Electrocatalytic Oxidation of Formate by [Ni(PR_2NR_2)(CH_3CN)]^{2+} Complexes


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Supporting Information

ABSTRACT: [Ni(PR_2NR_2)(CH_3CN)]^{2+} complexes with R = Ph, R’ = 4-MeOPh or R = Cy, R’ = Ph, and a mixed-ligand [Ni(PF_2NR_2)(PF_2NR_2)(CH_3CN)]^{2+} with R = Cy, R’ = Ph, R” = Ph, have been synthesized and characterized by single-crystal X-ray crystallography. These and previously reported complexes are shown to be electrocatalysts for the oxidation of formate in solution to produce CO_2, protons, and electrons, with rates that are first-order in catalyst and formate at formate concentrations below ∼0.04 M (34 equiv). At concentrations above ∼0.06 M formate (52 equiv), catalytic rates become nearly independent of formate concentration. For the catalysts studied, maximum observed turnover frequencies vary from <1.1 to 15.8 s^{-1} at room temperature, which are the highest rates yet reported for the oxidation of formate by homogeneous catalysts. These catalysts are the only base-metal electrocatalysts as well as the only homogeneous electrocatalysts reported to date for the oxidation of formate. An acetate complex demonstrating an η^1-OC(O)CH_3 binding mode to nickel has also been synthesized and characterized by single-crystal X-ray crystallography. Based on this structure and the electrochemical and spectroscopic data, a mechanistic scheme for electrocatalytic formate oxidation is proposed which involves formate binding followed by a rate-limiting proton and two-electron transfer step accompanied by CO_2 liberation. The pendant amines have been demonstrated to be essential for electrocatalysis, as no activity toward formate oxidation was observed for the similar [Ni(depe)]^{2+} (depe = 1,2-bis(diethylphosphino)ethane) complex.

INTRODUCTION

The temporal variation in the availability of renewable energy sources such as solar and wind makes storage of this energy in the form of fuels attractive. Water-splitting is one attractive route for energy storage, but the low volumetric energy density of H_2 has motivated efforts to store energy in the form of reduced carbon products with much higher volumetric energy densities, such as methanol or formic acid. Although formic acid has a lower energy density than methanol, current formic acid fuel cells can run at much higher concentrations than methanol fuel cells, with the result that the performance of formic acid fuel cells is competitive with the performance of methanol fuel cells.

Currently formic acid is mainly produced by carbonylation of methanol followed by hydrolysis. However, there is also much current work on the production of formic acid by direct electrochemical reduction of carbon dioxide or indirectly via water electrolysis to form hydrogen followed by hydrogenation of CO_2 to produce formic acid. Once viable methods become available for producing formic acid for energy storage, electrocatalysts for the oxidation of formic acid will be of interest. At present, however, the only electrocatalysts reported for this process are heterogeneous catalysts based upon precious metals such as platinum, palladium, or rhodium.

One possible pathway for formate oxidation involves the heterolytic cleavage of the C−H bond. Recent work in one of our laboratories has shown that [Ni(PF_2NR_2)(CH_3CN)]^{2+} complexes rapidly and reversibly promote the heterolytic cleavage of H_2 into a hydride and proton during H_2 oxidation using the nickel center as a hydride acceptor and the ligand as a proton acceptor. There is also a considerable body of information on the factors controlling the hydride acceptor abilities of this class of complexes. In fact, metal diphosphine complexes were used to determine the hydride donor ability of formate in acetonitrile solutions (44 ± 2 kcal/mol), and this transfer of a hydride from formate to generate CO_2 and a metal hydride can be viewed as the first step in the oxidation of formate. It was anticipated that [Ni(PF_2NR_2)(CH_3CN)]^{2+} complexes would be electrocatalysts for formate oxidation, as the hydride acceptor ability of [Ni(PF_2NR_2)(CH_3CN)]^{2+} complexes is in the appropriate range to accept a hydride from formate and can be systematically varied, and because the pendant bases can facilitate the oxidation of hydrides to protons.

Received: May 16, 2011
Published: June 21, 2011
In this article we examine the influence of different phosphorus and nitrogen substituents of [Ni(P2N2)2(CH3CN)]2+ complexes for catalytic formate oxidation and the role of a pendant base in this electrocatalytic process. The synthesis and characterization of new [Ni(P2N2)2(CH3CN)]2+ complexes are described. The formation of nickel hydride species by reaction with hydrogen as well as with formate is also described, and the hydride donor abilities (ΔG°fH) of three new hydride complexes are reported. Finally, the activities for electrocatalytic oxidation of formate are discussed, both for the new complexes reported here as well as for previously reported complexes.

**RESULTS**

**Synthesis and Characterization of Ligands and Complexes.** The ligands used for this study differ in the substitution on the phosphorus (R) and the nitrogen atoms (R') of the eight-membered ring of the P2NR2 ligands, as shown in eq 1 in Chart 1. The synthesis of the ligands was performed according to literature procedures. The ligands used in this study were the following: P2N2R2BF4 (1,5-di(4-methoxyphenyl)-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane), P2N2R2BF4 (1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane), and P2N2R2BF4 (1,5-diphenyl-3,7-dicyclohexyl-1,5-diaza-3,7-diphosphacyclooctane).

Using these ligands, the two homoleptic complexes, [Ni(P2N2)2(CH3CN)]2+ (BF4)2, were prepared by the reaction of [Ni(CH3CN)6]2+ complexes [Ni(P2N2)2(CH3CN)]2+ and [Ni(PCy3)2(CH3CN)]2+ with an excess of formate or by reaction with 2 equiv of the ligand [Ni(Ph2PCH2Ph)]2+. This disproportionation reaction is presumably accompanied by the formation of hydrogen gas as shown in eq 4.
X-ray Diffraction Studies. Crystal structures of the four dicationic complexes \([\text{Ni}(\text{PPh}_2\text{NPhOMe}_2)\text{CH}_3\text{CN}]\)(BF_4)_2, \([\text{Ni}(\text{PCy}_2\text{NPh}_2)\text{CH}_3\text{CN}]\)(BF_4)_2, \([\text{Ni}(\text{PCy}_2\text{NPh}_2)\text{PPh}_2\text{NPh}_2]\text{CH}_3\text{CN}]\)(BF_4)_2, and \([\text{Ni}(\text{PCy}_2\text{NPh}_2)]\text{CH}_3\text{CN}]\)(BF_4)_2 as well as the structure of the neutral complex \([\text{Ni}(\text{PPh}_2\text{NPhOMe}_2)]\text{CH}_3\text{CN}]\) were obtained, as shown in Figure 1, and selected bond lengths and angles are in the Supporting Information. The crystals of the three nickel(II) bis-diphosphine complexes were all grown from acetonitrile solutions of the complexes layered with diethyl ether at −35 °C. All three structures show a trigonal bipyramidal coordination geometry around the nickel(II) center. In each of these complexes, both P2N2 ligands are coordinated via the phosphorus donor atoms to axial and equatorial positions on the nickel(II). The third equatorial ligand is an acetonitrile molecule. The bond lengths and angles, as well as the bite angles, are comparable to those of previously reported structures, but there are some differences in the boat/chair conformations of the rings, likely due to packing effects.

The structure of the zero-valent complex \([\text{Ni}(\text{PPh}_2\text{NPhOMe}_2)]\text{CH}_3\text{CN}]\) was determined with crystals grown from vapor diffusion of pentane into a THF solution of the complex at −35 °C. As expected for a nickel(0) complex, the structure shows a tetrahedral coordination geometry. The same coordination geometry was observed for the recently published \([\text{Ni}(\text{PPh}_2\text{NPhOMe}_2)]\text{CH}_3\text{CN}]\) complex, and in fact, the bond lengths and angles are very similar to those reported in the literature.

Crystals of \([\text{Ni}(\text{PCy}_2\text{NPh}_2)]\text{CH}_3\text{CN}]\)(BF_4)_2 suitable for X-ray diffraction were grown from an acetonitrile solution of the compound layered with diethyl ether at room temperature. The structure can be described as a distorted square planar coordination geometry around the nickel center. The square plane is spanned by the two phosphorus atoms of the PCy_2NPh ligand and two nitrogen atoms of two coordinated acetonitrile molecules. Selected bond lengths and angles are in the Supporting Information.

The nickel \(\eta^1\)-acetate complex, \([\text{Ni}(\text{PPh}_2\text{NBn}_2)(\text{OAc})](\text{BF}_4)\) (Bn = benzyl), was synthesized by adding 1 equiv of tetrabutylammonium acetate (NBu_4OAc) to a solution of \([\text{Ni}(\text{PPh}_2\text{NBn}_2)]\text{CH}_3\text{CN}]\)(BF_4)_2 in THF and [Ni(PCy_2NPh)_2](CH_3CN)](BF_4)_2 (synthesized as previously described) in the Supporting Information.

Figure 1. Thermal ellipsoid plots of the crystal structures of the complexes. Thermal ellipsoids are shown at the 50% probability level. For clarity, hydrogen atoms and uncoordinated counterions and solvent molecules are omitted, and only the first carbon of the nitrogen and phosphorus substituents are shown: \([\text{Ni}(\text{PPh}_2\text{NPhOMe}_2)]\text{CH}_3\text{CN}]\)(BF_4)_2, \([\text{Ni}(\text{PCy}_2\text{NPh}_2)]\text{CH}_3\text{CN}]\)(BF_4)_2, \([\text{Ni}(\text{PCy}_2\text{NPh}_2)\text{PPh}_2\text{NPh}_2]\text{CH}_3\text{CN}]\)(BF_4)_2, and \([\text{Ni}(\text{PCy}_2\text{NPh}_2)]\text{CH}_3\text{CN}]\)(BF_4)_2. (Et_2O, where P(1) and P(2) belong to the PPh_2NPh ligand and P(3) and P(4) belong to the PCy_2NPh ligand; [Ni((\text{PPh}_2\text{NPhOMe}_2)]\text{CH}_3\text{CN}]\)(BF_4)_2, THF; and [Ni((\text{PPh}_2\text{NPh}_2)]\text{CH}_3\text{CN}]\)(BF_4)_2, CH_3CN.

Figure 2. Perspective thermal ellipsoid plot of the crystal structure of [Ni(PPh_2NPhOMe)_2(\text{OAc})](\text{BF}_4). Thermal ellipsoids are shown at the 50% probability level. The Ni1–O1 distance is 2.09 Å, whereas Ni1–O2 is 3.56 Å. For clarity, hydrogen atoms and uncoordinated counterions are omitted, and only the first carbon of the nitrogen and phosphorus substituents is shown.
benzonitrile. The complex crystallizes as a distorted trigonal bipyramid with the acetate bound through a single oxygen in the equatorial plane, as shown in Figure 2. Bond distances and angles are shown in the Supporting Information. The trigonal plane is distorted, with one oxygen–nickel–phosphine angle being 122.05° and the other angle being 99.58°. There are no known structures of analogous nickel(II) tetraphosphine acetate complexes with which to compare directly. However, the Ni–O bond length of 2.092 Å is slightly longer (2.055 and 2.050 Å) than those of other nickel(II) acetate complexes in the literature, with the Ni–O–C bond angle being similar to those of other nickel η1-acetate complexes.

**Electrochemical Studies.** Representative cyclic voltammograms for complexes [Ni(pPh2NPhOme)2(CH3CN)]2+, [Ni(Cy2NPh2)(CH3CN)]2+, and [Ni(Cy2NPh2)(pPh2NPhOme)(CH3CN)]2+ in acetonitrile solutions are shown in Figure 3 by traces a, b, and c, respectively. They consist of two reversible one-electron waves assigned to the Ni(II/I) and Ni(I/0) couples. This behavior is consistent with previous studies of [Ni(diphosphine)2]2+ complexes, and the potentials for these couples are listed in Table 1, together with related values from the literature. It can be seen from Figure 3 and Table 1 that the potentials of the Ni(II/I) couple are particularly sensitive to the nature of the substituents on phosphorus, shifting to more positive potentials as the number of cyclohexyl substituents increases. This positive shift is somewhat counter-intuitive, in that replacing phenyl substituents on phosphorus with more electron-donating cyclohexyl groups would be expected to shift the potentials more negative on the basis of simple inductive effects. However, the increased steric bulk of the cyclohexyl substituents produces larger distortions toward tetrahedral geometry that lead to a lower energy for the lowest unoccupied molecular orbital (LUMO), as discussed elsewhere. The lower energy of the LUMO results in a more positive potential for the Ni(II/I) couple.

Finally, it is of interest to compare the cyclic voltammogram of the hydride complex [HNi(pPh2NPhOme)2]2+ (Figure 4) to that of [Ni(pPh2NPhOme)2(CH3CN)]2+ (Figure 3a). Scanning anodically, [HNi(pPh2NPhOme)2]2+ shows a well-defined irreversible 2e− oxidation at −0.47 V. The return cathodic scan shows reduction waves that correspond to the Ni(II/I) and Ni(I/0) couples of [Ni(pPh2NPhOme)2(CH3CN)]2+. This result suggests that the oxidation of [HNi(pPh2NPhOme)2]2+ is followed by rapid proton loss and a second electron transfer to generate [Ni(pPh2NPhOme)2(CH3CN)]2+, which is reduced on the return scan. At variable scan rates of 50 mV/s to 20 V/s, the wave at −0.47 V is irreversible, suggesting that proton transfer to the pendant amine following this oxidation is fast (k > 50 s−1). Similar behavior is observed for [HNi(depe)2](BF4) (depe = 1,2-bis(diethylphosphino)ethane), but in that case the irreversible oxidation occurs at 0.0 V (the oxidation is irreversible at all observed scan rates, up to 100 V/s). This result suggests that the presence of a pendant base in [HNi(pPh2NPhOme)2]2+ results in a 0.5 V negative shift in potential. This potential shift is attributed to the pendant base assisting proton transfer upon oxidation of [HNi(pPh2NPhOme)2]2+, as previously observed for other...
complexes containing diphosphine ligands with pendant amine bases.5 It should be noted that the potentials for the nickel(II/1) and nickel(I/0) couples for Ni(depe)2 are actually an average of 0.25 V more negative than for [Ni(PPh2)2NMe2(CH3CN)2]+, suggesting that the presence of the pendant amine may result in an even larger shift than simply the difference between the corresponding hydride oxidation potentials.

**Table 1. Thermodynamic and Electrochemical Data in Acetonitrile and Benzonitrile**

<table>
<thead>
<tr>
<th>NiL2(CH3CN)2+ ligands</th>
<th>ΔG°H− (kcal/mol)</th>
<th>E1/2(NiII/I) (V vs CpFe+/0)</th>
<th>E(NiI/0) (V vs CpFe+/0)</th>
<th>pKa of HNiL2+</th>
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<tr>
<td>p5C5N5H10b</td>
<td>63.7</td>
<td>−0.62 (−0.60)</td>
<td>−1.09 (−1.10)</td>
<td>17.3</td>
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<td>p5C5N5H10b</td>
<td>60.5</td>
<td>−0.76 (−0.75)</td>
<td>−1.05 (−1.07)</td>
<td>16.5</td>
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<tr>
<td>p5C5N5H10</td>
<td>58.6</td>
<td>−0.87 (−0.87)</td>
<td>−1.07 (−1.08)</td>
<td>17.4</td>
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<tr>
<td>p5C5N5H10</td>
<td>59.0</td>
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<tr>
<td>p5C5N5H10</td>
<td>61.4</td>
<td>−0.74</td>
<td>−0.89</td>
<td>13.8</td>
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<tr>
<td>p5C5N5H10</td>
<td>57.1</td>
<td>−0.94</td>
<td>−1.19</td>
<td>19.4</td>
</tr>
<tr>
<td>p5C5N5H10</td>
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<td>−0.98</td>
<td>−1.14</td>
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<tr>
<td>p5C5N5H10</td>
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<td>−0.80</td>
<td>−1.28</td>
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<td>p5C5N5H10</td>
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<td>−1.04</td>
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<td>dppp</td>
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<td>−1.16 (−1.13)</td>
<td>−1.29 (−1.30)</td>
<td>23.8</td>
</tr>
<tr>
<td>depe</td>
<td>−0.89 (−0.86)</td>
<td>−1.33 (−1.32)</td>
<td>23.9</td>
<td></td>
</tr>
</tbody>
</table>

Values in parentheses are in benzonitrile. |a| Estimated from Ni(I/0) couple using pKa = −18.6 E1/2 = −2.65; see Figure 6. |b| Fraze et al.12 Estimated from Ni(II/I) couple using ΔG°H− = 20.8 E1/2 + 76.8; see Figure 5. |c| Yang et al.18,19 dppp = 1,3-bis(diphenylphosphino)propane, depe = 1,2-bis(diethylphosphino)ethane, dmpp = 1,2-bis(dimethylphosphino)propane. Berning et al.20

**Thermodynamic Properties of Complexes [HNi(PPh2)2NMe2(CH3CN)2]+, [HNi(PCy2)2NMe2(CH3CN)2]+, and [HNi(PCy2)2NPh2(CH3CN)2]+.** The hydride donor ability (ΔG°H−) in acetonitrile for each of the three complexes was calculated from the observed equilibrium concentrations of the hydride with the starting complex using the thermodynamic cycle shown in Scheme 1. The equilibrium between the hydride complex [HNi(PPh2)2NMe2(CH3CN)2]+ and [Ni(PPh2)2NMe2(CH3CN)2]+ was measured by 31P NMR spectroscopy using an appropriate base under 1 atm of hydrogen (eq 5). The sum of reactions 5−7 is reaction 8 (the heterolytic cleavage of the Ni−H bond to form H+ and the corresponding Ni(II) complex), and the free energy associated with this reaction is ΔG°H−, the hydride donor ability. The reverse reaction corresponds to the hydride acceptor ability of Ni(PPh2)2NMe2(CH3CN)2+. Larger values of ΔG°H− correspond to better hydride acceptors and lower values to better hydride donors. This information is summarized in Table 1, together with data for selected additional complexes from the literature.

For the new complexes considered here, [HNi(PCy2)2NMe2(CH3CN)2]+ is the poorest hydride donor, with ΔG°H− = 63.7 kcal/mol, and [HNi(PPh2)2NPh2(CH3CN)2]+ is the best hydride donor, with ΔG°H− = 58.6 kcal/mol. The hydride donor ability for the heteroleptic complex [HNi(P5C5N5H10b)(P5C5N5H10)(CH3CN)]+, 60.5 kcal/mol, is only slightly poorer than the hydride donor ability of the homoleptic complex [HNi(P5C5N5H10)(CH3CN)]+, 60.5 kcal/mol. The pKa values for the [HNi(P5C5N5H10)(CH3CN)]+ complexes were determined through thermochemical cycles using the hydride donor abilities and the electrochemical potentials for the Ni(II/I) and Ni(I/0) couples in acetonitrile, as previously reported for similar complexes.31 The hydride donor abilities of the nickel complexes show the expected linear trend with the Ni(II/I) couple, and the pKa values for the metal hydrides also exhibit a linear trend with the Ni(I/0) couple, as shown in Figures 5 and 6. These trends are very similar to the trends previously observed for nickel bis-diphosphine complexes with no pendant bases.30 The heteroleptic complex is not shown in Figures 5 and 6, but the data for this complex is consistent with the trends observed for the homoleptic complexes.

**Reactivity toward H2 and CO2 using High Pressure NMR Spectroscopy.** The three new bis-P2N4 complexes [Ni(P5C5N5H10b)(CH3CN)]2+, [Ni(PCy2)2NMe2(CH3CN)]2+, and [Ni(PCy2)2NPh2(CH3CN)]2+ did not demonstrate any catalytic activity for CO2 reduction under high pressures of CO2 and H2. The complexes were dissolved in acetonitrile-d3, and the solutions were placed in a high-pressure PEEK NMR tube.32,33 No reaction could be observed after applying 21 atm of a 1:1 mixture of CO2/H2. Even the independently synthesized hydride complex [HNi(PCy2)2NPh2(CH3CN)]2+ did not react observably with 21 atm of carbon dioxide. For complex [Ni(P5C5N5H10b)(CH3CN)]2+, the formation of a hydride species could be observed without the addition of an external base, but no evidence for formation of formate or formic acid could be observed via NMR spectroscopy. These results are consistent

**Scheme 1. Determination of Hydride Donor Abilities for [HNi(P5C5N5H10b)(CH3CN)]2+ Complexes**
with thermodynamic data discussed in more detail below, where-in the transfer of a hydride to CO₂ to generate formate (ΔG_{f}^{0} = 44 ± 2 kcal/mol) is thermodynamically unfavorable.

**Electrocatalytic Oxidation of Formate.** The complexes [Ni(P²⁺₂N²⁺₂)(CH₃CN)]²⁺, [Ni(P²⁺₂N²⁺₂₂)(CH₃CN)]²⁺, and [Ni(P²⁺₂N²⁺₂₂)(P²⁺₂N²⁺₂)(CH₃CN)]²⁺ were also examined for their activity for electrocatalytic formate oxidation. The left-hand side of Figure 7 shows cyclic voltammograms of [Ni(P²⁺₂N²⁺₂₂)(P²⁺₂N²⁺₂)(CH₃CN)]²⁺ as a function of formate concentration (added as NBu₄HCO₂-HCO₂H). The reversible wave at ~1.33 V is due to the cobaltocenium/cobaltocene couple, used as an internal standard. This compound was used instead of ferroene because the ferrocenium/ferroene couple overlaps the catalytic waves observed for formate oxidation. The reversible wave at ~−1.1 V is assigned to the Ni(I/0) couple as discussed above. The negative shift in potential is consistent with a fast following step that is first-order in formate to one that is independent of formate. The initially linear region of this plot implies a first-order dependence of the TOF on formate concentration. The formate-independent region indicates a change in the rate-determining step from one that is first-order in formate to one that is independent of formate. The slow decrease above ~0.08 M is due to catalyst decomposition. Test of P²⁺₂N²⁺₂ ligand from the nickel complex has been observed at high formate concentrations after hours in solution or in the presence of excess acetate, as indicated by the appearance of free P²⁺₂N²⁺₂ ligand in the ³¹P NMR spectrum.

A plot of the TOF of the catalyst versus the concentration of formate (as NBu₄HCO₂-HCO₂H) is shown on the right-hand side of Figure 7. It can be seen that the TOF initially increased linearly as a function of formate concentration, became independent of formate concentration between ~0.04 and 0.06 M, and slowly decreased at higher formate concentrations. The initially linear region of this plot implies a first-order dependence of the TOF on formate concentration. The formate-independent region indicates a change in the rate-determining step from one that is first-order in formate to one that is independent of formate. The TOF has been observed at high formate concentrations after hours in solution or in the presence of excess acetate, as indicated by the appearance of free P²⁺₂N²⁺₂ ligand in the ³¹P NMR spectrum. The left-hand side of Figure 8 shows a series of cyclic voltammograms recorded in benzonitrile solutions of [Ni(P²⁺₂N²⁺₂₂)(P²⁺₂N²⁺₂)(CH₃CN)]²⁺ as a function of catalyst concentration in the presence of excess formate (0.15 M NBu₄HCO₂-HCO₂H). It can be seen that the catalytic current increases as the concentration of the catalyst increases. On the right-hand side of Figure 8 is a plot of the catalytic current (i_{cat}) as a function of the catalyst concentration obtained from the data on the left-hand side of the figure. The linear dependence of this plot on catalyst concentration implies that the catalytic reaction is first-order in catalyst. The data taken together imply that at low formate concentrations, the rate-determining step includes the reaction of formate with the catalyst, while at high formate concentrations the rate of reaction is still first-order in catalyst but appears to become independent of formate concentration. However, decay of the TOF at high formate concentration, likely
Due to NBu₄HCO₂·HCO₂H being a simple, soluble, crystalline solid, this was used as the formate source throughout the present studies. This soluble salt does contain a co-crystallized formic acid that is homoconjugated with the formate; however, the formic acid was not expected to have a substantial effect on catalysis. In order to evaluate the effect of the formic acid, the electrocatalytic formate oxidation was repeated for [Ni(PCH₂NMe₂)₂(CH₃CN)]²⁺ with a solution containing NBu₄HCO₂·HCO₂H with an equimolar amount of DBU to deprotonate the formic acid and thereby generate formate and formate ions to compete with the formic acid homoconjugate for the coordination site of the catalyst.

Table 2. Electrocatalytic TOFs and Thermochemical Data

<table>
<thead>
<tr>
<th>Liq. (CH₃CN)²⁺ ligands</th>
<th>TOF (s⁻¹)ᵃ</th>
<th>ΔG°ₚ₉ (kcal/mol)b</th>
<th>pKₐ of HNiL₂⁺ c</th>
<th>pKₐ of free RNH₃⁺ d</th>
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<tr>
<td>p⁴P₂NMe₂⁺</td>
<td>15.8</td>
<td>56.4</td>
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<td>p⁴P₂N₃⁺</td>
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<td>57.1</td>
<td>19.9</td>
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<td>p⁴P₂NC₅Me₂⁺</td>
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<td>60.7</td>
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<td>p⁴P₂NC₅Me₂⁺</td>
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<td>1.5</td>
<td>56.0</td>
<td>23.8</td>
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</tbody>
</table>

ᵃ Data collected in benzonitrile with ~1 mM complex and 0.2 M NBu₄OTf, where value shown is the maximum observed TOF. ᵇ Thermochromic values in acetonitrile. ᶜ Yang et al.⁵⁻²⁸ ᵈ Fraze et al.⁹ ᵉ Kilgore et al.¹⁶ ᶠ depe = 1,2-bis(diethylphosphino)ethane. Berning et al.³⁰ ᵍ Estimated from Ni(II/1) couple using ΔG°₁₅ = 20.8 E₁/₂ + 76.8; see Figure 5. ʰ Estimated from Ni(I/0) couple using pKₐ = −18.6 E₁/₂ = −2.65; see Figure 6. ᵢ Izutsu.³⁷ ｊ Kaljurand et al.³⁸

Figure 7. Left: CVs of the titration of [Ni(PCH₂NMe₂)₂(PCH₂N₃⁺)₂(CH₃CN)]²⁺, with NBu₄HCO₂·HCO₂H. Right: Corresponding turnover frequency versus [NBu₄HCO₂·HCO₂H]. Conditions: 1.2 mM catalyst solution in benzonitrile, 0.2 M NBu₄OTf as supporting electrolyte, glassy carbon working electrode, scan rate 50 mV/s. Potentials are referenced with respect to the ferrocenium/ferrocene couple (0.00 V) using the cobaltocenium/cobaltocene couple as a secondary reference (−1.33 V).

Figure 8. Left: CVs of the titration of NBu₄HCO₂·HCO₂H with [Ni(PCH₂NMe₂)₂(PCH₂N₃⁺)₂(CH₃CN)]²⁺. Right: iₜot vs the concentration of [NBu₄HCO₂·HCO₂H]. Conditions: 0.15 M NBu₄HCO₂·HCO₂H solution in benzonitrile, 0.2 M NBu₄OTf as supporting electrolyte, glassy carbon electrode, scan rate 50 mV/s. Potentials are referenced with respect to the ferrocenium/ferrocene couple using cobaltocenium as a secondary internal reference.

a result of catalyst decomposition, complicates the interpretation of the formate concentration-independent region.
protonated DBU. The result of using 1 equiv of DBU per NBu4HCO2•H2O was a very similar overall catalytic TOF of 10.6 s−1 with DBU vs 8.5 s−1 using NBu4HCO2•H2O without DBU (see Experimental Section for additional details).

To determine that CO2 was indeed the product of the catalytic reaction, a controlled potential electrolysis was carried out using [Ni(P(Ph2N)n)2]+, which shows a 2e− oxidation at ~0 V vs Cp2Fe+/02+ process at this [HNi(depe)2]2+ potential range over which the catalytic process was observed. Quantification of the CO2 indicated a current efficiency of 93 ± 5% for this reaction. The protons were presumably trapped by formate to produce formic acid.

For comparison, the complex [Ni(depe)2]2+ was also studied to determine if a similar complex without a pendant amine would be a catalyst for formate oxidation. As seen in Figure 9, addition of increasing amounts of NBu4HCO2•H2O to acetonitrile solutions of [Ni(depe)2]2+ results in the formation of [HNi(depe)2]2+ in which shows a 2e− oxidation at ~0 V vs Cp2Fe/0 (Cp2Fe+0 used as the internal reference). The lack of current enhancement beyond the 2e− process at this [HNi(depe)2]2+ oxidation indicates no measurable catalytic activity (~0.4 s−1).

This result indicates that the pendant amines play an important role in the observed catalytic activity of Ni(P(2NR2)n)22+ complexes.

**DISCUSSION**

The development of inexpensive and energy-efficient electrocatalysts for formate oxidation is essential for the utilization of formic acid fuel cells (the anodic half-reaction involved is shown in eq 13). In this reaction, formic acid is oxidized by two electrons, with the release of CO2 and two protons. As with other multi-electron and multi-proton processes, the management of proton movement for catalysts of this type is of paramount importance. In previous work it has been demonstrated that pendant bases incorporated in the second coordination sphere of first-row transition metal complexes can serve as proton relays for catalytic oxidation and production of H2 and for O2 reduction.10,17 In addition, the hydride donor abilities of Ni(P(2NR2)n)22+ complexes are known to be in the range of 57–67 kcal/mol,30 and the hydride donor ability of formate anion in acetonitrile is 44 ± 2 kcal/mol.11 These data indicated that the formate anion should readily transfer a hydride to nickel to form CO2 and a nickel hydride, and that these hydrides are the same intermediates involved in the oxidation of H2 by Ni(P(Ph2N)n)2(CH3CN)2+ complexes. As a result, it was anticipated that these complexes would be catalysts for formate oxidation.

\[
\text{HCO}_2\text{H} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- \tag{13}
\]

A series of [Ni(P(2NR2)n)2(CH3CN)]2+ complexes were synthesized, characterized, and tested for electrocatalytic oxidation of formate. Systematic variation of the substituents at phosphorus and nitrogen allowed control over the hydride donor abilities and pKa values for the corresponding nickel hydrides, which correlate with the reduction potentials for the Ni(II/1) and Ni(1/0) couples, respectively (as shown in Figures 5 and 6). These correlations provide estimates of the hydride donor abilities and pKa values of the nickel hydrides from simple electrochemical potentials, which are more easily measured. The observed correlation is similar to the one previously reported for nickel bis-diphosphine complexes lacking a pendant base.30

Our initial expectation was that the catalytic rates of formate oxidation would parallel the hydride acceptor ability of the nickel catalyst, where in this series [Ni(P(Cy)2N(Ph3)O)2(CH3CN)]2+ is the best hydride acceptor and [Ni(P(Ph2N)n)2(CH3CN)]2+ is the worst. To test this hypothesis, we carried out a series of kinetic studies that showed that the TOF for each catalyst was dependent on formate concentrations below ~0.04 M (34 equiv NBu4HCO2•H2O) and that above this concentration the TOF became formate concentration independent. In addition, the onset of the catalytic current was observed near the Ni(II/1) couple, consistent with no reaction of nickel(0) or nickel(I) with formate, followed by immediate reaction after oxidation to nickel(II). This interpretation is supported by NMR spectroscopic studies that demonstrate the nickel(II) complexes [Ni(P(Ph2N)n)2(CH3CN)]2+, [Ni(P(Cy)2N(Ph3)O)2(CH3CN)]2+, [Ni(P(Cy)2N(Ph3)O)2(CH3CN)]2+, and [Ni(P(Cy)2N(Ph3)O)2(CH3CN)]2+, all react with formate to form the corresponding hydride complexes. However, the concentration range over which the catalytic rates are dependent on formate concentration is small. At concentrations above ~0.06 M formate (52 equiv of NBu4HCO2•H2O), where catalysis is most likely to be performed under practical conditions, the catalytic rate appears to become independent of formate concentration.

For the pendant base-containing complexes tested, [Ni(P(2NR2)n)2(CH3CN)]2+ is the best hydride acceptor and yet the least active catalyst. In fact, the catalytic rates correlate poorly with the hydride acceptor abilities of these complexes, as shown in Table 2. The failure of the catalytic rate to correlate with the hydride acceptor ability is inconsistent with a rate-determining step involving direct hydride transfer from formate to the nickel center. The observation that [Ni(depe)2]2+ shows no observable catalytic activity in the presence of excess formate (as shown in Figure 9) indicates that the presence of the pendant amine is essential for catalysis.

To probe the binding of formate with the nickel center, [Ni(P(Ph2N)n)2(CH3CN)]2+ was synthesized as previously reported and reacted with acetate to isolate a five-coordinate
nickel acetate complex. The nickel acetate complex is stable, whereas the formate complex is not. This instability of the formate complex is attributed to the possible net hydride transfer to liberate CO$_2$ and generate the nickel hydride. Higher concentrations of acetate led to almost complete displacement of the phosphine ligands from nickel. This favorable binding of acetate suggests that formate may also bind through oxygen to form a complex analogous to the structurally characterized acetate complex, $[\text{Ni}(\text{PPh}_3\text{N}^\text{H}_2)_2(\text{OAc})]^+$ (Figure 2), as shown in step B of the proposed catalytic cycle shown in Scheme 2.

For catalysts with a phenyl substituent at phosphorus, the catalytic activity correlates with the $pK_a$ of the conjugate acid ($\text{R}^0\text{NH}_3^+$) of the free amine used to make the corresponding $\text{P}^\text{R}_2\text{N}^\text{H}_2$ ligand (see the blue data and line in Figure 10). This correlation and the lack of catalytic activity for Ni(depe)$_2^{2+}$ suggest that the rate-determining step requires the presence of the pendant amine. In addition, the homoletic complexes with the bulkier cyclohexyl substituents at phosphorus exhibit lower TOFs than their phenyl analogues, indicating that increased steric bulk decreases catalytic activity. A mechanism that is consistent with all of the above observations is shown in Scheme 2. In this scheme, the oxidation of Ni(I) to Ni(II) is followed by a fast reaction with formate to generate $[\text{Ni}(\text{P}^\text{R}_2\text{N}^\text{H}_2)_2(\text{O}_2\text{CH})]^+$, with formate binding through one oxygen. The steric retardation of the catalytic rate for cyclohexyl vs phenyl substituents at phosphorus may be the result of this equilibrium step being shifted to disfavor formate association. As illustrated in steps C and D of Scheme 2, the oxygen-bound formate complex is thought to undergo a proton transfer from the carbon atom of formate to a pendant nitrogen atom with a concomitant transfer of two electrons to nickel and the release of CO$_2$. It is this heterolytic cleavage of formate that is proposed as the rate-limiting step in the overall catalytic cycle. Subsequent deprotonation and re-oxidation of the resulting nitrogen protonated Ni(0) complex appears to be fast and leads to the reformation of Ni(I), as in step E of Scheme 2.

Regardless of the precise mechanistic features, which are still under investigation, a comparison of the TOFs observed for formate oxidation by the nickel-based catalysts used in this study with those of catalytic thermal formate oxidations show that the rates observed here (from <1 to 16 s$^{-1}$) at room temperature are comparable to those of the best molecular catalysts for formate oxidation reported to date in the literature: ruthenium complexes with TOFs of $3600$ h$^{-1}$ (1 s$^{-1}$) at 40 °C and $18000$ h$^{-1}$ (5 s$^{-1}$) at 120 °C,$^7,39,40$ and iridium complexes with TOFs as high as $14000$ h$^{-1}$ (4 s$^{-1}$) at 90 °C.$^{41,42}$ In addition, the failure to observe any measurable catalytic currents for analogous nickel diphosphine complexes lacking pendant amines illustrates the importance of the resulting nitrogen protonated Ni(0) complex appearing to be fast and leads to the reformation of Ni(I), as in step E of Scheme 2.

Figure 10. Correlation of TOF for electrocatalytic formate oxidation with the $pK_a$ of the free primary ammonium ($\text{R}^0\text{NH}_3^+$) used to synthesize the corresponding $\text{P}^\text{R}_2\text{N}^\text{H}_2$ ligands for each Ni($\text{P}^\text{R}_2\text{N}^\text{H}_2)_2^-$ ($\text{CH}_3\text{CN})^{2+}$ complex. The data point labels in the figure refer to the $\text{R}$ and $\text{R}'$ substituents, respectively, and the trend line and corresponding equation are only for $\text{R} = \text{Ph}$.
of the pendant amines in catalytic reactions involving multi-electron and multi-proton processes.

**SUMMARY AND CONCLUSIONS**

Thermodynamic considerations of the hydride donor abilities of the formate ion and the hydride acceptor abilities of [Ni(diphosphine)₂]⁺⁺ complexes suggested that hydride transfer from formate to these nickel complexes should occur. In addition, pendant amines were incorporated in the diphosphine ligands to assist in proton transfer reactions that were expected to occur during the catalytic reactions. Using these guidelines, new [Ni(P⁵⁺,N⁵⁺)₂(CH₃CN)]²⁺ and previously reported complexes were prepared that allowed a systematic variation in the hydride acceptor ability of the metal and the basicity of the pendant amine. These [Ni(P⁵⁺,N⁵⁺)₂(CH₃CN)]²⁺ complexes were demonstrated to be catalysts for the electrocatalytic oxidation of formate, and mechanistic studies demonstrated that the pendant amine plays an important role in the rate-determining step that is thought to involve proton transfer from the formate carbon atom to a pendant amine of the ligand. The catalytic TOFs for these electrocatalysts are as high as any reported thermal formate/formic acid oxidation catalysts, and to our knowledge, the present catalysts are the first electrocatalysts to utilize a base metal, nickel, rather than the more typical platinum, palladium, or rhodium. Furthermore, these are the first homogeneous complexes reported for the electrocatalytic oxidation of formate.

**EXPERIMENTAL SECTION**

**Materials and Methods.** All chemicals were purchased from commercial sources and used as received unless otherwise specified. The complexes [Ni(P⁵⁺,N⁵⁺)₂(CH₃CN)]²⁺(BF₄)₂, [Ni(P⁵⁺,N⁵⁺)₂(CH₃CN)][BF₄]₂, [Ni(P⁵⁺,N⁵⁺)₂(CH₃CN)][BF₄]₂, and [Ni(P⁵⁺,N⁵⁺)₂(CH₃CN)][BF₄]₂ were prepared as previously described. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of nitrogen. Acetonitrile and tetrahydrofuran (THF) were sparged with pure nitrogen and dried over basic alumina with a custom dry solvent system. Acetonitrile and tetrahydrofuran (THF) were sparged with pure nitrogen and dried over basic alumina with a custom dry solvent system.

**X-ray Structural Analysis for [Ni(PPh₃)₂(CH₃CN)][BF₄]₂.** Kilgore et al. very recently reported the synthesis of [Ni(PPh₃)₂(CH₃CN)][BF₄]₂ using a similar procedure. For details of the synthesis used for the present work, see the Supporting Information. Single crystals suitable for X-ray diffraction were obtained after several days by layering a concentrated acetonitrile solution with diethyl ether at −35 °C. H and 31P NMR data matched the previously reported data. 1H NMR (CD₃CN, 200 MHz) δ [ppm]: 5.94 (s, 1H, H₂/N₃/C₄), 4.23 (s, 3H, methyl), 2.36 (s, 3H, methyl), 2.24 (s, 3H, methyl). 31P NMR δ [ppm]: 57.16 (s, 1P, Pₕₕₕₕₕₕ). The asymmetric unit contains one [Ni(PPh₃)₂(CH₃CN)][BF₄]₂ cation, one [BF₄]⁻ anion, and one molecule of Et₂O solvent located on general positions, yielding Z = 4 and Z = 1. No non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogens were treated as idealized contributions. The goodness-of-fit on F² was 1.022, with R₁ (wR₂) = 0.0429 (0.0889) for [H > 2σ(H)] and with largest difference peak and hole of 0.653 and −0.327 e/Å³.

**Synthesis of [Ni(PPh₃)₂(N₃/C₄)]²⁺(OAc)²⁺(OAc)⁻(CH₃CN)⁻(BF₄)⁺.** Kilgore et al. very recently reported the synthesis of [Ni(PPh₃)₂(N₃/C₄)]²⁺(OAc)⁺(CH₃CN⁻)⁻(BF₄)⁺ using a similar procedure. For details of the synthesis used for the present work, see the Supporting Information. Single crystals suitable for X-ray diffraction were obtained after several days by layering a concentrated acetonitrile solution with diethyl ether at −35 °C. H and 31P NMR data matched the previously reported data. 1H NMR (CD₃CN, 200 MHz) δ [ppm]: 5.94 (s, 1H, H₂/N₃/C₄), 4.23 (s, 3H, methyl), 2.36 (s, 3H, methyl), 2.24 (s, 3H, methyl). 31P NMR δ [ppm]: 57.16 (s, 1P, Pₕₕₕₕₕₕ). The asymmetric unit contains one [Ni(PPh₃)₂(N₃/C₄)]²⁺(OAc)⁺(CH₃CN⁻)⁻(BF₄)⁺ cation, one [BF₄]⁻ anion, and one molecule of Et₂O solvent located on general positions, yielding Z = 4 and Z = 1. No non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogens were treated as idealized contributions. The goodness-of-fit on F² was 1.022, with R₁ (wR₂) = 0.0429 (0.0889) for [H > 2σ(H)] and with largest difference peak and hole of 0.653 and −0.327 e/Å³.
Synthesis of [Ni(P\textsubscript{2}N\textsubscript{ph}\textsubscript{2})(P\textsubscript{2}N\textsubscript{ph})(CH\textsubscript{2}CN)](BF\textsubscript{4})\textsubscript{2}. Method a: [Ni(P\textsubscript{2}N\textsubscript{ph} \textsubscript{2}O苯酮\textsubscript{2})(CH\textsubscript{2}CN)](BF\textsubscript{4})\textsubscript{2} (63.2 mg, 48.5 μmol) was dissolved in acetonitrile in a glovebox, and this solution was added to a vial containing excess sodium formate. The red solution turned yellow over 20 min. The excess sodium formate was removed by filtration, and the product was isolated by removing the solvent under vacuum. The resulting solid was washed twice with pentane and dried under vacuum.

**Method b:** The hydride complex [Ni(P\textsubscript{2}N\textsubscript{ph} \textsubscript{2}O苯酮\textsubscript{2})(CH\textsubscript{2}CN)](BF\textsubscript{4})\textsubscript{2} (101.6 mg, 78 μmol) and 1 equiv of sodium trimethoxyborohydride (NaB(O\textsubscript{3}Me)\textsubscript{3}H) (10.0 mg, 78 μmol) instead of sodium formate. 31P\textsuperscript{1}H NMR (CD\textsubscript{3}CN, 20 °C, 400 MHz) δ ppm: 7.62–7.61 (m, 8H, C\textsubscript{arom} C\textsubscript{0}N), 7.46 (4H, J = 7.4 Hz, C\textsubscript{arom} H\textsubscript{N}), 7.26 (2H, J = 7.6 Hz, C\textsubscript{arom} H\textsubscript{P}), 7.03 (3d, 8H, J = 9 Hz, C\textsubscript{arom} N\textsubscript{D}), 6.89 (9H, J = 9.2 Hz, C\textsubscript{arom} H\textsubscript{N}), 3.89 (d, 8H, J = 12.8 Hz, P\textsubscript{Ph} CN\textsubscript{N}), 3.78 (s, 12H, P\textsubscript{Ph} CN\textsubscript{N}), 3.42 (d, 8H, J = 13.2 Hz, P\textsubscript{Ph} CN\textsubscript{N}), –8.05 (quintet, 1H, J = 30.3 Hz, Ni-H). 31P\textsuperscript{1}H NMR (CD\textsubscript{3}Cl\textsubscript{2}, 20 °C, 162 MHz) δ ppm: 15.1 (s).

Synthesis of [Ni(P\textsubscript{2}N\textsubscript{ph} \textsubscript{2}O苯酮\textsubscript{2})(OAc)](BF\textsubscript{4})\textsubscript{2}·EtO\textsubscript{2}O. A solution of tetrabutyllammonium acetate (14.5 mg, 0.049 mmol) in benzyl alcohol was added to a solution of [Ni(P\textsubscript{2}N\textsubscript{ph} \textsubscript{2}O苯酮\textsubscript{2})(CH\textsubscript{2}CN)](BF\textsubscript{4})\textsubscript{2} (60 mg, 0.048 mmol) in benzyl alcohol. The solution immediately changed from red to dark purple. Vapor diffusion of diethyl ether into the crude reaction mixture at room temperature afforded dark red crystals suitable for X-ray crystallography; yield, 38% (21 mg, 0.018 mmol).

Elemental analysis: C/H/N calcd for NiC\textsubscript{21}H\textsubscript{20}N\textsubscript{P}\textsubscript{2}B\textsubscript{2}F\textsubscript{8}: 57.74/6.93/5.80; found, 57.78/6.92/6.11.

Synthesis of [HNI(P\textsubscript{2}N\textsubscript{ph} \textsubscript{2}O苯酮\textsubscript{2})\textsubscript{2}](BF\textsubscript{4})\textsubscript{2}. Method a: [Ni(P\textsubscript{2}N\textsubscript{ph} \textsubscript{2}O苯酮\textsubscript{2})(CH\textsubscript{2}CN)](BF\textsubscript{4})\textsubscript{2} (63.2 mg, 48.5 μmol) was dissolved in acetonitrile in a glovebox, and this solution was added to a vial containing excess sodium formate. The red solution turned yellow over 20 min. The excess sodium formate was removed by filtration, and the product was isolated by removing the solvent under vacuum. The resulting solid was washed twice with pentane and dried under vacuum.

**Method b:** The hydride complex [HNI(P\textsubscript{2}N\textsubscript{ph} \textsubscript{2}O苯酮\textsubscript{2})(CH\textsubscript{2}CN)](BF\textsubscript{4})\textsubscript{2} (101.6 mg, 78 μmol) and 1 equiv of sodium trimethoxyborohydride (NaB(O\textsubscript{3}Me)\textsubscript{3}H) (10.0 mg, 78 μmol) instead of sodium formate. 31P\textsuperscript{1}H NMR (CD\textsubscript{3}CN, 20 °C, 400 MHz) δ ppm: 7.62–7.61 (m, 8H, C\textsubscript{arom} C\textsubscript{0}N), 7.46 (4H, J = 7.4 Hz, C\textsubscript{arom} H\textsubscript{N}), 7.26 (2H, J = 7.6 Hz, C\textsubscript{arom} H\textsubscript{P}), 7.03 (3d, 8H, J = 9 Hz, C\textsubscript{arom} N\textsubscript{D}), 6.89 (9H, J = 9.2 Hz, C\textsubscript{arom} H\textsubscript{N}), 3.89 (d, 8H, J = 12.8 Hz, P\textsubscript{Ph} CN\textsubscript{N}), 3.78 (s, 12H, P\textsubscript{Ph} CN\textsubscript{N}), 3.42 (d, 8H, J = 13.2 Hz, P\textsubscript{Ph} CN\textsubscript{N}), –8.05 (quintet, 1H, J = 30.3 Hz, Ni-H). 31P\textsuperscript{1}H NMR (CD\textsubscript{3}Cl\textsubscript{2}, 20 °C, 162 MHz) δ ppm: 15.1 (s).
8.4 H, N(CH$_2$CH$_3$CH$_2$CH$_3$)$_4$), 1.70 (m, 8.4 H, N(CH$_2$CH$_3$CH$_2$CH$_3$)$_4$), 1.43 ( sextet, 8.2 H, J$_{HH}$ = 6.0 Hz, N(CH$_2$CH$_3$CH$_2$CH$_3$)$_4$), 1.04 (t, 12.0 H, J$_{H}$ = 6.0 Hz, N(CH$_2$CH$_3$CH$_2$CH$_3$)$_4$). Elemental analysis: C/H/N calcd for C$_{18}$H$_{33}$N$_6$O$_4$C, 64.82; H, 11.79; N, 4.20; found, C, 64.22; H, 11.53; N, 4.29.

General Procedure for Hydricity Determination by Heterolytic H$_2$ Cleavage: [Ni($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$]$_2$(CH$_3$CN) ($\text{BF}_4$)$_2$. In a typical experiment, [Ni($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$]$_2$(CH$_3$CN) ($\text{BF}_4$)$_2$ (15 mg, 0.0012 mmol) and p-anisidine (60 mg, 0.049 mmol) were dissolved in 0.5 mL of dry acetonitrile-d$_3$ and transferred to an NMR tube equipped with a septum. Hydrogen gas was bubbled through the solution for 20 min. After an additional 10 min, the sample was analyzed by $^1$H and $^{31}$P NMR spectroscopy. The weighted averages of the aromatic proton chemical shifts of p-anisidine/p-anisidine oxide were used to determine the ratio of acid to base for the reference, and the ratio of [Ni($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$]$_2$(CH$_3$CN) ($\text{BF}_4$)$_2$ to [HNi($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$]$_2$ was determined by $^{19}$F NMR spectroscopy. These ratios were then used to determine the equilibrium constant. The samples were run again after 24 h to ensure equilibration. For [Ni($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$]$_2$(CH$_3$CN) ($\text{BF}_4$)$_2$, p-bromanilone was used as the base, and for [Ni($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$](CH$_3$CN) ($\text{BF}_4$)$_2$, aniline was used as the base.

Reactivity toward NBu$_4$HCO$_2$·HCO$_2$H: General Procedure for NMR Titration. In a glovebox, a solution of [Ni($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$]$_2$(CH$_3$CN) ($\text{BF}_4$)$_2$ (5.0 mg, 0.0038 mmol) in 0.1 mL of acetonitrile was prepared by dissolving 331 mg (0.99 mmol) in a second 4 mL vial. The NMR tube was shaken thoroughly, and $^1$H and $^{31}$P NMR spectra are shown in the Supporting Information. For NBu$_4$HCO$_2$·HCO$_2$H solution, the acid concentration of 1.0 M was used to determine the ratio of acid to base that was used to determine the order with respect to catalyst, as shown in Figure 8. 

Bulk Electrolysis. A multineck conical flask was used for the bulk electrolysis experiment. A stainless steel mount was attached to one neck, and to this mount a cylinder of reticulated vitreous carbon was attached as the working electrode. Two of the other necks of the flask were fitted with glass tubes terminating with 7 mm Vycor frits (Princeton Applied Research). One tube was used for the reference electrode and the other tube for the counter electrode. Both were filled with electrolyte solutions (0.2 M NBu$_4$OTf in benzonitrile), and the reference cell contained a silver chloride-coated silver wire, whereas a Nichrome wire was used in the countercell. With the fittings attached, the cell had a total volume of 328 mL. The cell was filled with stock solutions of catalyst and NBu$_4$HCO$_2$·HCO$_2$H to give 20 mL of a solution that was 0.76 mM in [Ni($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$]$_2$(CH$_3$CN) ($\text{BF}_4$)$_2$, 0.086 M in NBu$_4$HCO$_2$·HCO$_2$H, and 0.2 M in NBu$_4$OTf. Controlled-potential coulometry was performed at ~100 mV positive of the peak for the catalytic current. After 16.3 C of charge had passed, samples of the gas in the headspace of the flask were removed via a gastight syringe and analyzed by gas chromatography. The percentages of N$_2$ and CO$_2$ in the headspace were determined through calibration against gas standards of a known composition. From these data, 5.3 mol of CO$_2$ per mole of catalyst was produced, a current efficiency of 93 ± 5% was calculated for CO$_2$ production, and no H$_2$ was observed.

ASSOCIATED CONTENT

Supporting Information. Crystallographic structure for NBu$_4$HCO$_2$·HCO$_2$H and crystallographic data and CIF files for NBu$_4$HCO$_2$·HCO$_2$H, [Ni($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$]$_2$(CH$_3$CN)] ($\text{BF}_4$)$_2$, [Ni($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$] ($\text{BF}_4$)$_2$, [Ni($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$](CH$_3$CN) ($\text{BF}_4$)$_2$, [Ni($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$] ($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$(CH$_3$CN) ($\text{BF}_4$)$_2$, and [Ni($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$] ($\text{P}^{(\text{X})}_2\text{N}^{\text{PhMe}}$)$_2$(CH$_3$CN) ($\text{BF}_4$)$_2$. Crystallographic data and CIF files are available from the Cambridge Crystallographic Data Center through the Open Database, http://www.ccdc.cam.ac.uk.

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ACKNOWLEDGMENT

Funding by Deutsche Forschungsgemeinschaft (J.S.), the NSF GRFP (C.S.), and by the Helios Solar Energy Research Center, which is supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, is gratefully acknowledged. B.R.G., J.C.L., A.M.A., and D.L.D. were supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Biosciences and Geosciences. J.A.S.R., M.L.H., U.J.K., and J.Y.Y. were supported as part of the Center for Molecular Electrocatlysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under FWP S5073. Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy.
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