in 4/1 H_2O/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 $Co(dmpe)_2H$ (dmpe = 1,2-bis(dimethylphosphino)ethane) is an active catalyst for CO_2 hydrogenation.[42,43] In the presence of Verkade's base (2,8,9-triisopropyl-2,5,8,9-tetraaza-1-phosphobicyclo [3.3.3]-undecane), $Co(dmpe)_2H$ catalyzes hydrogenation of CO_2 with a TOF (turnover frequency) of 3400 h^{-1} at room temperature using 1 atm of a 1/1 mixture of H_2 and CO_2.[42,43] In 2015, the first catalysts based on copper for the hydrogenation of CO_2 were reported.[50−52] The Cu(I) complex of the branched triphos ligand hydrogenates CO_2 to formate in

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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.[33] 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 $[Cp^*Ir(L_{NN})(OH_2)]^{2+}$ (L_{NN} = bpy, bisimidazoline, bipyrimidine, azole-pyrimidine) have been well studied for CO_2 hydrogenation in aqueous solution.[18,62] 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.[63] These factors need to be balanced to ensure catalyst longevity and activity.

Hydricity ($\Delta G°_{H^-}$) is defined as the Gibbs free energy for cleavage of an M−H bond to give a hydride (H^-), as illustrated in eq 1.[64,65] 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 ($\Delta G°_{H^-}$) of formate, which has been estimated to be 44 kcal/mol in acetonitrile and 24 kcal/mol in H_2O.[66−68] Transition-metal hydrides that are more hydridic than formate (have $\Delta G°_{H^-}$ 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]

$$M{-}H(solv) \rightleftharpoons M^+(solv) + H^-(solv) \qquad (1)$$

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 ΔG_{H^-}) to add a hydride to CO_2 in organic solvent; however, we have overcome this limitation by moving to water, in which $[HNi(dmpe)_2]^+$ 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 $[HNi(dmpe)_2]^+$ 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 $\Delta G°_{H^-}$, we have sought a complex that is a weaker hydride donor (higher $\Delta G°_{H^-}$) to enable regeneration of the hydride complex in the presence of CO_2. For this reason we synthesized $[Ni\mathbf{L}_2][BF_4]_2$ (L = 1,2-[bis(dimethoxypropyl)phosphino]ethane; see Chart 1). The alkyl arms of the water-soluble phosphine **L** should decrease the hydricity of the metal monohydride relative to $[HNi(dmpe)_2]^+$. Here we report that $[HNi\mathbf{L}_2]^+$ is an active catalyst for CO_2 hydrogenation in water.

Scheme 1. Catalytic Cycle for CO_2 Hydrogenation Using Bis(diphosphine) Complexes[42,43]

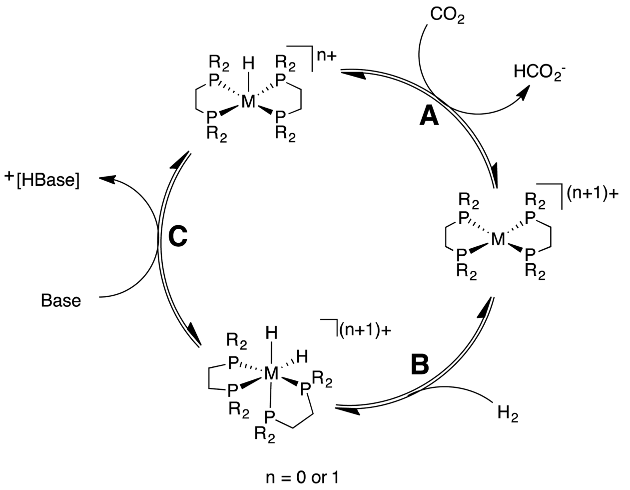
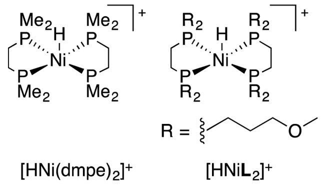


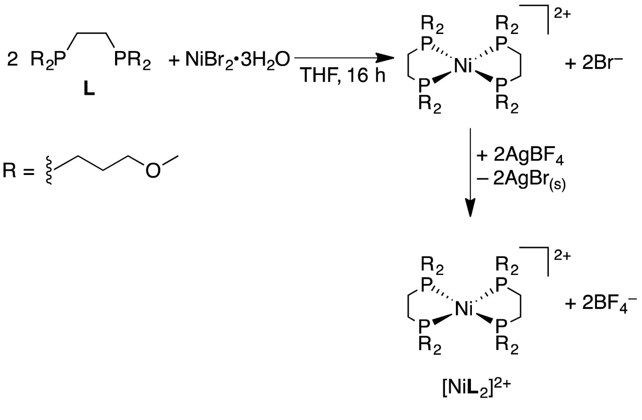
Chart 1. Bis(diphosphine) Complexes of Nickel Hydrides Described in This Study



■ RESULTS

The diphosphine ligand L was synthesized according to the literature procedure.[76] The Ni complex $[Ni\mathbf{L}_2](BF_4)_2$ was prepared as shown in Scheme 2. A THF suspension of $NiBr_2\cdot 3H_2O$ was added dropwise to a solution of L in THF. The

Scheme 2. Synthesis of $Ni\mathbf{L}_2^{2+}$



resulting mixture was stirred at room temperature for 16 h. Pure $[NiL_2](Br)_2$ was obtained as a red oil after addition of cold ether. A salt metathesis reaction between $[NiL_2](Br)_2$ and $AgBF_4$ gave $[NiL_2](BF_4)_2$. The $^{31}P\{^1H\}$ NMR spectrum of $[NiL_2](BF_4)_2$ in $CDCl_3$ contains a single resonance at 55.96 ppm for the phosphine complex.

The addition of cesium formate to an acetonitrile solution of NiL_2^{2+} gave $HNiL_2^+$ after 45 min at room temperature. A characteristic hydride resonance is observed at −14.12 ppm in the ^1H NMR spectrum of $HNiL_2^+$. The $^{31}P\{^1H\}$ NMR resonance for $HNiL_2^+$ is shifted 17 ppm upfield of that for NiL_2^{2+} to 43.0 ppm, and the $^{13}C\{^1H\}$ NMR spectrum showed the presence of CO_2.

The hydricity ($\Delta G°_{H^-}$) of $HNiL_2^+$ was determined by heterolysis of H_2 using two different sets of measurements.[65,67] In the first method an aqueous solution of NiL_2^{2+} in 0.8 M $NaHCO_3(aq)$ was charged with 1 atm of H_2 and heated at 80 °C for 3 h. After the mixture was cooled to room temperature, the concentration of $HNiL_2^+$ relative to the starting NiL_2^{2+} was determined by integration of the corresponding resonances in the $^{31}P\{^1H\}$ NMR spectrum. The pH of the reaction solution was measured using a pH meter that had been calibrated with pH 7 and pH 10 buffers. The hydricity of $HNiL_2^+$ was determined from the measured equilibrium between NiL_2^{2+} and $HNiL_2^+$, the pressure of H_2, the solution pH, and the free energy for heterolysis of H_2 (34.2 kcal/mol) (Scheme 3). The average $\Delta G°_{H^-}$ value from three independent trials was 23.0(3) kcal/mol.

Scheme 3. Standard Method Used To Determine the Hydricity of $HNiL_2^+$

$$\begin{array}{lll} NiL_2^{2+} + H_2 \rightleftharpoons HNiL_2^{+} + H^+ & & -1.364(\log K_{eq}) \\ H^+ + H^- \rightleftharpoons H_2 & & -34.2\ \text{kcal/mol} \\ \hline NiL_2^{2+} + H^- \rightleftharpoons HNiL_2^{+} & & -\Delta G°_{H-}\ \text{(hydride acceptor value)} \end{array}$$

$$K_{eq} = \frac{[HNiL_2^+][H^+]}{[NiL_2^{2+}]P_{H2}}$$

The hydricity of $HNiL_2^+$ in water was also determined by measuring the equilibrium between NiL_2^{2+} and $HNiL_2^+$ in water containing TAPS buffer (TAPS = 3-[[1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl]amino]propane-1-sulfonic acid, $pK_a = 8.4$). $HNiL_2^+$ was synthesized by pressurizing an aqueous solution of NiL_2^{2+} containing TAPS sodium salt with H_2 (1 atm). The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy until equilibration. The reaction required 18 days to reach equilibrium in the forward direction (Scheme 3, line 1). Addition of TAPS shifted the equilibrium back toward $NiL_2^{2+} + H_2$. The solution re-equilibrated after an additional 19 days following this addition. Both measured equilibria were utilized to calculate the hydricity value of 23.5 kcal/mol for this trial (see the Supporting Information for additional details).

In acetonitrile the transfer of a hydride from $HNiL_2^+$ to CO_2 is thermodynamically unfavorable. For the NiL_2^{2+} system, changing the reaction solvent to water provided a means to favor the transfer of a hydride from $HNiL_2^+$ to CO_2. When excess sodium formate was added to a solution of NiL_2^{2+} in water, no reaction was detected after 24 h at room temperature; however, $HNiL_2^+$ was detected by $^{31}P\{^1H\}$ NMR spectroscopy after heating at 70 °C for less than 24 h. Approximately 50% conversion to $HNiL_2^+$ was observed after heating at 70 °C for 24 h. The slow reaction kinetics are consistent with the measured hydricity ($\Delta G°_{H^-}$) being close to thermoneutral for the NiL_2^{2+} system.

The catalytic activity of NiL_2^{2+} for the hydrogenation of CO_2 was investigated by measuring the turnover frequency (TOF) as a function of temperature. Specifically, operando NMR spectroscopy was performed in custom high-pressure PEEK cells to examine the hydrogenation of CO_2 using NiL_2^{2+} in H_2O with 0.8 M $NaHCO_3$. The TOF for the hydrogenation of CO_2 was measured at several different temperatures (40, 60, 80, and 100 °C) using 0.029 M NiL_2^{2+} in H_2O with 0.8 M $NaHCO_3$ at 34 atm of a 1/1 mixture of H_2 and CO_2, as shown in Table 1.

Table 1. Catalytic Performance for NiL_2^{2+} as a Function of Temperature[a]

temp (°C)	TOF (h^{-1})	TOF (s^{-1})
40	$[2.2(2)] \times 10^{-2}$	$[6.2(7)] \times 10^{-6}$
60	$[8(3)] \times 10^{-2}$	$[2.3(8)] \times 10^{-5}$
80	$[4.0(5)] \times 10^{-1}$	$[1.1(1)] \times 10^{-4}$
100	$[6(4)] \times 10^{-1}$	$[2(1)] \times 10^{-4}$

[a] Average TOF for formate production using NiL_2^{2+} (0.029 M) using a 1/1 mixture of H_2 and CO_2 (34 atm) in H_2O buffered with 0.8 M of sodium bicarbonate to pH 9.0 at various temperatures.

The TOF was observed to increase with temperature (Table 1). An Eyring plot gave the apparent activation parameters of $\Delta H^\ddagger = 13(5)$ kcal mol^{-1} and $\Delta S^\ddagger = -40(15)$ cal mol^{-1} K^{-1} (Figure 1). Using the values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ determined from the Eyring plot, the $\Delta G^\ddagger$ value at 80 °C was calculated to be 27 kcal/mol.

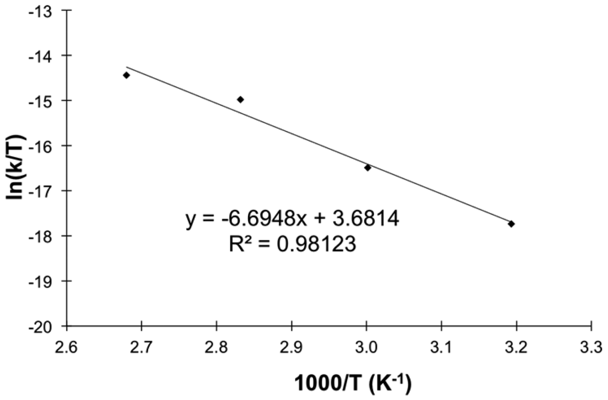


Figure 1. Eyring plot for CO_2 hydrogenation using NiL_2^{2+} using a 1/1 mixture of CO_2 and H_2 (34 atm) in H_2O buffered with 0.8 M of sodium bicarbonate to pH 9.0 ($R^2 = 0.98$, temperatures ranged from 40 to 100 °C).

To determine the effect of CO_2 and H_2 on the catalytic CO_2 hydrogenation using NiL_2^{2+}, the reaction was carried out at several different mixtures of H_2 and CO_2, as shown in Table S1 of the Supporting Information. Very similar TOFs of $[4.0(5)] \times 10^{-1}$ and $[3.4(3)] \times 10^{-1}$ h^{-1} were obtained using 1/1 and 3/1 mixtures of H_2 and CO_2, respectively. Slower TOFs were observed but not quantifiably reproduced with a 15/85 mixture of H_2 and CO_2. Regardless, the rate slowed with an increasing percentage of CO_2 at the same total pressure of H_2/CO_2, suggesting that the reaction is inhibited by either CO_2 or the solution acidification resulting therefrom. Lowering the total gas pressure of a 1/1 mixture of H_2 and CO_2 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 H_2 and CO_2 was increased from 34 to 51 atm. The observed decrease in rate with decreased H_2 pressure suggests that H_2 addition is rate limiting. The lack of rate enhancement upon increasing the fraction of H_2 from 1/1 to 3/1 or increasing the total pressure from 34 to 51 atm with a 1/1 mixture of H_2 and CO_2 could be a result of saturation kinetics for the rate dependence on the pressure of H_2. Similarly, Ogo and co-workers have reported saturation behavior in H_2 for CO_2 hydrogenation with $[Cp^*Ir^{III}(L)(H)_2]^+$ (Cp^* = η^5-C_5Me_5, L = 2,2′-bipyridine, 4,4′-dimethoxy-2,2′-bipyridine).[55] 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 CO_2. Addition of only H_2 (34 atm) to a solution of NiL_2^{2+} in H_2O buffered with 0.8 M of sodium bicarbonate gave 3 turnovers of formate after heating at 80 °C for ~28 h, resulting in a TOF of 7.9×10^{-2} h^{-1}. This is ~5 times slower than what was observed in the presence of CO_2, specifically, 34 atm of a 1/1 mixture of H_2 and CO_2 (see the Supporting Information for additional details). This observation is consistent with CO_2 being hydrogenated through an equilibrium between bicarbonate and CO_2, rather than direct hydrogenation of bicarbonate.

To elucidate the dependence on catalyst concentration, catalytic CO_2 hydrogenation in water with 0.8 M $NaHCO_3(aq)$ at 80 °C and 34 atm of a 1/1 mixture of H_2 and CO_2 was investigated using several concentrations of NiL_2^{2+} (0.014, 0.029, 0.057 M). The TOF remains constant, which suggests that the reaction is first order in NiL_2^{2+} concentration (see the Supporting Information). During catalysis a mixture of NiL_2^{2+} and $HNiL_2^+$ is detected by $^{31}P\{^1H\}$ NMR spectroscopy. When catalysis was monitored by operando $^{31}P\{^1H\}$ NMR spectroscopy, starting with NiL_2^{2+} the ratio of $HNiL_2^+$ to NiL_2^{2+} was observed to increase for the first 3.9 h, reaching a maximum of 1/4.05 NiL_2^{2+} to $HNiL_2^+$. At this point in time ≤1 equiv of formate had been generated. The amount of Ni−H then began to decrease until reaching a ratio of 1/0.63 NiL_2^{2+} to Ni−H. We predict that the decline in Ni−H concentration after 3.9 h might be a result of a decreasing pH because of the reaction shown in eq 2. The decrease in pH would therefore change the equilibrium concentration of $HNiL_2^+$, as illustrated by Scheme 3, line 1.

$$H_2(g) + CO_2(g) \rightleftharpoons H^+ + HCO_2^- \quad (2)$$

■ DISCUSSION

There are three factors that determine whether or not a transition-metal complex will serve as a CO_2 hydrogenation catalyst: (1) the complex has to be able to activate dihydrogen, (2) the acidity of the H_2 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 CO_2. For $Co(dmpe)_2^+$, the acidity of the H_2 addition product was critical, because a very strong base (Verkade's base, pK_a of the conjugate acid in acetonitrile is 33.6) was needed to deprotonate $H_2Co(dmpe)_2^+$ to generate $HCo(dmpe)_2$.[42,43,77] For bis(diphosphine) complexes of Ni, the acidity of the H_2 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 CO_2 is favorable, this complex is not catalytic for the hydrogenation of CO_2 because the hydride could not be regenerated, even at pH 11.8.[63] Essentially, stronger hydride donors require higher basicity to regenerate the hydride through heterolysis of H_2. On the basis of the hydricity ($\Delta G°_{H^-}$), 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 $HNi(dmpe)_2^+$).[65,78] 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 was still hydridic enough to transfer a hydride to CO_2 ($\Delta G°_{H^-}$ < 24 kcal/mol in H_2O) 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.[76,79] The hydricity of $HNi(dmpe)_2^+$ in water has been determined to be 16 kcal/mol.[63] The hydricity of $HNiL_2^+$ in water has now been determined to be 23.2 kcal/mol, corresponding to a 7 kcal/mol difference in hydricity in comparison to $HNi(dmpe)_2^+$ resulting from replacement of the methyl groups with 3-methoxypropyl substituents. As a result, the transfer of a hydride from $HNiL_2^+$ to CO_2 is favorable by 1 kcal/mol.

An induction period (~2 h at 80 °C) was observed for catalytic CO_2 hydrogenation to formate using NiL_2^{2+} (0.029 M) in H_2O with added $NaHCO_3$ (0.8 M) and a 1/1 mixture of H_2 and CO_2 (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 H_2 and CO_2 (34 atm total pressure) at 100 °C. 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 ^{31}P NMR spectroscopy. One possible explanation for the observed induction period is that the initial formation of $HNiL_2^+$ is limiting. The only two species observed by operando $^{31}P\{^1H\}$ NMR spectroscopy during the course of the reaction are NiL_2^{2+} and $HNiL_2^+$. 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 H_2 and CO_2 (34 atm total pressure), but this induction period was not observed when a 3/1 mixture of H_2 and CO_2 was used (34 atm total pressure). This result supports the hypothesis that a certain amount of $HNiL_2^+$ may need to be formed before catalysis is observed because the increased pressure of H_2 leads to faster formation of Ni−H. Interestingly, a still unexplained induction period ranging from 15 min to >2 h was observed for catalytic CO_2 hydrogenation using $Co(dmpe)_2^+$ in the presence of DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene).[43]

The induction period observed for CO_2 hydrogenation with NiL_2^{2+} is still observed when Na_2CO_3 (0.12 M) is added to 0.8 M $NaHCO_3(aq)$. Addition of Na_2CO_3 would increase the basicity of the starting solution. The results suggest that the pH at the start of the reaction is not the cause of the observed induction period. The induction period was also present when 0.6 equiv of $NiBF_4 \cdot 6H_2O$ was added to NiL_2^{2+}. This result suggests that the catalytic activity is not a result of loss of ligand or degradation of starting NiL_2^{2+} to generate paramagnetic, NMR-silent species such as $NiL(solvent)_2^{2+}$. The length of the induction period was observed to decrease with increasing temperatures and H_2 pressures. These features are consistent with the induction period resulting from the formation of $HNiL_2^+$.

The pH of the solution decreased as the CO_2 hydrogenation reaction progressed. Water buffered with either a carbonate or phosphate buffer is still acidified upon addition of CO_2, inherently leading to a solution with a pH near 8.[63] Due to acidification with CO_2, the simplest choice of a base is bicarbonate, which leads to a solution buffered by the CO_2/HCO_3^- acid/base pair. For a solution with 1 M bicarbonate and under 1 atm of CO_2 the resulting solution pH should be ~7.8, on the basis of the solubility and acidity of CO_2. For the catalytic studies, three concentrations of $NaHCO_3$ were screened (0.2, 0.4, and 0.8 M) at 80 °C and 17 atm of a 1/1 mixture of H_2 and CO_2. The TOF for formate production was observed to increase with increasing base concentration, with 0.8 M $NaHCO_3$ generating the most formate (see the Supporting Information). Higher concentrations of $NaHCO_3$ in water led to precipitation of NiL_2^{2+}. Other bases (NEt_3, $NHEt_2$, DBU, and KOH) were also investigated; however, $NaHCO_3$ gave superior results. Specifically, minimal formate (≤2 turnovers) was obtained with NEt_3, $NHEt_2$, and DBU. KOH was not a suitable base for this reaction, as a solid was formed upon addition of KOH to a solution of NiL_2^{2+} 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,[63] because the use of phosphate inhibited catalysis.

On the basis of the above data, NiL_2^{2+} appears to operate under the same mechanism as shown in Scheme 1. More specifically, the proposed catalytic cycle for CO_2 hydrogenation to formate in aqueous $NaHCO_3$ involves the addition of H_2 to NiL_2^{2+} to give unobserved $H_2NiL_2^{2+}$, which is quickly deprotonated by base to form the Ni−H complex $HNiL_2^+$. Hydride transfer from $HNiL_2^+$ to CO_2 gives formate and regenerates the starting material. NiL_2^{2+} and $HNiL_2^+$ are the only two species observed by NMR spectroscopy during catalysis. Despite the slow rates of catalysis, NiL_2^{2+} and $HNiL_2^+$ appear to be stable under the reaction conditions for long periods of time (~50 h).

■ SUMMARY AND CONCLUSIONS

The bis(diphosphine) complex of nickel NiL_2^{2+} is an active catalyst for CO_2 hydrogenation in water, with $NaHCO_3$ as the only added base. Catalytic turnover of this complex was enabled by balancing the hydride donor ability of $HNiL_2^+$ with the ability to regenerate the hydride at a near-neutral pH. The driving force for hydride transfer from $HNiL_2^+$ to CO_2 is small (1 kcal/mol), which enables catalysis to occur, at slow catalytic rates.

NiL_2^{2+} is the first homogeneous nickel catalyst for the hydrogenation of CO_2 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 CO_2 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 N_2 for 2 h. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were dried using a PureSolv system using CuO and molecular sieves under N_2. All other reaction solvents were purified and dried according to the literature.[80] H_2 and CO_2 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 ^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% H_3PO_4 in D_2O or neat H_3PO_4 (δ 0 ppm). The temperature of the NMR probe was calibrated using a PEEK NMR tube filled with ethylene glycol and the equation $T\ (K) = (4.218 - \Delta)/0.009132$, where Δ is the shift difference (ppm) between the CH_2 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 $[NiL_2](Br)_2$. To a blue-brown suspension of $NiBr_2 \cdot 3H_2O$ (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 Et_2O, causing separation of a red oil. The Et_2O layer was decanted off, and the red oil was collected as the pure complex (1.747 g, 85.6%). ^1H NMR (300 MHz, $CDCl_3$): 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). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 52.02. HRMS (ES+-TOF) *m*/*z*: $[M^+]$ calcd for $[C_{36}H_{80}BrNiO_8P_4]^+$ 901.3341; found 901.3334.

Synthesis of $[NiL_2](BF_4)_2$. To a solution of $[NiL_2](Br)_2$ (0.883 g, 0.898 mmol) in 50 mL of THF was added a solution of $AgBF_4$ (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 Et_2O, causing separation of an orange oil. The Et_2O layer was decanted off, and the orange oil was collected as the pure complex (535 mg, 59.6%). ^1H NMR (500 MHz, $CDCl_3$): 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, $CDCl_3$): δ −0.77. $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN): δ 72.75, 58.85, 25.38, 23.53, 22.25. $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 55.96. HRMS (ES+-TOF) *m*/*z*: $[M^+]$ calcd for $[C_{38}H_{80}F_3NiO_8P_4S]^+$ 1011.2779; found 1011.2783. Anal. Calcd for $C_{36}H_{80}B_2F_8O_8P_4Ni$: C, 43.36; H, 8.09. Found: C, 42.83; H, 8.06.

Synthesis of $[\mathrm{HNiL_2}]BF_4$ from Cesium Formate. $[\mathrm{NiL_2}](BF_4)_2$ (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. ^{1}H 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). ^{13}C{^{1}H} NMR (126 MHz, D_2O): δ 71.74, 70.96, 56.85, 24.08, 23.27, 21.12. ^{13}C{^{1}H} NMR (126 MHz, CD_3CN): δ 125.77, 73.46, 58.77, 26.50, 26.40, 25 0.70. ^{31}P{^{1}H} NMR (202 MHz, H_2O): δ 43.00 (s). ^{19}F 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.[81,82] *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 $[\mathrm{NiL_2}](BF_4)_2$. The resulting solution was added to a PEEK cell containing a capillary with C_6D_6 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. ^{1}H 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_6D_5H resonance in the C_6D_6 internal standard.

Determining Concentration Dependences Using PEEK NMR Spectroscopy Cells. To determine the dependence of the catalytic rate on the concentration of catalyst, a 0.063 M stock solution of $[\mathrm{NiL_2}](BF_4)_2$ in 0.8 M aqueous $NaHCO_3$ was prepared in a 2 mL volumetric flask. Using the stock solution, 350 μL solutions of 0.014, 0.029, and 0.057 M were prepared. All samples were stored in vials at −65 °C until ready for use. After the solutions were thawed and warmed to room temperature, a 300 μL portion of the sample was transferred to a PEEK NMR spectroscopy tube using a syringe. A C_6D_6 capillary was added as an internal standard. High-pressure reactions in PEEK NMR spectroscopy cells were carried out at 80 °C and 34 atm of a 1/1 mixture of H_2 and CO_2 using the general method for PEEK NMR spectroscopy experiments described above. The results are shown in Table S4 in the Supporting Information.

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 $[\mathrm{NiL_2}](BF_4)_2$ (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 ^{31}P{^{1}H} NMR spectroscopy after 26 h. The reaction was periodically monitored by ^{31}P{^{1}H} 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 ^{31}P{^{1}H} 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. $[\mathrm{NiL_2}](BF_4)_2$ (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 $\mathrm{HNiL_2}^+$ was measured by ^{31}P{^{1}H} NMR spectroscopy. The pH of the solution was measured, and the $\Delta G°_{\mathrm{H}^-}$ 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)

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Notes

The authors declare no competing financial interest.

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