Pages: 9



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A Ni^{II}–Bis(diphosphine)–Hydride Complex Containing Proton Relays – Structural Characterization and Electrocatalytic Studies

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The synthesis of the 1,5-diphenyl-3,7-diisopropyl-1,5-diaza-3,7-diphosphacyclooctane ligand, $P^{iPr}_2N^{Ph}_2$, is reported. Two equivalents of the ligand react with $[Ni(CH_3CN)_6](BF_4)_2$ to form the bis(diphosphine)–Ni^{II} complex $[Ni(P^{iPr}_2N^{Ph}_2)_2]$ - $(BF_4)_2$, which acts as a proton reduction electrocatalyst. In addition to $[Ni(P^{iPr}_2N^{Ph}_2)_2]^{2+}$, we report the synthesis and structural characterization of the Ni⁰ complex $Ni(P^{iPr}_2N^{Ph}_2)_2$

Introduction

The production and oxidation of H_2 can be used as a reversible cycle to store electricity. Widespread use of electrocatalytic cells for the storage of electrical energy from renewable sources is currently limited by the scarcity and high cost of platinum, the predominantly used catalyst. As a result, there is much interest in the development of both hetero- and homogeneous catalysts based on earth-abundant metals to replace platinum as the primary catalyst in fuel cells.^[1-3] Efforts in our group have focused on the rational design of earth-abundant transition metal complexes for their use as molecular electrocatalysts for the production and use of chemical fuels.^[4] For the production and oxidation of H₂, we have used a modular, energy-based approach to design catalysts based on the functional components of the [FeFe]-hydrogenase enzymes.^[5] Namely, the first coordination sphere around the metal center is primarily used to tune the redox potential, hydride donor ability, and pK_a of the metal center. The second coordination sphere, those atoms attached to the ligand structure that do not directly interact with the metal center, is used to relay protons between the surrounding solvent matrix and the metal. Recent work pioneered by Shaw and co-workers has extended the design of molecular catalysts to include the use of the outer coordination sphere to influence redox po-

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and the Ni^{II}-hydride complex [HNi(P^{iPr}₂N^{Ph}₂)₂]BF₄. The [HNi(P^{iPr}₂N^{Ph}₂)₂]BF₄ complex represents the first Ni^{II}-hydride in the [Ni(P^R₂N^{R'}₂)₂]²⁺ family of compounds to be structurally characterized. In addition to the experimental data, the mechanism of electrocatalysis facilitated by [Ni-(P^{iPr}₂N^{Ph}₂)₂]²⁺ is analyzed by using linear free energy relationships recently established for the [Ni(P^R₂N^{R'}₂)₂]²⁺ family.

tentials and to control the movement of protons over longer distances.^[6–8] The rational design of coordination spheres around metal complexes, from the primary coordination sphere to the outer coordination sphere, illustrates one aspect of the progress made from Werner's original work to modern coordination chemistry 100 years later.

A major focus of our group has been the development of Ni^{II} catalysts containing 1,5-diaza-3,7-diphosphacyclooctane (PR2NR'2) ligands.^[5,9-12] These ligands are suitable for substitution at both the phosphorus (R) and nitrogen (\mathbf{R}') atoms to aid in tuning the electronic and steric properties of their metal complexes. Formation of Ni^{II} complexes with P^R₂N^{R'}₂ ligands results in bis(diphosphine) complexes, $\{[Ni(P_2^R N^{R'}_2)_2]^{2+}\}$, with N atoms in proximity, but not bound to the Ni center. The positioned pendant amines are suitable for relaying protons to and from the metal center to exogenous acids and bases in solution.^[13,14] The ability to tune the free energy of H₂ addition ($\Delta G^{\circ}_{H_2}$) in the $[Ni(P_2^R N_2^{R'})_2]^{2+}$ family of compounds has resulted in proton reduction, H₂ oxidation, and bidirectional catalysts.^[5] The mechanism of electrocatalysis for the production and oxidation of H₂ facilitated by the $[Ni(P^{R}_{2}N^{R'}_{2})_{2}]^{2+}$ complexes has been extensively studied and consists of a series of electron transfer and inter- and intramolecular proton transfer steps.^[13,14] Recent computational work from our group has established the linear free energy relationships between the pK_a of the pendant amine, Ni(II/I), and (I/0) couples that predict the energy landscape of the catalytic cycle.[15] These relationships enable a thorough mechanistic analysis of catalysis by complexes of these types.

In this work we report the synthesis of a new $P_2^R N_2^{R'_2}$ ligand, 1,5-diphenyl-3,7-diisopropyl-1,5-diaza-3,7-diphos-

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phacyclooctane ($P^{iPr}_2N^{Ph}_2$), and its Ni^{II} complex. We also report the synthesis and structural characterization of the Ni^{II}-hydride complex, [HNi($P^{iPr}_2N^{Ph}_2$)₂]BF₄. Additionally, we report the electrochemical properties of the complex and analyze the mechanism for H₂ production by using computationally derived free energy landscapes.

Results

Synthesis and Structural Characterization

The $P_2^{IPr_2}N^{Ph_2}$ ligand was synthesized through in situ generation of $iPrPH_2$ and bis(hydroxymethyl)isopropylphosphine, $[iPrP(CH_2OH)_2]$, followed by condensation with one equivalent of aniline (PhNH₂) to form the cyclic diazadiphosphine (Scheme 1). The ligand was isolated as a white solid in more than 40% yield and fully characterized by NMR spectroscopy and elemental analysis. Additional characterization was performed by X-ray analysis of a single crystal of Ni($P_2^{IPr_2}N^{Ph_2}$)Cl₂, obtained from the reaction of $P_2^{IPr_2}N^{Ph_2}$ and NiCl₂ as reported in the Supporting Information (Figure S1).



Scheme 1. Synthesis of P^{*i*Pr}₂N^{Ph}₂.

Formation of the Ni^{II} complex, $[Ni(P^{iPr}_2N^{Ph}_2)_2](BF_4)_2$, was achieved by reaction of two equivalents of $P^{iPr}_2N^{Ph}_2$ with $[Ni(CH_3CN)_6](BF_4)_2$ in CH₃CN (Scheme 2). The Ni^{II} complex was isolated as a crystalline red solid in 82% yield and characterized by NMR spectroscopy and mass spectrometry. Formation of the Ni⁰ complex, Ni($P^{iPr}_2N^{Ph}_2)_2$, was accomplished through reduction of $[Ni(P^{iPr}_2N^{Ph}_2)_2]$ -(BF₄)₂ with KC₈ in THF. The complex was isolated as a yellow solid in 90% yield (Scheme 2). The Ni($P^{iPr}_2N^{Ph}_2)_2$ complex was characterized by ³¹P{¹H} and ¹H NMR spectroscopy and by single-crystal X-ray diffraction analysis (Figure 1).

In addition to the Ni^{II} and Ni⁰ complexes described above, the Ni^{II}-hydride, [HNi($P^{iPr_2}N^{Ph_2}$)₂]BF₄, was also synthesized through the reaction of [Ni($P^{iPr_2}N^{Ph_2}$)₂](BF₄)₂ with Na[HB(OMe)₃] (Scheme 2). The hydride was isolated in more than 85% yield and identified through its ³¹P{¹H} and characteristic ¹H NMR spectra (Figure S2) that showed the hydride resonance as a quintet (² $J_{PH} = 18$ Hz) at -11.2 ppm. In addition to the spectroscopic data, singlecrystal X-ray analysis of [HNi($P^{iPr_2}N^{Ph_2}$)₂]BF₄ was performed (Figure 1). Formation of [HNi($P^{iPr_2}N^{Ph_2}$)₂]⁺ was also accomplished through protonation of the Ni⁰ complex



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Scheme 2. Synthesis of $[Ni(P'^{Pr}{}_2N^{Ph}{}_2)_2](BF_4)_2,\ Ni(P'^{Pr}{}_2N^{Ph}{}_2)_2]$ and $[HNi(P'^{Pr}{}_2N^{Ph}{}_2)_2]BF_4.$



Figure 1. Thermal ellipsoid plots rendered at 50% probability of the structures of $Ni(P^{iPr}_2N^{Ph}_2)_2$ (top) and $[HNi(P^{iPr}_2N^{Ph}_2)_2]$ -BF₄ (bottom). Hydrogen atoms and the BF₄⁻ anion in [HNi-(P^{iPr}_2N^{Ph}_2)_2]BF₄ have been omitted for clarity.

Date: 23-06-14 14:06:20

Ni($P^{iPr_2}N^{Ph_2}$)₂ with one equivalent of [(DMF)H]⁺ or by reaction of [Ni($P^{iPr_2}N^{Ph_2}$)₂]²⁺ with H₂ and a strong base such as *p*-anisidine (see the Supporting Information for complete

details). Compounds Ni(P^{iPr}₂N^{Ph}₂)₂ and [HNi(P^{iPr}₂N^{Ph}₂)₂]BF₄ were characterized by single-crystal X-ray crystallography, and the structures are presented in Figure 1. Table 1 contains selected average bond lengths and angles for these compounds. The structures of the complexes show a tetrahedral coordination environment around the Ni center with a dihedral angle between the planes formed from the P1-Ni-P2 and P3-Ni-P4 atoms of 89.0° for Ni(P^{iPr}₂N^{Ph}₂)₂ and 88.0° for $[HNi(P^{iPr}_2N^{Ph}_2)_2]^+$. In both structures, each phosphine ligand forms two six-membered chelate rings; the metal center has a boat conformation in one ring and a chair conformation in the other. In Ni(P^{iPr}₂N^{Ph}₂)₂, the average Ni····N_{boat} nonbonding distance is observed to be 3.417 Å, and the Ni···N_{chair} nonbonding distance averages 3.766 Å. The average Ni···N_{boat} nonbonding distance in $[HNi(P^{iPr}_2N^{Ph}_2)_2]^+$ is observed to be 3.365 Å, and the Ni···N_{chair} nonbonding distance averages 3.822 Å. The average Ni-P bond length increases by 0.078 Å from Ni- $(P^{iPr}_2N^{Ph}_2)_2$ to $[HNi(P^{iPr}_2N^{Ph}_2)_2]^+$. The average P-Ni-P chelate bond angle for $Ni(P^{iPr}_2N^{Ph}_2)_2$ is 85.7°, and that for $[HNi(P^{iPr}_2N^{Ph}_2)_2]^+$ is 83.6°. In $[HNi(P^{iPr}_2N^{Ph}_2)_2]^+$, the Ni-H hydrogen atom was not located in the difference map; however, after collection of the X-ray data, the single crystal was dissolved in CD₃CN and the characteristic peaks of Ni-hydride were observed in the ³¹P{¹H} and ¹H NMR spectra. Complete crystal data and bond lengths and angles are presented in the Supporting Information (Tables S1-S7).

Table 1. Selected average bond angles (°) and lengths (Å) for Ni- $(P'^{\rm Pr}_2N^{\rm Ph}_2)_2$ and $[HNi(P'^{\rm Pr}_2N^{\rm Ph}_2)_2]^+.$

	$Ni(P^{iPr}_2N^{Ph}_2)_2$	$[HNi(P^{iPr}_2N^{Ph}_2)_2]^+$
P-Ni-P bite angle	85.72	83.61
Dihedral angle between		
P-Ni-P ligand planes	89.02	88.90
Ni–P distance	2.135	2.213
Ni…N _{boat} distance	3.417	3.365
Ni…N _{chair} distance	3.766	3.822

Electrochemical Studies

The cyclic voltammogram of $[Ni(P^{iP_2}N^{Ph_2})_2]^{2+}$ shows two reversible redox couples with $E_{1/2}$ values of -0.63 V (Ni^{II/I} couple) and -1.06 V (Ni^{I/0} couple) vs. the ferrocenium/ferrocene (Cp₂Fe^{+/0}) couple (Figure 2). A plot of the peak current (i_p) vs. the square root of the scan rate shows a linear correlation, which implies diffusion-controlled electrochemical processes. The difference between the potential of cathodic and anodic peaks (ΔE_p) at a scan rate of 0.1 V s⁻¹ is measured to be 65 mV, where the ΔE_p of Cp₂Fe^{+/0} is 68 mV, which indicates a one-electron process for the two couples.



FULL PAPER



Figure 2. Cyclic voltammogram of $1.0 \text{ mm} [\text{Ni}(\text{P}^{i\text{Pr}_2}\text{N}^{\text{Ph}_2})_2]^{2+}$ in 0.10 m [*n*Bu₄N][PF₆]/CH₃CN. Conditions: 1 mm glassy carbon working electrode; scan rate 0.10 V s⁻¹ at 25 °C.

The cyclic voltammogram of $[\text{HNi}(\text{P}^{i\text{P}_2}\text{N}^{\text{Ph}_2})_2]^+$ shows an irreversible oxidation peak at $E_p = -0.28$ V at a scan rate of 0.1 V s⁻¹ (Figure 3). The wave remains irreversible at all scan rates that were studied (0.5–10 V s⁻¹, Figure S3). The peak potential for this oxidation is observed to shift in the positive direction as a function of scan rate, which is indicative of a kinetic potential shift caused by a rapidly following chemical step. This data is consistent with the previously reported irreversible oxidation of $[\text{HNi}(\text{P}^{i\text{Bu}}_2\text{N}^{\text{R}}_2)_2]^+$ (R = Bn, Ph), attributed to rapid intramolecular proton movement of the hydride to the pendant amine, followed by intermolecular deprotonation of the oxidized species.^[16]



Figure 3. Cyclic voltammogram of $1.0 \text{ mM} [\text{HNi}(\text{P}^{iP_2}\text{N}^{\text{Ph}_2})_2]^+$ in $0.10 \text{ M} [n\text{Bu}_4\text{N}][\text{PF}_6]/\text{CH}_3\text{CN}$. Conditions: 1 mm glassy carbon working electrode; scan rate 0.10 V s^{-1} at 25 °C.

Electrocatalysis

When electrochemical measurements on $[Ni(P'^{Pr}_{2}-N^{Ph}_{2})_{2}]^{2+}$ were carried out in the presence of acid, an in-

Pages: 9

Date: 23-06-14 14:06:20

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crease in the cathodic current was observed (Figure 4). Prior to the addition of acid, enough H₂O was added to result in a 1.1 M H₂O concentration in CH₃CN, which was previously shown to increase the rate of catalysis. In the presence of 1.0 mM $[Ni(P^{iPr}_2N^{Ph}_2)_2]^{2+}$ and 5.4 mM [(DMF)H]OTf ($pK_a = 6.1$ in MeCN), an increase in the cathodic current was observed with a peak potential at -0.67 V (Figure 4, top), indicative of proton reduction to form H₂. Electrochemical measurements carried out in the presence of 1.0 mM $[Ni(P^{iPr}_2N^{Ph}_2)_2]^{2+}$ and 5.4 mM HOTf $(pK_a = 2.6 \text{ in})^{2+1}$ MeCN) resulted in an increase in the cathodic current with a peak potential at -0.60 V (Figure 4, bottom).^[17] In the presence of either acid, a second wave in the cyclic voltammogram near -1.2 V is observed. Over time the wave at -1.2 V increases with a corresponding decrease in the catalytic wave, which indicates decomposition of the complex (Figure S4). The decomposition of $[Ni(P^{iPr}_2N^{Ph}_2)_2]^{2+}$ in the presence of acid was confirmed by ³¹P{¹H} NMR spec-



troscopy (Figure S5). Rapid catalyst decomposition in the presence of acid prevented us from obtaining quantitative rate data for the catalytic process.

Discussion

Synthesis and Structural Characterization

Due to the volatility of *i*PrPH₂ required in the synthesis of the $P^{iPr}_2N^{Ph}_2$ ligand, the primary phosphine was generated in situ by reaction of K[P(TMS)₂] with *i*PrCl to form *i*PrP(TMS)₂ followed by protonation with EtOH, which was used as the solvent in the next step.^[18] Reaction of *i*PrPH₂ with paraformaldehyde results in formation of *i*PrP(CH₂OH)₂, which is then treated with PhNH₂ to form the $P^{iPr}_2N^{Ph}_2$ ligand. The ligand was obtained in an overall yield of 42% as a white crystalline solid that was characterized by heteronuclear NMR spectroscopy and elemental analysis.

Formation of [Ni(P^{iPr}2N^{Ph}2)2](BF4)2 was achieved through the reaction of [Ni(CH₃CN)₆](BF₄)₂ with two equivalents of $P'^{Pr}_2 N^{Ph}_2$, as is common in the synthesis of the $[Ni(P_2^R N_2^{R'})_2]^{2+}$ family of compounds. In addition to the Ni^{II} complex, the Ni⁰ and the Ni^{II}-hydride complex were also obtained. The Ni^{II}-hydride, [HNi(P^{*i*Pr}₂N^{Ph}₂)₂]⁺, represents the first isolated and structurally characterized hydride in the $[Ni(P_2^R N_2^{R'})_2]^{2+}$ family of compounds. Structural data for the Ni⁰ and Ni^{II}-hydride complexes were obtained by single-crystal X-ray analysis. Both structures show similar distorted tetrahedral geometry around the Ni centers, a notable difference being in the average Ni-P bond lengths. The average Ni-P bonds in the [HNi- $(P^{iPr}_2 N^{Ph}_2)_2]^+$ structure are 0.078 Å longer than those observed in Ni(P^{iPr}₂N^{Ph}₂)₂. The increase in Ni–P bond length is inconsistent with the expected trend based on a more electron-poor Ni^{II}-hydride metal center than Ni⁰. Additionally, the Ni Nboat nonbonding distance of the pendant amine in the boat confirmation of [HNi(P^{*i*Pr}₂N^{Ph}₂)₂]⁺ is shorter than that in $Ni(P^{iPr}_2N^{Ph}_2)_2$, where the Ni···N_{chair} nonbonding distance is longer. The increase in Ni-P bond length and changes in the Ni…N nonbonding distances are consistent with the interaction of the nitrogen atom of the pendant amine in the boat confirmation with the hydride ligand on the metal center (Figure 5). The interaction between the pendant amine and the hydride ligand has been observed previously in spectroscopic and computational



Figure 4. Cyclic voltammogram of $1.0 \text{ mm} [\text{Ni}(\text{P}^{/\text{Pr}}_2\text{N}^{\text{Ph}}_2)_2]^{2+}$ in 0.10 m [*n*Bu₄N][PF₆]/CH₃CN with 1.1 m H₂O before and after addition of [(DMF)H]⁺ (top) and HOTf (bottom). Conditions: 1 mm glassy carbon working electrode; scan rate 0.10 V s⁻¹ at 25 °C.

Figure 5. Illustration of the ligand distortion observed in the crystal structure of $[HNi(P^{iPr}_2N^{Ph}_2)_2]^+$ relative to that of Ni- $(P^{iPr}_2N^{Ph}_2)_2$. Only a single $P^{iPr}_2N^{Ph}_2$ ligand is shown, and the substituents on the P and N atoms are omitted for clarity.

data of other $[HNi(P^{R}_{2}N^{R'}_{2})_{2}]^{+}$ complexes.^[13] The structural comparison of $Ni(P^{iPr}_{2}N^{Ph}_{2})_{2}$ and $[HNi(P^{iPr}_{2}N^{Ph}_{2})_{2}]^{+}$ further supports this interaction.

Electrocatalytic Pathways

The free energy of H₂ addition ($\Delta G^{\circ}_{H_2}$) for [Ni(P^R₂- $N^{R'}_{2}_{2}_{2}^{2+}$ complexes can be calculated as the sum of the hydride donor ability of $[HNi(P^{iPr}_2N^{Ph}_2)_2]^+$, the pK_a of $[HNi(P^{iPr}_2N^{Ph}_2 H)(P^{iPr}_2N^{Ph}_2)]^{2+}$, and the heterolytic bond cleavage energy of H₂ in CH₃CN (Figure 6). By using the reported free energy relationships, the hydride donor ability of $[HNi(P^{iPr}_2N^{Ph}_2)_2]^+$ was found to be 63.8 kcal mol⁻¹ and the p K_a of $[HNi(P^{iPr}_2N^{Ph}_2H)(P^{iPr}_2N^{Ph}_2)]^{2+}$ was found to be 6.78.^[15] These numbers are consistent with the experimentally determined values for other [Ni(P^R₂N^{Ph}₂)₂]²⁺ complexes (R = Ph, alkyl). Using these values, the $\Delta G^{\circ}_{H_{2}}$ for $[Ni(P^{iPr}_2N^{Ph}_2)_2]^{2+}$ was calculated to be 2.95 kcal mol⁻¹ (Figure 6). Although the poor hydride donor ability of [HNi- $(P^{iPr}_2 N^{Ph}_2)_2$ biases the catalyst towards H₂ oxidation, the low pK_a of the N–Ph group provides compensation, which results in a positive $\Delta G^{\circ}_{H_2}$ and a catalyst biased for H₂ production.^[5]

As shown in Figure 4, $[Ni(P^{iPr}_2N^{Ph}_2)_2]^{2+}$ can function as an electrocatalyst for the production of H₂ as previously observed for other $[Ni(P^R_2N^{Ph}_2)_2]^{2+}$ (R = Ph, alkyl) compounds. The mechanism for H₂ production by $[Ni(P^R_2N^{R'}_2)_2]^{2+}$ complexes has been well studied and consists of alternating electron (E) and proton transfer (C) steps.^[19–21] As shown in the mechanism outlined in Figure 7, there are two possible pathways for catalysis; the most direct pathway (black arrows) proceeds through electron and protonation transfer steps to form endo-protonated isomers, leading to H_2 elimination. A second pathway (gray arrows) proceeds through proton-transfer steps that result in exo-protonated isomers, requiring isomerization steps before H_2 elimination can occur.

A recent publication from our laboratories highlights a set of linear free energy relationships that can be used to calculate free energy landscapes for the catalytic pathways.^[15] Analysis of the thermodynamic properties of [Ni- $(P^{iPr}_2N^{Ph}_2)_2$]²⁺ complexes and the endo pathway (Figure 7, black arrows) for using either [(DMF)H]⁺ or HOTf are discussed below (see Figures S6 and S7 in the Supporting Information for the exo pathway).

The free energy landscape for the ECEC endo pathway (Figure 7, black arrows) is illustrated in Figure 8. Catalysis can proceed through different sequences of proton and electron transfer steps (i.e. EECC, CCEE, ECCE, etc.); however, previous experimental and computational results indicate that an ECEC mechanism is the likely pathway.^[12,14,20,21] Although quantitative rate data for electrocatalysis in this system were not obtained, qualitative analysis of the cyclic voltammograms in Figure 4 indicates that catalysis with HOTf is significantly faster (greater than or equal to five times current enhancement) than that observed with [(DMF)H]⁺ under identical conditions. Analysis of the free energy landscapes illustrates the driving force for H_2 production with HOTf (Figure 8, red) to be much greater than that with [(DMF)H]⁺ (Figure 8, blue). As expected, the major difference between the two free energy landscapes occurs in the protonation steps. Specifically, the

$$[\text{Ni}(\text{P}^{i\text{Pr}}_{2}\text{N}^{\text{Ph}}_{2})_{2}]^{2^{+}} + \text{H}^{-} \iff [\text{HNi}(\text{P}^{i\text{Pr}}_{2}\text{N}^{\text{Ph}}_{2})_{2})]^{+} -\Delta G^{\circ}_{\text{H}^{-}} = -63.8 \text{ kcal/mol}$$

$$[\text{HNi}(\text{P}^{i\text{Pr}}_{2}\text{N}^{\text{Ph}}_{2})_{2})]^{+} + \text{H}^{+} \iff [\text{HNi}(\text{P}^{i\text{Pr}}_{2}\text{N}^{\text{Ph}}_{2}\text{H})(\text{P}^{i\text{Pr}}_{2}\text{N}^{\text{Ph}}_{2})]^{2^{+}} \Delta G^{\circ} = -1.364 \text{ x pK}_{a} = -9.25 \text{ kcal/mol}$$

$$H_{2} \iff H^{-} + H^{+} \Delta G^{\circ} = 76.0 \text{ kcal/mol}$$

$$[\text{Ni}(\text{P}^{i\text{Pr}}_{2}\text{N}^{\text{Ph}}_{2})_{2}]^{2^{+}} + H_{2} \iff [\text{HNi}(\text{P}^{i\text{Pr}}_{2}\text{N}^{\text{Ph}}_{2}\text{H})(\text{P}^{i\text{Pr}}_{2}\text{N}^{\text{Ph}}_{2})]^{2^{+}} \Delta G^{\circ}_{\text{H}_{2}} = 2.95 \text{ kcal/mol}$$

Figure 6. Calculation of the free energy of H₂ addition $(\Delta G^{\circ}_{H_2})$ to $[Ni(P^{iPr}_2N^{Ph}_2)_2]^{2+}$ in CH₃CN.



Figure 7. Proposed mechanism for catalysis facilitated by [Ni(P^{*i*Pr}₂N^{Ph}₂)₂]²⁺.

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Date: 23-06-14 14:06:20

Pages: 9



 $+H^+$

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Ni(II) proton/hydride -19.18 $Ni(II) + H_2$ -20 Figure 8. Free energy landscape for electrocatalytic production of H₂ by $[Ni(P^{iPr}_2N^{Ph}_2)_2]^{2+}$. Free energy values are calculated at 1 atm H₂,

an applied potential of 0.63 V, and [(DMF)H]+ (blue) and HOTf (red) as the protonating acid.

protonation steps with HOTf are significantly more favored than those with $[(DMF)H]^+$ because of the difference in the pK_a values of the two acids. In addition to the increase in rate when using HOTf, a kinetic potential shift in the catalytic wave of about 70 mV is observed, which indicates a fast following chemical reaction after the electron transfer event. When the free energy landscapes of the two acids are compared, the first protonation step in the case of [(DMF) H]⁺ is uphill by 1.63 kcalmol⁻¹, whereas the same step with HOTf is -3.42 kcalmol⁻¹ downhill. This is one possible source of the shift observed in the catalytic wave when using HOTf as the protonating acid. Regardless of the precise mechanism, protonation by the stronger acid, HOTf, of catalytic intermediates will be more favored than that by a weaker acid like [(DMF)H]⁺, which has been demonstrated both experimentally and computationally.

Conclusions

Synthesis of $[Ni(P^{iPr}_2N^{Ph}_2)_2]^{2+}$ has enabled the isolation and first structural characterization of Ni^{II}-hydride in the $[Ni(P_2^R N_2^{R'})_2]^{2+}$ family of catalysts. Structural analysis of $[HNi(P^{iPr}_2N^{Ph}_2)_2]^+$ shows that the pendant amine in the boat confirmation likely interacts with the hydride ligand, which is consistent with previous spectroscopic and computational results. Although the catalyst decomposes in the presence of acid, qualitative analysis of the experimental data coupled with computationally derived free energy landscapes yields insight into the mechanism for H₂ production facilitated by $[Ni(P^{iPr}_2N^{Ph}_2)_2]^{2+}$.

Experimental Section

Materials and Methods: All chemicals and materials were purchased from Aldrich and were used without additional purification unless otherwise noted. Tris(trimethylsilyl)phosphine was obtained from Strem Chemicals, Inc. (Newburyport, MA), and used as received. Tetrabutylammonium hexafluorophosphate, [nBu₄N][PF₆], was obtained from Tokyo Chemical Industries (TCI), America

(Portland, OR), and was recrystallized three times from ethanol. The ultra-high purity grade hydrogen gas used in this study was from OXARC Inc. (Spokane, WA) and was passed through a hydrogen purification column from Vici Metronics (Poulsbo, WA). All manipulations were carried out under an inert atmosphere by either vacuum/Schlenk techniques or in an inert atmosphere glovebox. K[P(SiMe₃)₂],^[18] [(DMF)H]OTf,^[22] and [Ni(CH₃CN) $_{6}](BF_{4})_{2}^{[23]}$ were prepared according to the literature procedures.

Instrumentation: NMR spectra were recorded with a Varian Inova spectrometer (500 MHz for ¹H, 200 MHz for ³¹P) at 25 °C unless noted otherwise. ¹H NMR spectra were referenced against the proteo impurity in the deuterated solvent. The ³¹P{¹H} NMR spectra were referenced to external phosphoric acid. Exact mass spectrometric analysis was performed by using an Exactive mass spectrometer (Thermo Scientific, San Jose, CA) equipped with a custom electrospray ionization (ESI) interface. Electrospray emitters were custom-made by using 360 μ m o.d. \times 20 μ m i.d. chemically etched fused silica. The ion transfer tube temperature and spray voltage were 250 °C and 2.2 kV, respectively. The mass spectrometer was set to acquire data in the positive mode; data were collected from 300 to 1200 m/z units at an ultra-high resolution of 100k or between 200-600 m/z units at an ultra-high resolution of 100k, AGC target set to ultimate mass accuracy, 5×10^5 . Samples diluted in either methanol or acetonitrile to a concentration of 0.1 mM were directly injected with a 250 µL Hamilton syringe at a flow rate of $1 \ \mu L \ min^{-1}$.

Crystallography

Each crystal was coated in Paratone, affixed to a micromount, and placed under streaming nitrogen (100 K) for analysis with a Bruker KAPPA APEX II CCD diffractometer with 0.71073 Å Mo- K_{α} radiation. Space groups were determined on the basis of systematic absences and intensity statistics. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 . Anisotropic displacement parameters were determined for all non-hydrogen atoms. Hydrogen atoms were placed at idealized positions and refined with fixed isotropic displacement parameters, by using a riding model.

The following programs were used: SAINT^[24] for data reduction and cell refinement; SADABS^[25] for scaling and multi-scan absorption correction; SHELXS-2013 and SHELXL-2013^[26] for structure solution and refinement (respectively); OLEX2^[27] was used as the graphical user interface in which structure solution and refinement

were performed. Crystal data and information about data collection and refinement are listed in Table S1.

CCDC-1000237 [for Ni($P^{Pr_2}N^{Ph_2}$)Cl₂], -1000238 [for Ni($P^{Pr_2}N^{Ph_2}$)₂], and -1000239 [for {HNi($P^{Pr_2}N^{Ph_2}$)₂}BF₄] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

P'Pr₂N^{Ph}₂: To a stirring solution of 2-bromopropane (1.35 g, 0.011 mol) in THF (20 mL) was added dropwise a solution of K[P(SiMe₃)₂] (1.943 g, 0.011 mol) in THF (20 mL). The resulting solution was stirred at room temperature for 30 min, and a white solid of potassium iodide was formed on the solution. The solid was removed by filtration to yield a colorless solution. The solution was concentrated to dryness and dissolved in EtOH (20 mL). To this solution, a suspension of paraformaldehyde (0.685 g, 0.022 mol) in ethanol was added. The resulting mixture was stirred at 70 °C for 15 h to yield a colorless solution of isopropylbis-(hydroxymethyl)phosphine. To this solution, aniline was added dropwise over the course of 15 min, and the resulting solution was stirred at 70 °C for 17 h. Cooling the reaction solution to room temperature resulted in crystallization of the ligand as a white solid. The ligand (0.922 g, 42% overall yield) was isolated as a white solid through filtration and washed with cold EtOH. P^{iPr}₂N^{Ph}₂, C₂₂H₃₂N₂P₂ (386.45): calcd. C 68.37, H 8.35, N 7.25; found C 68.34, H 8.17, N 7.32. ³¹P{¹H} NMR (CD₂Cl₂, 202.2 MHz): δ = -37.1 (s) ppm. ¹H NMR (CD₂Cl₂, 499.9 MHz): δ = 7.16 (t, J = 5 Hz, 4 H, ArH), 6.67 (d, J = 5 Hz, 4 H, ArH), 6.62 (t, J = 5 Hz, 2 H, ArH), 4.30 (t, J = 15 Hz, 4 H, PCH₂N), 3.58 (d, J = 5 Hz, 2 H, PCH₂N), 3.55 (d, J = 5 Hz, 2 H, PCH₂N), 1.77 (m, 2 H, *i*PrCH), 1.29 (dd, J = 10 Hz, 12 H, *i*PrCH₃) ppm.

[Ni(P^{*i***Pr}₂N^{Ph}₂)₂](BF₄)₂:** To a stirring solution of the P^{*i*Pr}₂N^{Ph}₂ ligand (0.225 g, 0.582 mmol) in CH₃CN (20 mL), was added dropwise a solution of [Ni(CH₃CN)₆](BF₄)₂ (0.139 g, 0.291 mmol) in CH₃CN (10 mL). The resulting mixture was stirred for 1 h, after which the volume of the solution was reduced by 50% under vacuum. Addition of Et₂O (10 mL) resulted in the formation of red crystals of [Ni(P^{*i*Pr}₂N^{Ph}₂)₂](BF₄)₂ (0.240 g, 82% yield), which were isolated by filtration. ³¹P{¹H} NMR (CD₃CN, 121.4 MHz): δ = 16.0 (s) ppm. ¹H NMR (CD₃CN, 299.9 MHz): δ = 7.47 (t, *J* = 8 Hz, 8 H, Ar*H*), 7.20 (d, *J* = 8 Hz, 8 H, Ar*H*), 7.14 (t, *J* = 8 Hz, 4 H, Ar*H*), 4.02 (d, *J* = 14 Hz, 8 H, PCH₂N), 3.60 (t, *J* = 15 Hz, 8 H, PCH₂N), 2.68 (m, 4 H, *i*PrC*H*), 1.29 (broad, 24 H, *i*PrC*H*₃) ppm. HRMS (ESI): calcd. for [Ni(P^{*i*Pr}₂N^{Ph}₂)₂]²⁺ 415.1717; found 415.1719.

Ni($P^{PP}_{2}N^{Ph}_{2}$)₂: The [Ni($P^{PP}_{2}N^{Ph}_{2}$)₂(BF₄)₂ complex (0.096 g, 0.095 mmol) was dissolved in THF (10 mL), and a suspension of KC₈ (0.026 g, 0.095 mmol) in THF (10 mL) was added in a drop-wise manner. The resulting solution was stirred overnight and filtered to remove excess solids to yield a golden yellow solution. Removal of solvents led to a pale yellow solid that was recrystallized from benzene to yield Ni($P^{PP}_{2}N^{Ph}_{2}$)₂ (0.071 g, 90% yield). ³¹P{¹H} NMR (C₆D₆, 202.2 MHz): δ = 18.9 (s) ppm. ¹H NMR (C₆D₆, 499.9 MHz): δ = 7.23 (t, *J* = 7 Hz, 8 H, Ar*H*), 7.02 (d, *J* = 8 Hz, 8 H, Ar*H*), 6.86 (t, *J* = 7 Hz, 4 H, Ar*H*), 4.02 (d, *J* = 14 Hz, 8 H, PCH₂N), 3.60 (t, *J* = 15 Hz, 8 H, PCH₂N), 1.34 (m, 4 H, *i*PrCH), 1.29 (dd, *J* = 14 Hz, 24 H, *i*PrCH₃) ppm.

[HNi(P^{*i***Pr}₂N^{Ph}₂)2](BF₄):** To a stirring solution of [Ni(P^{*i* $Pr}₂N^{Ph}₂)2]-(BF₄)_2 (0.086 g, 0.086 mmol) in CH₃CN (5 mL) was added a slurry of sodium trimethoxyborohydride (0.011 g, 0.086 mmol) in CH₃CN (5 mL). The resulting mixture was stirred for 30 min at room temperature. The mixture was filtered to yield a yellow solution, and the solvent was removed by vacuum. The pale yellow solid was washed three times with pentane (5 mL) to recover pure$

[HNi($P^{iPr}_2N^{Ph}_2)_2$](BF₄) (0.067 g, 85% yield). ³¹P{¹H} NMR (CD₃CN, 202.4 MHz): δ = 22.9 (s) ppm. ¹H NMR (CD₃CN, 499.9 MHz): δ = 7.28 (t, J = 8 Hz, 8 H, Ar*H*), 7.12 (d, J = 9 Hz, 8 H, Ar*H*), 6.92 (t, J = 8 Hz, 4 H, Ar*H*), 3.62 (d, J = 14 Hz, 8 H, PC*H*₂N), 3.57 (t, J = 14 Hz, 8 H, PC*H*₂N), 2.19 (m, 4 H, *i*PrC*H*), 1.13 (m, 24 H, *i*PrC*H*₃), -11.2 (quintet, J = 18 Hz, 1 H, Ni-*H*) ppm.

Supporting Information (see footnote on the first page of this article): Experimental details for alternative syntheses of [HNi- $(P^{Pr}_2N^{Ph}_2)_2](BF_4)$ and additional crystallographic, spectroscopic, cyclic voltammetry, and thermodynamic analyses.

Acknowledgments

Pages: 9

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Pages: 9

Nickel Hydride Electrocatalysts

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A Ni^{II}–Bis(diphosphine)–Hydride Complex Containing Proton Relays – Structural Characterization and Electrocatalytic Studies

Keywords: Homogeneous catalysis / Hydrogen / Proton transport / Nickel / Diphosphine



A new member of the $[Ni(P^{R}_{2}N^{R'}_{2})_{2}]^{2+}$ family of electrocatalysts is reported. Complex $[Ni(P'^{Pr}_{2}N^{Ph}_{2})_{2}]^{2+}$ is an electrocatalyst for proton reduction to form H₂. Additionally, we have isolated and structurally characterized the Ni^{II}-hydride [HNi- $(P'^{Pr}_{2}N^{Ph}_{2})_{2}]^{+}$.