# **ORGANOMETALLICS**

# Stabilization of Nickel Complexes with Ni<sup>0</sup>…H–N Bonding Interactions Using Sterically Demanding Cyclic Diphosphine Ligands

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## **Supporting Information**



**ABSTRACT:** The series of complexes  $Ni(P_{2}^{rBu}N_{2}^{R})_{2}$   $[Ni(P_{2}^{rBu}N_{2}^{R})_{2}]BF_{4}$   $[HNi(P_{2}^{rBu}N_{2}^{R})_{2}]BF_{4}$  and  $[Co(P_{2}^{rBu}N_{2}^{P})_{2}]BF_{4}$   $(P_{2}^{rBu}N_{2}^{R})_{2}]BF_{4}$   $[P_{2}^{rBu}N_{2}^{R})_{2}]BF_{4}$  and  $[Co(P_{2}^{rBu}N_{2}^{P})_{2}]BF_{4}$   $(P_{2}^{rBu}N_{2}^{R})_{2}]BF_{4}$  results  $[P_{2}^{rBu}N_{2}^{R}]_{2}]BF_{4}$  and  $[Co(P_{2}^{rBu}N_{2}^{P})_{2}]BF_{4}$  and  $[Co(P_{2}^{rBu}N_{2}^{P})_{2}]BF_{4}$  results and characterized. Spectroscopic, electrochemical, and X-ray diffraction studies indicate these complexes are stable as a result of the tetrahedral arrangement of the two diphosphine ligands. Electrochemical oxidation of  $[HNi(P_{2}^{rBu}N_{2}^{Ph})_{2}]BF_{4}$  results in rapid proton transfer from nickel at a rate faster than can be observed on the CV time scale. Double protonation of  $Ni(P_{2}^{rBu}N_{2}^{Ph})_{2}$  forms the endo-endo, endo-exo, and exo-exo isomers of  $[Ni(P_{2}^{rBu}N_{2}^{Ph}N_{2}^{Ph})_{2}](BF_{4})_{2}$ , which were found to be more stable toward loss of  $H_{2}$  than previously observed for similar complexes. The presence of  $Ni^{0}...HN$  hydrogen bonds at the endo protonation sites of  $[Ni(P_{2}^{rBu}N_{2}^{Ph}N_{2}^{Ph})_{2}](BF_{4})_{2}$  results in significant differences in the Ni(I/0) oxidation potentials of each of the isomers. The differences in  $E_{1/2}(I/0)$  values correspond to bond free energies of 7.4 and 3.7 kcal/mol for the first and second  $Ni^{0}...HN$  hydrogen bonds of the endo-exo and endo-endo isomers, respectively. Computational studies give bond dissociation energies of the  $Ni^{0}...HN$  bonds that are within 1-2 kcal/mol of the experimentally determined values.

# INTRODUCTION

Nickel(II) complexes containing two cyclic diphosphine ligands of the type shown in structure 1 have been found to function as highly effective electrocatalysts for hydrogen oxidation and proton reduction to produce hydrogen.<sup>1-4</sup> The nature of the substituents on the phosphorus atoms of the ligands controls the hydricity of the metal.<sup>5-7</sup> When the metal hydricity is matched with the proton acceptor ability of the pendant amines, the driving force for hydrogen addition to, or release from, the complex can be tuned to achieve the desired direction of the catalytic reaction. The proposed mechanism for the catalytic reactions proceeds through Ni(I) and Ni(0) intermediates and is also proposed to involve nickel hydrides.<sup>1-4</sup> The pendant amines of the ligands have been shown to function as efficient proton relays. The role of the bases in promoting rapid intramolecular proton exchange between the amines and the metal center in intermediate stages of the reaction, as well as intermolecular proton transfer between the nickel complex and the solution during the course



of the catalytic cycles, has been discussed in previous papers.  $^{\rm 8-13}$ 

Addition of  $H_2$  to selected hydrogen oxidation catalysts in this class has led to the reduction of Ni(II) and formation of diprotonated Ni(0) species, and these intermediates in the catalytic cycle have been identified by multinuclear NMR studies.<sup>10</sup> We postulated that the introduction of steric bulk to the phosphorus in the cyclic diphosphine ligands of the nickel catalysts might enable us to spectroscopically detect and characterize additional intermediates proposed for the catalytic

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reactions. We report here the syntheses and spectroscopic and electrochemical characterizations of Ni(0), Ni(I), and Ni(II) hydride derivatives containing  $P^{tBu}_{2}N^{R}_{2}$  ligands (R = Ph, Bn), as well as additional important electrochemical characterizations of the three isomers of  $[Ni(P^{tBu}_{2}N^{Bn}HN^{Bn})_{2}](BF_{4})_{2}$ , a doubly protonated Ni(0) complex in which two of the ligand nitrogen atoms have been protonated. The results provide valuable insights into factors that influence the stabilities of reduced intermediates and the rates of the catalytic cycles.

## RESULTS

Synthesis and Characterization of Metal Complexes. The reaction between Ni(COD)<sub>2</sub> and 2–3 equiv of the ligand  $P^{tBu}_{2}N^{Ph}_{2}$  or  $P^{tBu}_{2}N^{Bn}_{2}$  affords the complexes Ni( $P^{tBu}_{2}N^{Ph}_{2}$ )<sub>2</sub>



and Ni(P<sup>fBu</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)<sub>2</sub> (eq 1). During the course of the reaction to make Ni(P<sup>fBu</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)<sub>2</sub>, an intermediate is observed that is assigned as Ni(COD)(P<sup>fBu</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>) on the basis of its <sup>1</sup>H NMR spectrum. The transformation of this intermediate into Ni(P<sup>fBu</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)<sub>2</sub> is somewhat sluggish; therefore, the reaction mixture is heated to 60 °C for ca. 24 h to facilitate complete conversion to Ni(P<sup>fBu</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)<sub>2</sub>. The conversion to Ni(P<sup>fBu</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)<sub>2</sub> is faster, and full conversion to Ni(P<sup>fBu</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)<sub>2</sub> can be achieved at room temperature. Both compounds display some light sensitivity in solution, and so the reactions were conducted in the dark. A single resonance is observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at 20.11 ppm for Ni(P<sup>fBu</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)<sub>2</sub> and at 15.45 ppm for Ni(P<sup>fBu</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)<sub>2</sub>, as expected for tetrahedral bis(diphosphine) nickel(0) complexes.

Both Ni( $P^{fBu}_2N^{Ph}_2$ )<sub>2</sub> and Ni( $P^{fBu}_2N^{Bn}_2$ )<sub>2</sub> are oxidized by  $[Fe(C_5Me_5)_2]BF_4$  to afford the Ni(I) complexes [Ni- $(P^{fBu}_2N^{Ph}_2)_2]BF_4$  and  $[Ni(P^{fBu}_2N^{Bn}_2)_2]BF_4$ , as shown in eq 1. By using a slight excess of the nickel complex,  $[Ni(P^{fBu}_2N^{Ph}_2)_2]$ -BF<sub>4</sub> and  $[Ni(P^{fBu}_2N^{Bn}_2)_2]BF_4$  are easily purified by washing with toluene followed by crystallization. Magnetic moments of 1.71 and 1.78  $\mu_B$  were determined for  $[Ni(P^{fBu}_2N^{Ph}_2)_2]BF_4$  and  $[Ni(P^{fBu}_2N^{Bn}_2)_2]BF_4$ , respectively, using the Evans method. These values are close to the spin-only value of 1.73  $\mu_B$  expected for a d<sup>9</sup> metal complex containing a single unpaired electron.

Acetonitrile solutions of  $[Ni(P^{fBu}_2N^{Ph}_2)_2]BF_4$  are purple to red, while  $[Ni(P^{fBu}_2N^{Bn}_2)_2]BF_4$  affords yellow solutions. The UV-vis spectrum of  $[Ni(P^{fBu}_2N^{Ph}_2)_2]BF_4$  in CH<sub>3</sub>CN contains two bands at 386 nm ( $\varepsilon = 1503 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 515 nm ( $\varepsilon =$ 264 M<sup>-1</sup> cm<sup>-1</sup>) which are assigned as metal-to-ligand charge transfer and d-d transitions, respectively (Figure 1). A third, very intense band at less than 360 nm is observed in the spectrum of  $[Ni(P^{fBu}_2N^{Ph}_2)_2]BF_4$  and arises from  $\pi - \pi^*$ transitions within the phenyl groups of the ligands. A single band is observed for  $[Ni(P^{fBu}_2N^{Bn}_2)_2]BF_4$  at 385 nm ( $\varepsilon = 1439$ M<sup>-1</sup> cm<sup>-1</sup>), which is assigned to a metal-to-ligand charge transfer in analogy to  $[Ni(P^{fBu}_2N^{Ph}_2)_2]BF_4$  (Figure 1). The charge transfer band of  $[Ni(P^{fBu}_2N^{Bn}_2)_2]BF_4$  does appear to contain a small shoulder extending into the visible region,



Figure 1. UV–vis spectra of 1.0 mM  $[Ni(P^{tBu}_2N^{Ph}_2)_2]BF_4$  (red trace) and 1.0 mM  $[Ni(P^{tBu}_2N^{Bn}_2)_2]BF_4$  (blue trace) in acetonitrile.

which could belong to a d-d transition that is obscured by the more intense charge transfer and  $\pi - \pi^*$  bands. A d-d transition for  $[\text{Ni}(\text{P}^{t\text{Bu}}_2\text{N}^{\text{Bn}}_2)_2]\text{BF}_4$  that is blue-shifted relative to  $[\text{Ni}(\text{P}^{t\text{Bu}}_2\text{N}^{\text{Ph}}_2)_2]\text{BF}_4$  is consistent with  $\text{P}^{t\text{Bu}}_2\text{N}^{\text{Bn}}_2$  being a stronger field ligand than  $\text{P}^{t\text{Bu}}_2\text{N}^{\text{Ph}}_2$  as a result of inductive effects of the NR groups.

Attempts were made to synthesize the Ni(II) complexes  $[Ni(P^{fBu}_2N_2^R)_2](BF_4)_2$  through two routes. In the first route, 2 equiv of  $P^{fBu}_2N_2^R$  was added to  $[Ni(CH_3CN)_6](BF_4)_2$ ; in the second route,  $Ni(P^{fBu}_2N_2^R)_2$  was oxidized with 2 equiv of  $[FeCp_2]PF_6$ . However, all attempts resulted in a complex mixture of products, as observed by  ${}^{31}P{}^{1}H$  NMR spectroscopy, and the mixture of products could not be purified. An isoelectronic cobalt complex,  $[Co(P^{fBu}_2N^{Ph}_2)_2]BF_4$ , was formed by reduction of  $[Co(P^{fBu}_2N^{Ph}_2)^{2}](CH_3CN)_3](BF_4)_2^{14}$  with an



excess of zinc in the presence of 1 equiv of  $P_{2}^{fBu}N_{2}^{Ph}$  (eq 2). Unlike other  $[Co(diphosphine)_{2}]^{+}$  complexes,<sup>15,16</sup>  $[Co-(P_{2}^{fBu}N_{2}^{Ph})_{2}]BF_{4}$  is paramagnetic with a magnetic moment of 2.85  $\mu_{B}$ , as determined by the Evans method. This value is close to the spin-only value of 2.83  $\mu_{B}$  expected for an S = 1 ground state, which indicates that  $[Co(P_{2}^{fBu}N_{2}^{Ph})_{2}]BF_{4}$  is a high-spin d<sup>8</sup> complex that is significantly distorted from a square-planar geometry. Two bands are observed in the UV–vis spectrum of  $[Co(P_{2}^{fBu}N_{2}^{Ph})_{2}]BF_{4}$  at 390 nm ( $\varepsilon = 501 M^{-1} cm^{-1}$ ) and 690 nm ( $\varepsilon = 93 M^{-1} cm^{-1}$ ), both of which are assigned to d–d transitions (see Figure S1 in the Supporting Information).

The hydride complexes  $[HNi(P^{fBu}_2N^{Ph}_2)_2]BF_4$  and  $[HNi-(P^{fBu}_2N^{Bn}_2)_2]BF_4$  were prepared by protonation of the Ni(0) complexes Ni( $P^{fBu}_2N^{Ph}_2)_2$  and Ni( $P^{fBu}_2N^{Bn}_2)_2$  with slightly less than 1 equiv of pyridinium tetrafluoroborate and 2,6-lutidinium tetrafluoroborate, respectively, isolated as pure products, and characterized spectroscopically (eq 3). The hydride ligands give diagnostic <sup>1</sup>H NMR signals at -12.46 ppm for  $[HNi-(P^{fBu}_2N^{Ph}_2)_2]BF_4$  and at -11.63 ppm for  $[HNi(P^{fBu}_2N^{Bn}_2)_2]$ -BF<sub>4</sub>. Coupling between the hydride and four phosphorus atoms causes the hydride resonance to appear as a quintet, which collapses to a singlet in the <sup>1</sup>H{<sup>31</sup>P} NMR spectrum.



These data are consistent with those for other nickel hydride complexes containing P2N2 ligands, which have been observed and characterized in situ but not isolated.<sup>5,9,17</sup> Complexes  $[HNi(P_2^{fBu}N_2^{Ph})_2]BF_4$  and  $[HNi(P_2^{fBu}N_2^{Bn})_2]BF_4$  are stable indefinitely in the solid state at -30 °C, but acetonitrile solutions of  $[HNi(P_2^{HB_1}N_2^{Ph_2})_2]BF_4$  and  $[HNi(P_2^{HB_1}N_2^{Bh_2})_2]BF_4$ slowly decompose to form [Ni(P<sup>tBu</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)<sub>2</sub>]BF<sub>4</sub> and [Ni- $(P^{tBu}_{2}N^{Bn}_{2})_{2}]BF_{4}$ . The decomposition of  $HNi^{II}$  into Ni<sup>I</sup> in CD<sub>3</sub>CN solution was monitored by <sup>1</sup>H NMR spectroscopy at room temperature (24  $\pm$  2 °C), and after 7 days 64% of  $[HNi(P^{tBu}_2N^{Ph}_2)_2]BF_4 \text{ and } 77\% \text{ of } [HNi(P^{tBu}_2N^{Bn}_2)_2]BF_4$ remained. Additional data on the rate of decomposition is found in Figure S2 of the Supporting Information. No firm conclusions can be drawn about the mechanism of this transformation. It is clear, however, that  $[HNi(P^{tBu}N^{Ph})_2]^+$ and  $[HNi(P^{tBu}_{2}N^{Bn}_{2})_{2}]^{+}$  are sufficiently stable for isolation and characterization and that the decomposition is slow enough that it does not significantly affect the studies reported here.

Treatment of  $Ni(P^{tBu}_2N^{Bn}_2)_2$  with 2.1 equiv of *p*cyanoanilinium tetrafluoroborate at room temperature afforded the doubly protonated complex  $[Ni(P^{tBu}_2N^{Bn}HN^{Bn})_2](BF_4)_2$ (2A-2C), which was not isolated but generated in situ (eq 4).



The three observed isomers of  $[Ni(P^{fBu}_2N^{Bn}HN^{Bn})_2](BF_4)_2$  are assigned as endo-endo (2A), endo-exo (2B), and exo-exo (2C) isomers by comparison of the observed <sup>31</sup>P{<sup>1</sup>H} NMR resonances to those for  $[Ni(P^{Cy}_2N^{Bn}HN^{Bn})_2](BF_4)_2$ , which has been characterized thoroughly by NMR spectroscopy.<sup>10</sup> At a reaction time of about 10 min, the isomer distribution consists of 36% 2A, 29% 2B, and 35% 2C. After 2 h at room temperature the solution reaches an equilibrium isomer distribution of 74% 2A, 24% 2B, and 2% 2C that does not change further over a period of days. In this system, the exo-exo isomer 2C is the kinetic product that is formed at short reaction times and is isomerized to the thermodynamically preferred isomers 2A and 2B. This isomerization is likely facilitated by pcyanoaniline that is present in solution, since isomerization of exo-exo isomers in related systems is known to be very slow.<sup>11</sup> Experiments on the role of bases in accelerating isomerizations in closely related Ni complexes are underway and will be reported separately.

Unlike other  $[Ni(P_2^RN^R'HN^{R'})_2](BF_4)_2$  complexes, 2A-2C do not eliminate  $H_2$  to generate  $[Ni(P^{fBu}_2N^{Bn}_2)_2](BF_4)_2$  but instead decompose slowly to form the Ni(I) complex  $[Ni(P^{tBu}_2N^{Bn}_2)_2]$ -BF<sub>4</sub>. For example, after 17 days a solution of 2A-2C consisted of approximately 13% [Ni(P<sup>tBu</sup>2N<sup>Bn</sup>2)2]BF4. This process is attributed to decomposition of a trace amount (<1%) of the hydride complex  $[HNi(P^{tBu}_{2}N^{Bn}_{2})_{2}]BF_{4}$ , which is consistently observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectra to be in equilibrium with 2A-2C. Because of the equilibrium, small amounts of the nickel hydride impurity can lead to larger amounts of the Ni(I) complex as a decomposition product. In addition to  $[Ni(P^{tBu}_{2}N^{Bn}_{2})_{2}]BF_{4}$ , a second paramagnetic product is observed in the <sup>1</sup>H NMR spectrum of 2A-2C after partial decomposition has occurred. The new compound displays a broad resonance at 9.6 ppm in the <sup>1</sup>H NMR spectrum, which is slightly downfield from the tert-butyl resonance for [Ni- $(P_{2}^{fBu}N_{2}^{Bn})_{2}$ BF<sub>4</sub> at 8.1 ppm. The same resonance is observed when *p*-bromoanilinium tetrafluoroborate is added to [Ni- $(P^{tBu}_{\phantom{t}2}\!N^{Bn}_{\phantom{t}2})_2]BF_4\!,$  indicating that the Ni(I) complex has been protonated on at least one of the pendant amines. Definitive spectroscopic characterization of this protonated Ni(I) species has remained elusive, due to its paramagnetic nature and lack of distinctive bands in its UV-vis spectrum.

**Structural Studies.** Yellow crystals of Ni $(P_{2}^{\text{fBu}}N_{2}^{\text{Bn}})_{2}$  suitable for an X-ray diffraction study were grown by slow evaporation of a pentane solution. A drawing of the molecule is shown in Figure 2a, and selected bond distances and angles are given in Table 1. The molecule has a pseudotetrahedral geometry with Ni–P bond lengths of 2.14–2.15 Å and  $P_{2}^{\text{fBu}}N_{2}^{\text{Bn}}$  bite angles of 86.4 and 86.7°. The dihedral angle ( $\alpha$ ) between the two planes formed by the two phosphorus atoms of each diphosphine ligand and the Ni atom is 89°, which is close to the 90° angle expected for an ideal tetrahedral complex. These metrical parameters are very similar to those observed for Ni $(P_{2}^{\text{Ph}}N_{2}^{\text{Me}})_{2}^{18}$  and for the  $P_{2}^{\text{Ph}_{2}}N_{2}^{\text{Bn}}$  ligand of Ni $(dppp)(P_{2}^{\text{Ph}_{2}}N_{2}^{\text{Bn}})_{2}^{9}$ 

Orange crystals of  $[\text{Ni}(\text{P}^{f\text{Bu}}_{2}\text{N}^{\text{Bn}}_{2})_{2}]\text{BF}_{4}$  were grown from a solution of CH<sub>3</sub>CN and Et<sub>2</sub>O at -35 °C. The crystal consists of a discrete  $[\text{Ni}(\text{P}^{f\text{Bu}}_{2}\text{N}^{\text{Bn}}_{2})_{2}]^{+}$  cation, a BF<sub>4</sub><sup>-</sup> anion, and solvent molecules. A drawing of the cation is shown in Figure 2b, and selected bond distances and angles are given in Table 1. The Ni–P bonds are all similar and range in length from 2.21 to 2.23 Å and are longer than the Ni–P bonds of Ni(P^{f\text{Bu}}\_{2}\text{N}^{\text{Bn}}\_{2})\_{2}] by 0.07–0.09 Å. The P–Ni–P bite angles of  $[\text{Ni}(\text{P}^{f\text{Bu}}_{2}\text{N}^{\text{Bn}}_{2})_{2}]$ -BF<sub>4</sub> (84.4, 85.3°) are slightly smaller than the corresponding angles in Ni(P^{f\text{Bu}}\_{2}\text{N}^{\text{Bn}}\_{2})\_{2} (86.7, 86.4°) as a result of the greater Ni–P bond length of  $[\text{Ni}(\text{P}^{f\text{Bu}}_{2}\text{N}^{\text{Bn}}_{2})_{2}]$ BF<sub>4</sub>.

Green crystals of  $[Co(P^{fBu}_2N^{Ph}_2)_2]BF_4$  were grown by vapor diffusion of Et<sub>2</sub>O into a CH<sub>3</sub>CN solution of the complex. The crystals contain two crystallographically independent molecules of  $[Co(P^{fBu}_2N^{Ph}_2)_2]BF_4$  in the asymmetric unit, one of which lies on a crystallographic inversion center. A drawing of one of the molecular cations is shown in Figure 2c, and selected bond distances and angles are given in Table 1. The Co–P bonds range in length from 2.24 to 2.26 Å and are about 0.03 Å longer than the Ni–P bond lengths of  $[Ni(P^{fBu}_2N^{Bn}_2)_2]BF_4$ , both of which are formally in the 1+ oxidation state. This trend mirrors that observed for the pairs  $[Co(P^{fBu}_2N^{Ph}_2)(CH_3CN)_3]^{2+}/$  $[Ni(P^{fBu}_2N^{Ph}_2)(CH_3CN)_3]^{2+}$  and  $[Co(P^{fBu}_2N^{Bn}_2)_ (CH_3CN)_3]^{2+}/[Ni(P^{fBu}_2N^{Bn}_2)(CH_3CN)_2]^{2+}$ , where the Co–P bond lengths are longer than the corresponding Ni–P bond lengths by 0.03 Å.<sup>14</sup> In accordance with the greater M–P bond lengths of  $[Co(P^{fBu}_2N^{Ph}_2)_2]BF_4$ , the observed P–Co–P bite



**Figure 2.** X-ray crystal structure diagrams of (a)  $Ni(P^{fBu}_2N^{Bn}_2)_{2^{j}}$  (b) the molecular cation of  $[Ni(P^{fBu}_2N^{Bn}_2)_2]BF_4$ , and (c) one of the two molecular cations of  $[Co(P^{fBu}_2N^{Ph}_2)_2]BF_4$ . Only the ipso carbons of the phenyl rings and the quaternary carbons of the *tert*-butyl groups on phosphorus are shown for clarity. Thermal ellipsoids are shown at 50% probability.

angles (82.7–83.4°) of  $[Co(P^{fBu}_2N^{Ph}_2)_2]BF_4$  are smaller than the corresponding bite angles in  $[Ni(P^{fBu}_2N^{Bn}_2)_2]BF_4$ . Dihedral angles ( $\alpha$ ) of 85 and 77° are measured for the two molecular cations of  $[Co(P^{fBu}_2N^{Ph}_2)_2]BF_4$ . It is well-known that for d<sup>8</sup>  $[M(diphosphine)_2]^{n+}$  complexes  $\alpha$  increases as the diphosphine bite angle increases. In the case of  $[Co(P^{fBu}_2N^{Ph}_2)_2]BF_4$ , the small bite angle of 83° should result in a nearly square-planar geometry at Co on the basis of electronic factors. This scenario is observed for  $[Ni(P^{Ph}_2N^{C6H4Me}_2)_2]^{2+}$  ( $\alpha = 24^{\circ}$ ),  $[Ni-(P^{Ph}_2N^{C6H4OMe}_2)_2]^{2+}$  ( $\alpha = 29^{\circ}$ ), and  $[Ni(P^{Cy}_2N^{fBu}_2)_2]^{2+}$  ( $\alpha = 23^{\circ}$ ).<sup>12,19</sup> The *tert*-butyl groups of the  $P^{tBu}_2N^R_2$  ligand clearly result in large steric effects in the coordination sphere of  $[Co(P^{tBu}_2N^{Ph}_2)_2]BF_4$ , as evidenced by the large dihedral angles observed for this complex.

Table 1. Selected Bond Distances (Å) and Angles (deg)

$\mathrm{Ni}(\mathrm{P}^{\mathrm{fBu}}_{2}\mathrm{N}^{\mathrm{Bn}}_{2})_{2}$							
Ni(1) - P(1)	2.1451(10)	Ni(1)	-P(3)	2.1469(9)			
Ni(1) - P(2)	2.1374(9)	Ni(1)	-P(4)	2.1421(9)			
P(1)-Ni(1)-P	(2) 80	6.70(4)	$\alpha^{a}$	89			
P(3)-Ni(1)-P	(4) 80	ó.41(3)					
	[Ni(P <sup>tBu</sup>	$_{2}N_{2}^{Bn})_{2}]BF_{4}$					
Ni(1) - P(1)	2.2289(15)	Ni(1)-	-P(3)	2.2124(17)			
Ni(1) - P(2)	2.2292(16)	Ni(1)-	-P(4)	2.2113(15)			
P(1)-Ni(1)-P	(2) 85	5.31(6)	$\alpha^{a}$	84			
P(3)-Ni(1)-P	(4) 84	1.42(6)					
	[Co(P <sup>tBu</sup>	$[N_{2}^{Ph}]_{2}]BF_{4}^{b}$					
Co(1)-P(1)	2.2597(8)	Co(1)-	-P(4)	2.2628(9)			
Co(1) - P(2)	2.2522(8)	Co(2)-	-P(5)	2.2363(9)			
Co(1) - P(3)	2.2606(8)	Co(2)	-P(6)	2.2585(8)			
P(1)-Co(1)-P	(2) 82	2.71(3)	$\alpha(1)^a$	85			
P(3)-Co(1)-P	(4) 83	3.35(3)	$\alpha(2)^a$	77			
P(5)-Co(2)-P	(6b) 83	3.13(3)					

 ${}^{a}\alpha$  is the dihedral angle between the two planes formed by the two phosphorus atoms of each diphosphine ligand and the metal ion.  ${}^{b}$ The asymmetric unit of  $[Co(P^{fBu}_2N^{Ph}_2)_2]BF_4$  contains two crystallographically independent molecular cations. Co(2) lies on an inversion center; therefore, only the unique bonds and angles are listed.

 $pK_a$  Measurements. Addition of benzylamine (BnNH<sub>2</sub>) to a benzonitrile solution of  $[HNi(P_2^{Hu}N_2^{Ph})_2]BF_4$  resulted in an equilibrium between  $[HNi(P_2^{Hu}N_2^{Ph})_2]BF_4$  and Ni- $(P_{2}^{HBu}N_{2}^{Ph})_{2}$ , as determined by  ${}^{31}P{}^{1}H{}$  NMR spectroscopy. The resonances for Ni $(P_{2}^{HBu}N_{2}^{Ph})_{2}$  were broader than those observed in solutions of pure  $Ni(P^{fBu}_{2}N^{Ph}_{2})_{2}$ , and the amount of broadening increased with time. This broadening can be attributed to degenerate electron exchange between Ni- $(P^{fBu}_2N^{Ph}_2)_2$  and a trace amount of  $[Ni(P^{fBu}_2N^{Ph}_2)_2]BF_4$  that is formed from decomposition of  $[HNi(P^{fBu}_2N^{Ph}_2)_2]BF_4$ . Over a time period of 1–2 h, decomposition to  $[Ni(P^{fBu}_2N^{Ph}_2)_2]BF_4$ . is negligible, and the ratios of  $[HNi(P^{fB_2}N^{Ph}_2)_2]BF_4$  and  $Ni(P_{2}^{Hu}N_{2}^{Ph})_{2}$  were determined by integration of the  ${}^{31}P{}^{1}H$ NMR resonances. Determination of the ratios of BnNH<sub>2</sub> and  $[BnNH_3]BF_4$  by mass balance allows an equilibrium constant of  $1.5 \pm 0.3$  to be calculated for the deprotonation of  $[HNi(P_{2}^{tBu}N_{2}^{ph})_{2}]BF_{4}$ . Previous studies have shown that relative  $pK_a$  values in acetonitrile and benzonitrile are the same within experimental error.<sup>20</sup> Therefore, the measured equilibrium constant and a  $pK_a$  value of 16.91 for BnNH<sub>3</sub><sup>+</sup> in acetonitrile<sup>21</sup> were used to determine a pK<sub>a</sub> value of 16.7  $\pm$  0.4 for  $[HNi(P^{tBu}_2N^{Ph}_2)_2]BF_4$ . Similar treatment of [HNi- $(P^{tBu}_{2}N^{Bn}_{2})_{2}]BF_{4}$  with pyrrolidine resulted in a measured equilibrium constant of  $0.028 \pm 0.005$ . Using this equilibrium constant and a pK<sub>a</sub> value of 19.56 for pyrrolidinium in acetonitrile,<sup>21</sup> a pK<sub>a</sub> value of 21.1  $\pm$  0.4 was determined for  $[\text{HNi}(P^{fBu}_2N^{Bn}_2)_2]BF_4. \text{ The } pK_a \text{ values for } [\text{HNi}(P^{fBu}_2N^{Ph}_2)_2]^ BF_4$  and  $[HNi(P^{Bu}_2N^{Bn}_2)_2]BF_4$ , along with the redox potentials of  $Ni(P_2^{fBu}N_2^{Ph})_2$  and  $Ni(P_2^{fBu}N_2^{Bn})_2$ , can be used to determine homolytic bond dissociation free energies ( $\Delta G^{\circ}_{H^{\bullet}}$ ) of 53.0 ± 0.5 kcal/mol for  $[HNi(P_2^{tBu}N_2^{Ph})_2]BF_4$  and 52.8  $\pm$  0.5 kcal/ mol for  $[HNi(P_{12}^{HBu}N_{2}^{Bn})_2]BF_4$  using well-known thermodynamic cycles.  $^{22-25}$  These values are similar to those determined for other [HNi(diphosphine)<sub>2</sub>]<sup>+</sup> species.<sup>5,7,20,26,27</sup>

When  $Ni(P^{tBu}_2N^{Bn}_2)_2$  is treated with a small excess of pyridinium (pyH<sup>+</sup>), an equilibrium between  $[HNi(P^{tBu}_2N^{Bn}_2)_2]BF_4$ 

and the endo-endo isomer of  $[Ni(P^{tBu}_2N^{Bn}HN^{Bn})_2](BF_4)_2$  (2A) is observed. The ratios of  $[HNi(P^{tBu}_2N^{Bn}_2)_2]BF_4$  and 2A were determined by <sup>31</sup>P NMR spectroscopy, and the ratios of pyH<sup>+</sup> and py were determined by mass balance. These data allow an equilibrium constant of 0.5 ± 0.1 to be calculated for this reaction. The measured equilibrium constant and the known pK<sub>a</sub> value of 12.53 for pyridinium in acetonitrile<sup>21</sup> were used to determine a pK<sub>a</sub> value of 12.2 ± 0.4 for 2A. Using the equilibrium constants for 2A with 2B and 2C, pK<sub>a</sub> values of 11.7 ± 0.4 for 2B and 10.6 ± 0.4 for 2C were determined.

**Electrochemical Studies.** Figure 3 shows a cyclic voltammogram recorded on a benzonitrile solution of  $Ni(P^{fBu}_2N^{Ph}_2)_2$ .



Figure 3. Cyclic voltammogram of a 2  $\times$  10<sup>-3</sup> M solution of Ni(P<sup>fBu</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)<sub>2</sub>. Conditions: scan rate 100 mV/s, 0.2 M NBu<sub>4</sub>OTf benzonitrile solution, glassy-carbon working electrode.

A reversible oxidation wave is observed at  $E_{1/2} = -1.03$  V, and a plot of the peak current  $(i_p)$  versus the square root of the scan rate for the wave is linear, indicating that this is a diffusion-controlled process.<sup>28</sup> This oxidation wave is assigned to the Ni(I/0) couple. An irreversible oxidation wave is observed at

 $E_{\rm p}$  = +0.23 V at a scan rate of 100 mV/s, and this wave is assigned to a Ni(II/I) couple and/or oxidation of the pendant amine of the diphosphine ligand that is accompanied by rapid decomposition. Decomposition of the analyte at the Ni(II) oxidation state results in a diminished peak current for the cathodic wave of the Ni(I/0) couple. Cyclic voltammograms of  $Ni(P_{2}^{tBu}N_{2}^{Bn})_{2}$  are very similar to those of  $Ni(P_{2}^{tBu}N_{2}^{Ph})_{2}$ except that both oxidation waves occur at more negative potentials due to the greater electron donor ability of the  $P^{tBu}_{2}N^{Bn}_{2}$  ligand. The cyclic voltammograms of the Ni(I) analogues [Ni(P<sup>tBu</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)<sub>2</sub>]BF<sub>4</sub> and [Ni(P<sup>tBu</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)<sub>2</sub>]BF<sub>4</sub> were recorded in acetonitrile, and these showed waves very similar to those observed for  $Ni(P^{\prime Bu}_{\ 2}N^{Ph}_{\ 2})_2$  and  $Ni(P^{\prime Bu}_{\ 2}N^{Bn}_{\ 2})_2$  in benzonitrile. Slight shifts in potentials were observed for the Ni(II/I) couples for the Ni(I) complexes recorded in acetonitrile, and these are given in Table 2.

A cyclic voltammogram recorded on an acetonitrile solution of  $[Co(P_{2}^{fBu}N_{2}^{Ph})_{2}]BF_{4}$  is shown in Figure 4. Reversible couples at -1.62 and -2.03 V are assigned to the Co(I/0) and Co(0/-I) couples by analogy to other  $[Co(diphosphine)_2]^{2+}$  complexes.<sup>15,29</sup> Each of these reductions is a diffusioncontrolled process, as determined from the linear relationship observed between the peak current and the square root of the scan rate. An irreversible oxidation is observed at a peak potential of -0.01 V and is assigned to an oxidation from Co(I) to Co(II). Associated with this irreversible oxidation is a cathodic wave at  $E_{\rm p}$  = -0.93 V. These two waves are assigned respectively to the oxidation of  $[Co(P^{tBu}_2N^{Ph}_2)_2]^+$  to [Co- $(P^{fBu}_{2}N^{Ph}_{2})_{2}]^{2+}$  followed by rapid dissociation of  $P^{fBu}_{2}N^{Ph}_{2}$  to form  $[Co(P_{2}^{fBu}N_{2}^{Ph})(CH_{3}CN)_{3}]^{2+}$ . The oxidation wave at  $E_{p} =$ +0.33 V is tentatively assigned to the Co(III/II) couple of  $\lceil Co(P^{tBu}_{2}N^{Ph}_{2})(CH_{3}CN)_{3} \rceil^{\bar{2}_{+}}$  and/or the oxidation of the pendant amine of the diphosphine ligands.<sup>14</sup>

Table	2.	Cyclic	Voltammetry	Data	for	Nickel	and	Cobalt	Complexes
		_ /							

complex	$E_{\mathrm{p}}(\mathrm{III}/\mathrm{II}) \ (\mathrm{irr})^{a,b}$	$\begin{array}{c} E_{1/2}(\mathrm{II/I}) \stackrel{a}{=} E_{\mathrm{p}}(\mathrm{II/I}) \\ (\mathrm{irr})^{b} \end{array}$	$ \begin{array}{c} E_{1/2}(\mathrm{I}/\mathrm{0})^a \ (\Delta E_{\mathrm{p}})^c \ [i_{\mathrm{a}}/i_{\mathrm{c}}]^d \ E_{\mathrm{p}}(\mathrm{I}/\mathrm{0}) \\ (\mathrm{irr})^b \end{array} $	$E_{1/2}(0/-I)^{a} (\Delta E_{p})^{c} [i_{a}/i_{c}]^{d}$	ref
$Ni(P^{tBu}_{2}N^{Ph}_{2})_2$		+0.23 $(irr)^e$	$-1.03^{e}$ (69) [1.0]		this work
$Ni(P^{\prime Bu}{}_2N^{Bn}{}_2)_2$		$-0.02 (irr)^{e}$	$-1.29^{e}$ (76) [1.0]		this work
$[Ni(P^{rBu}_{2}N^{Ph}_{2})_{2}]BF_{4}$		+0.18 (irr)	-1.02 (63) [1.0]		this work
$[\mathrm{Ni}(\mathrm{P}^{t\mathrm{Bu}}_{2}\mathrm{N}^{\mathrm{Bn}}_{2})_{2}]\mathrm{BF}_{4}$		-0.06 (irr)	-1.29 (76) [1.0]		this work
$[HNi(P^{iBu}_2N^{Bu}_2)_2]BF_4$ $[HNi(P^{iBu}_2N^{Bu}_2)_2]BF_4$	$-0.31 (\text{irr})^{f}$ $-0.67 (\text{irr})^{f}$				this work this work
$[\mathrm{Ni}(\mathrm{P^{tBu}}_{2}\mathrm{N^{Bn}}\mathrm{HN^{Bn}})_{2}](\mathrm{BF_{4}})_{2}$ endo-endo			$-0.12 (q)^{g}$		this work
[Ni(P <sup>tBu</sup> <sub>2</sub> N <sup>Bn</sup> HN <sup>Bn</sup> ) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> endo-exo			$-0.29 (q)^{g}$		this work
$[\mathrm{Ni}(\mathrm{P}^{t\mathrm{Bu}}_{2}\mathrm{N}^{\mathrm{Bn}}\mathrm{HN}^{\mathrm{Bn}})_{2}](\mathrm{BF}_{4})_{2}$ exo-exo			-0.61 (69) [1.5]		this work
$[Ni(P_{2}^{Ph}N_{2}^{Ph})_{2}(CH_{3}CN)](BF_{4})_{2}$		-0.84	-1.02		5
$[Ni(P_{2}^{Ph}N_{2}^{Bn})_{2}(CH_{3}CN)](BF_{4})_{2}$		-0.94	-1.19		14
$[Ni(P^{Cy}_{2}N^{Bn}_{2})_{2}](BF_{4})_{2}$		-0.80	-1.28		5
$[\mathrm{Co}(\mathrm{P^{tBu}}_{2}\mathrm{N^{Ph}}_{2})_{2}]\mathrm{BF}_{4}$		-0.01 (irr)	-1.62 (62) [1.0]	-2.30 (74) [0.8]	this work
$[Co(P_{2}^{Ph}N_{2}^{Ph})_{2}(CH_{3}CN)](BF_{4})_{2}$		-0.58	-2.04	-2.04	28
[Co(dppe) <sub>2</sub> (CH <sub>3</sub> CN)](BF <sub>4</sub> ) <sub>2</sub>		-0.70	-1.56	-2.03	12

<sup>*a*</sup>Half-wave potential in volts versus the  $FeCp_2^+/FeCp_2$  couple in 0.2 M NEt\_4BF\_4/CH\_3CN solutions unless noted otherwise. <sup>*b*</sup>Peak potential of irreversible couples at a scan rate of 100 mV/s. <sup>*c*</sup>Separation of cathodic and anodic peak potentials at a scan rate of 100 mV/s. Under these conditions the reference couple (ferrocene, decamethylferrocene, or cobaltocenium) exhibited  $\Delta E_p$  values of 70 ± 5 mV. <sup>*d*</sup>Ratio of anodic and cathodic peak currents at 100 mV/s. <sup>*c*</sup>In 0.2 M NBu<sub>4</sub>OTf/PhCN solution. <sup>*f*</sup>Oxidation is a formal Ni(III/II) oxidation. <sup>*g*</sup>These waves become quasi-reversible at scan rates above 10 V s<sup>-1</sup>.



Figure 4. Cyclic voltammogram of  $2 \times 10^{-3}$  M solution of  $[Co(P^{tBu}_2N^{Ph}_2)_2]BF_4$ . Conditions: scan rate 100 mV/s, 0.2 M NEt<sub>4</sub>BF<sub>4</sub> acetonitrile solution, glassy-carbon working electrode.

Figure 5a shows a cyclic voltammogram recorded on a 0.5 mM solution of  $[\text{HNi}(\text{P}^{f\text{Bu}}_2\text{N}^{\text{Bn}}_2)_2]\text{BF}_4$  in acetonitrile. At a scan rate of 100 mV/s, an irreversible oxidation of  $[\text{HNi}(\text{P}^{f\text{Bu}}_2\text{N}^{\text{Bn}}_2)_2]\text{BF}_4$  is observed at  $E_p = -0.67$  V, and this wave is accompanied by a reduction wave at  $E_p = -1.31$  V corresponding to the Ni(I/0) couple of Ni( $\text{P}^{f\text{Bu}}_2\text{N}^{\text{Bn}}_2)_2$ . Cyclic voltammograms recorded on 1.0-2.0 mM solutions of  $[\text{HNi}(\text{P}^{f\text{Bu}}_2\text{N}^{\text{Bn}}_2)_2]\text{BF}_4$  in acetonitrile show two additional quasi-reversible waves at  $E_{1/2} = -0.61$  V and  $E_{1/2} = -0.32$  V as the concentration of  $[\text{HNi}(\text{P}^{f\text{Bu}}_2\text{N}^{\text{Bn}}_2)_2]\text{BF}_4$  is increased. These waves correspond to isomers **2C** and **2B**, respectively, as discussed in the next paragraph. The absence of **2A** and **2B** in voltammograms recorded at low concentrations of  $[\text{HNi}(\text{P}^{f\text{Bu}}_2\text{N}^{\text{Bn}}_2)_2]\text{BF}_4$  suggests that they are formed via inter-



Figure 5. (a) Cyclic voltammogram of a 0.5 mM solution of  $[HNi(P^{IBu}_2N^{Bu}_2)_2]BF_4$ . (b) Cyclic voltammograms of a solution of  $[HNi(P^{IBu}_2N^{Bu}_2)_2]BF_4$  at varying concentrations. Conditions: scan rate 100 mV/s, 0.2 M NEt<sub>4</sub>BF<sub>4</sub> acetonitrile solution, glassy-carbon working electrode.

molecular proton transfer following oxidation of [HNi- $(P^{tBu}_{2}N^{Bn}_{2})_{2}]BF_{4}$ . Similar to the case for  $[HNi(P^{tBu}_{2}N^{Bn}_{2})_{2}]BF_{4}$ , electrochemical oxidation of [HNi(P<sup>tBu</sup>2N<sup>Ph</sup>2)2]BF<sub>4</sub> exhibits an irreversible oxidation wave at  $E_{\rm p}$  = -0.31 V accompanied by a reversible reduction wave at -1.02 V corresponding to the I/0 couple of  $Ni(P_2^{fBu}N_2^{Ph})_2$ . The oxidation couples for both [HNi(P<sup>tBu</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)<sub>2</sub>]BF<sub>4</sub> and [HNi(P<sup>tBu</sup><sub>2</sub>N<sup>Bn</sup><sub>2</sub>)<sub>2</sub>]BF<sub>4</sub> remain irreversible even at a scan rate of 100 V/s. Upon recording the oxidation couple of either  $[HNi(P^{fBu}_2N^{Ph}_2)_2]BF_4$  or [HNi- $(P^{tBu}_{2}N^{Bn}_{2})_{2}$ ]BF<sub>4</sub>, the only return cathodic wave observed occurs at the corresponding Ni(I/0) couple, which indicates that proton loss from the oxidized nickel complex is rapid. As a result, a kinetic potential shift is observed for oxidation of  $[HNi(P^{tBu}_{2}N^{Ph}_{2})_{2}]BF_{4}$  and  $[HNi(P^{tBu}_{2}N^{Bn}_{2})_{2}]BF_{4}$ , and the observed half-wave potentials were found to be dependent on the scan rate. For every 10-fold increase in scan rate, the halfwave potentials of [HNi(P<sup>tBu</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub>)<sub>2</sub>]BF<sub>4</sub> and [HNi- $(P^{tBu}_{2}N^{Bn}_{2})_{2}]BF_{4}$  shift to more positive potentials by approximately 30 mV.<sup>28</sup>

Figure 6a shows cyclic voltammograms recorded on a solution of  $[Ni(P^{tBu}_2N^{Bn}HN^{Bn})_2](BF_4)_2$  (2A-2C) at equilibrium. Three oxidations are observed on the anodic scan at potentials more negative than the irreversible II/I couple of the parent complex  $Ni(P^{tBu}_2N^{Bn}_2)_2$ . These oxidations are assigned to the I/0 couples of the isomers 2A-2C. The largest peak current is observed for the oxidation at  $E_p = -0.12$  V, which is assigned to the endo-endo isomer 2A, as the equilibrium mixture of isomers contains 74% of 2A, as discussed previously. The next largest peak current is observed for the oxidation at  $E_p = -0.29$  V, which is assigned to the endo-exo isomer (2B), and the smallest peak current is observed at  $E_{\rm p}$  = -0.59 V and is assigned to the exo-exo isomer (2C). The total measured anodic current consists of 70% 2A, 23% 2B, and 7% 2C, which is close to the equilibrium distribution of isomers as measured by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. At slow scan rates, the oxidations of 2A and 2B at -0.12 and -0.28 V are irreversible with no observable cathodic current on the return sweep. At scan rates of 10 V/s and higher, these couples begin to show quasireversible behavior (Figure 6b). In contrast, the oxidation of 2C at  $E_{1/2} = -0.61$  V is partially reversible at low scan rates (100 mV/s), as evidenced by the presence of a cathodic current upon scan reversal when only the oxidation of 2C is recorded (Figure 6c). The irreversible nature of the waves at -0.12 and -0.28 V suggest that proton loss from the oxidized products  $2A^+$  (endo-endo) and  $2B^+$  (endo-exo) is more rapid than for 2C<sup>+</sup> (exo-exo).

Two additional cathodic peaks are observed at  $E_{\rm p}$  = -0.88 V and  $E_p = -1.24$  V in voltammograms of 2A-2C (Figure 6a). The reduction at  $E_p = -1.24$  V is assigned to the I/0 couple of  $[Ni(P_{2}^{tBu}N_{2}^{Bn})_{2}]BF_{4}$  that is shifted to a slightly more positive potential through an EC mechanism, where the chemical reaction following the electrochemical oxidation is protonation of Ni( $P_{2}^{tBu}N_{2}^{Bn}$ ) in the diffusion layer. The reduction at  $E_{p}$  = -0.88 V is assigned to a monoprotonated Ni(I) species,  $[Ni(P^{{\rm fBu}}{}_2\!N^{Bn}HN^{Bn})(P^{{\rm fBu}}{}_2\!N^{Bn}{}_2)]^{1+}\!,$  that forms through proton loss upon oxidation of 2A-2C in the diffusion layer. These features can be reproduced by titration of small amounts of *p*-anisidinium tetrafluoroborate  $(pK_a = 11.86)^{21}$  into acetonitrile solutions of  $[Ni(P_2^{tBu}N_2^{Bn})_2]BF_4$  (Figure 7). The monoprotonated species is not observed when only 2C is oxidized (Figure 6c), which indicates that the monoprotonated species forms from 2A and/or 2B.



**Figure 6.** Cyclic voltammograms of a  $2 \times 10^{-3}$  M solution of  $[Ni(P^{fBu}_2N^{Bn}HN^{Bn})_2](BF_4)_2$  (2A–2C) showing (a) 2A–2C at scan rate 100 mV/s, (b) 2A–2C at scan rates 5, 10, and 25 V/s, and (c) 2C at scan rate 100 mV/s. Conditions: 0.2 M NEt<sub>4</sub>BF<sub>4</sub> acetonitrile solution, glassy-carbon working electrode.



**Figure 7.** Successive linear voltammograms of a  $2 \times 10^{-3}$  M solution of  $[Ni(P^{fBu}_2N^{Bn}_2)_2]BF_4$  in acetonitrile at increasing concentrations of *p*-anisidinium tetrafluoroborate. Conditions: scan rate 100 mV/s, 0.2 M NEt<sub>4</sub>BF<sub>4</sub> acetonitrile solution, glassy-carbon working electrode.

DFT calculations show that the calculated free energies for the diprotonated Ni(0) isomers increase in the order 2A < 2B < 2C, in agreement with the experimental equilibrium isomer distribution (Table 3). For the corresponding oxidized species

# Table 3. Calculated Relative Free Energies, Redox Potentials, and $d(Ni) \rightarrow \sigma^*(N-H)$ Interactions for Isomers 2A-2C

	$\Delta G$ (kcal/mol)		$\Delta E_{1/2}(\mathrm{I}/\mathrm{0})$ (V)		
	Ni(0)	Ni(I)	calcd	exptl	$d(Ni) \rightarrow \sigma^*(N-H)$ (kcal/mol) Ni(0)
endo-endo (2A)	0.0	8.4	0.53	0.49	15.4
endo-exo (2B)	2.4	4.2	0.24	0.32	8.1
exo-exo (2C)	3.9	0.0	0.00	0.00	0.0

the stability order is reversed:  $2A^+ > 2B^+ > 2C^+$  (Table 3). The higher free energy of  $2A^+$  and  $2B^+$  suggests that these species are more likely to be deprotonated to form monoprotonated species than  $2C^+$ , as experimentally observed. Reassured by these findings, we calculated the relative Ni(I/0) redox potentials for the three isomers. Our calculations are able to reproduce the shift toward more positive E(I/0) redox potentials on passing from isomer 2C to isomer 2A (Table 3) that was observed experimentally. The difference between theoretical prediction and experiment is within the accuracy of the adopted computational protocol (about 0.15 V).<sup>30,31</sup> A natural bond orbital (NBO) analysis<sup>32-39</sup> of three species 2A-2C indicates a significant charge transfer from occupied metal d orbitals to the antibonding  $\sigma^*(N-H)$  orbital when N-H is oriented toward the metal center. The magnitude of the hydrogen-bond-like  $d(Ni) \rightarrow \sigma^*(N-H)$  interaction has been estimated according to the NBO perturbative framework,<sup>38</sup> and these are reported in Table 3. As can be seen in Figure 8, there is a linear correlation between the



**Figure 8.** Correlation between the hydrogen-bond-like  $d(Ni) \rightarrow \sigma^*(N-H)$  interaction and the calculated redox potential for isomers **2C-A** (from left to right).

 $d(Ni) \rightarrow \sigma^*(N-H)$  interaction energy and the shift in the relative redox potential, which suggests that the Ni…HN hydrogen bond is the cause of the shift in the redox potential, as opposed to conformational differences in the ligands of the different isomers.

# DISCUSSION

**Syntheses, Structures, and Reactivity.** The syntheses of the  $P^{tBu}_2N_2^R$  ligands (R = Ph, Bn) and their reactions with  $[M(CH_3CN)_6]^{2+}$  (where M = Ni, Co) have been reported recently.<sup>14</sup> These complexes with sterically demanding *t*-Bu groups on the phosphines differ from other  $P_2N_2$  complexes that we have studied in that the Ni(II) and Co(II) products do not accommodate two of the  $P_2N_2$  ligands; only derivatives of the formula  $[M(P^{tBu}_2N^R_2)(CH_3CN)_x]^{2+}$  (x = 2, 3) have been isolated and characterized. The nickel derivatives were found to be inactive as catalysts for the electrochemical oxidation of hydrogen or reduction of protons.

In the present work we have prepared and characterized Ni(0) derivatives of the formula Ni $(P^{tBu}_{2}N^{R}_{2})_{2}$ . The tetrahedral structures of these complexes reduce steric interactions and permit coordination of two P2N2 ligands. These derivatives provide an entry into the syntheses of additional  $Ni(P_2N_2)_2$ complexes that are analogous to proposed intermediates in the catalytically active systems. For example, oxidation of Ni- $(P_{2}^{tBu}N_{2}^{R})_{2}$  with  $[Fe(C_{5}Me_{5})_{2}]^{+}$  results in the preparation of rather rare examples of Ni(I) derivatives,  $[Ni(P^{tBu}_2N^R_2)_2]^+$ , which have been characterized by magnetic measurements and elemental analyses. X-ray crystallographic data for complexes in two oxidation states,  $Ni(\dot{P}^{tBu}_{2}N^{\breve{Bn}}_{2})_{2}$  and  $[Ni(P^{tBu}_{2}N^{Bn}_{2})_{2}]^{+}$ , have been obtained and compared. The Ni-P bonds for the Ni(I) complex (2.21–2.23 Å) are longer than the Ni–P bonds of the Ni( $\hat{0}$ ) derivative by 0.07–0.09 Å, and they are similar to those observed for Ni(II) complexes containing  $P_2^R N_2^R$ ligands. An increase in the Ni-P bond length upon oxidation of nickel by one electron suggests that the Ni(I) cation possesses a weaker metal-to-ligand  $\pi$  bond. For a d<sup>9</sup> complex with local D<sub>2</sub> symmetry at nickel, a Jahn-Teller distortion is expected to remove the degeneracy of the  $d_{xy}$  and  $d_{xz}$  orbitals. This distortion is manifested in  $[Ni(P^{tBu}_2N^{Bn}_2)_2]BF_4$  in the observed dihedral angle of 84°, which is significantly less than the 89° angle observed for the d<sup>10</sup> complex Ni( $P^{tBu}_{2}N^{Bn}_{2}$ )<sub>2</sub>.

Protonation of the Ni(0) complexes results in the formation of Ni(II) hydride derivatives  $[HNi(P^{tBu}_{2}N^{R}_{2})_{2}]BF_{4}$ , which have been isolated and characterized by NMR spectroscopy and cyclic voltammetry. Although nickel hydride complexes with other  $P_2^R N_2^R$  ligands have been identified spectroscopically,<sup>5,9,17</sup>  $[HNi(P^{tBu}_2N^{Ph}_2)_2]BF_4$  and  $[HNi(P^{tBu}_2N^{Bn}_2)_2]BF_4$  are the first such hydrides to be isolated. The equilibrium constants for the reactions of each hydride complex with either benzylamine or pyrrolidine were determined by NMR spectroscopy and used to determine the pK<sub>a</sub> values for  $[HNi(P^{tBu}_{2}N^{Ph}_{2})_{2}]BF_{4}$  and  $[HNi(P_{2}^{tBu}N_{2}^{Bn})_{2}]BF_{4}$  of 16.7 and 21.1, respectively, in benzonitrile solution. These values are very similar to those determined previously for [HNi(P<sup>Ph</sup><sub>2</sub>N<sup>Ph'</sup><sub>2</sub>)<sub>2</sub>]<sup>+</sup> (16.3) and  $[HNi(P_{2}^{Cy}N_{2}^{Bn})_{2}]^{+}$  (21.0), generated in the same solvent.<sup>5</sup> The Ni(II) hydride products are stable indefinitely in the solid state at -30 °C but decompose in solution. At room temperature, the hydride complexes reacted slowly in acetonitrile solutions to form the Ni(I) derivatives  $[Ni(P_2^{Hu}N_2^{Ph})_2]BF_4$  and  $[Ni(P^{tBu}, N^{Bn})_2]BF_4$  and presumably H<sub>2</sub>, although the gaseous product was not detected in these NMR scale experiments. The homolytic bond dissociation free energies of 53.0 kcal/mol for  $[HNi(P_{2}^{tBu}N_{2}^{Ph})_{2}]BF_{4}$  and 52.8 kcal/mol for  $[HNi(P_{2}^{tBu}N_{2}^{Bn})_{2}]$ -BF4, together with the bond dissociation free energy of H2 (103.6 kcal/mol in acetonitrile)<sup>22</sup> indicate that loss of H<sub>2</sub> should be unfavorable for these two complexes by about 2 kcal/mol in the presence of 1.0 atm of  $H_2$  but favorable in the absence of  $H_2$ . The elimination of  $H_2$  and the formation of Ni(0) and Ni(II)

products have been recently characterized for the decomposition of a related Ni(II) hydride containing  $P^R_{\ 2}N^R_{\ 2}$  ligands.<sup>17</sup>

The addition of 2 equiv of an acid (p-cyanoanilinium) to  $Ni(P_{2}^{tBu}N_{2}^{Bn})_{2}$  in acetonitrile solution generates a mixture of diprotonated Ni(0) isomers, 2A-2C, as shown in eq 4. Although the exo-exo isomer 2C is a kinetic product that is formed at short reaction times, after 2 h at 20 °C, the isomer distribution reaches equilibrium with 74% 2A, 24% 2B, and 2% 2C. Analogous isomers have been synthesized and identified in the addition of hydrogen to  $[Ni(P^{Cy}_2N^{Bn}_2)_2]^{2+,10}$  [Ni- $(P^{Cy}_2N^{Bu}_2)_2]^{2+,19}$  and  $[Ni(P^{Ph}_2N^{Bn}_2)_2]^{2+,5}$  and in the protonation of  $[Ni(P^{Ph}_2N^{Bn}_2)_2]^{2+,13}$  Details of intramolecular proton transfer in these isomer mixtures and intermolecular proton exchange between isomers have been studied by NMR techniques.<sup>11</sup> Each of the previously studied systems displays catalytic activity for hydrogen oxidation or proton reduction, and H<sub>2</sub> elimination from the endo-endo isomer is facile. In the catalytically inactive system studied here, the diprotonated isomers are quite stable to  $H_2$  elimination over a period of days, permitting more detailed electrochemical characterizations of these systems, as discussed below.

Electrochemical Studies. In earlier studies, several nickel(0) complexes of the formula  $Ni(P_2^R N_2^R)_2$  have been characterized electrochemically, and typically two reversible oneelectron oxidations are observed that are assigned to the Ni(I/0)and Ni(II/I) couples. The new Ni(0) complexes described here display a reversible Ni(I/0) couple at -1.03 V for Ni( $P_{2}^{tBu}N_{2}^{Ph}$ )<sub>2</sub> and at -1.29 V for Ni( $P^{fB_{u}}_{2}N^{Bn}_{2}_{2}$ )<sub>2</sub>, but the corresponding Ni(II/ I) waves are irreversible with  $E_{p}$  at +0.23 V for Ni( $P^{fB_{u}}_{2}N^{Ph}_{2}_{2}$ )<sub>2</sub> and -0.02 V for Ni( $P_{2}^{fBu}N_{2}^{Bn}$ ); these peak currents are shifted to values much more positive than those observed for the reversible Ni(II/I) couples for related complexes, which occur in the region of -0.8 to -0.9 V (see Table 2). The cyclic voltammograms observed for the corresponding Ni(I) derivatives  $[Ni(P_2^{tBu}N_2^{Ph})_2]BF_4$ and  $[Ni(P_2^{tBu}N_2^{Bn})_2]BF_4$  are very similar to those described for  $Ni(P_{2}^{Hu}N_{2}^{Ph})_{2}$  and  $Ni(P_{2}^{Hu}N_{2}^{Bn})_{2}$ . The irreversible nature of the II/I oxidation wave and its anodic shift are attributed to the rapid decomposition of the Ni(II) complex and are consistent with our inability to synthesize stable  $[Ni(P^{tBu}_{2}N^{R}_{2})_{2}]^{2+}$  complexes. The hydride complexes  $[HNi(P_2^{fBu}N_2^R)_2]^+$  also display irreversible oxidation waves at -0.31 V for  $[HNi(P^{fBu}_2N^{Ph}_2)_2]BF_4$ and -0.67 V for  $[HNi(P^{fBu}_2N^{Bn}_2)_2]BF_4$  (scan rate 100 mV/s), and these waves remain irreversible at a scan rate of 100 V/s, indicating that proton loss from the oxidized products is very rapid. The formation of isomers 2A and 2B following oxidation of  $[HNi(P^{fBu}_{2}N^{Bn}_{2})_{2}]BF_{4}$  is also consistent with rapid intermolecular proton transfer following oxidation of the hydride complex.

The relative kinetic stabilities of the diprotonated Ni(0) isomers  $[Ni(P^{tBu}_2N^{Bn}HN^{Bn})_2]^{2+}$  (2A–2C) have allowed us to obtain for the first time cyclic voltammetric data on this type of isomeric mixture. The cyclic voltammograms show three distinct Ni(I/0) oxidation waves with relative intensities that roughly correspond to the equilibrium distribution of the isomers. The exo-exo isomer is the easiest to oxidize, and a reversible wave is observed with  $E_{1/2} = -0.59$  V. The d<sup>10</sup> Ni(0) centers in the endo-exo (2B) and endo-endo (2A) isomers are stabilized by interactions with the hydrogen of the protonated amine(s), and this shifts the potentials for the Ni(I/0) oxidation to more positive values, with  $E_{1/2}$  values of quasi-reversible waves at -0.28 (2B) and -0.12 V (2A). The data permit an evaluation of the strength of the hydrogen-bonding interactions in isomers 2A and 2B.

The difference in the  $E_{1/2}$  values for 2C, which has no Ni<sup>0</sup>...HN bonds, and 2B, which has a single Ni<sup>0</sup>...HN bond, is 0.32 V, which corresponds to 7.4 kcal/mol. Assuming that the small difference in the local geometry at the Ni center between isomers has little influence on the redox potential, this difference gives an estimate of the free energy of the Ni<sup>0</sup>…HN bond. Similarly, the free energy of the second Ni<sup>0</sup>…HN bond formed by isomerization from 2B to 2A is 3.7 kcal/mol. These values correlate well with the Ni<sup>0</sup>…HN bond strengths derived from computational studies. The experimentally observed redox potentials for the Ni(I/0) couples also agree very well with the theoretical values calculated for isomers 2A-2C. Hydrogen bonds involving transition metals and acids have been previously reported,<sup>40-42</sup> and in some cases these bond enthalpies have been estimated to range from 3 to 7 kcal/mol. Perhaps the M…HX bonds most relevant to these studies are those of [(HN(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>)Ni(CO)]<sup>+ 43</sup> and  $Co(CO)_3(PPh_2(o-C_6H_4CH_2NHMe_2))$ ,<sup>44</sup> as both complexes possess an intramolecular M···HN bond at a d<sup>10</sup> metal center.

The large stabilization energy resulting from hydrogen bonding (~11 kcal/mol) in 2A suggests that such intramolecular hydrogen bonding between the metal and nitrogen play important roles in determining the relative stability of intermediates and heights of activation barriers in catalytic reactions of closely related  $[Ni(P_2^RN_2^R)_2](BF_4)_2$  complexes. Ni(II), Ni(I), and Ni(0) oxidation states are known to be involved during the catalytic oxidation and production of  $H_{2}$ , and it is of interest to consider how changes in oxidation states of the metal might affect Ni…HN bonding during such a cycle. For example, protonation of the Ni(II) complex  $[Ni(P_{2}^{Ph}N_{2}^{Bn})_{2}]^{2+}$  with strong acids such as 2,6-dichloroanilinium results in the formation of the tetracation [Ni<sup>II</sup>(P<sup>Ph</sup><sub>2</sub>- $N^{Bn}HN^{Bn})_2$ <sup>4+</sup>, in which only the exo-exo isomer analogous to 2C is observed.<sup>13</sup> Because the Ni(II) site is much more electron-deficient compared to a Ni(0) center, formation of a Ni<sup>II</sup>...HN bond is not favorable. As a result, the endo-endo and endo-exo isomers are not stable for this oxidation state. The observation that the oxidation of 2C to  $2C^+$  is more reversible than the oxidations of 2A and 2B suggests that the Ni(I) intermediates  $2A^+$  and  $2B^+$  are less stable than  $2C^+$ . This is likely due to the loss in Ni…HN hydrogen bonding in the Ni(I) oxidation state. Thus Ni<sup>0</sup>…HN bonding likely stabilizes Ni(0) complexes during the catalytic cycles and plays a major role in determining the geometries of these complexes. Such interactions likely play a lesser role in higher oxidation states, although N…HN bonding (as opposed to Ni…HN bonding) does occur in the higher oxidation states. These interactions can have significant consequences for catalyst performance. For example, if during the oxidation of H<sub>2</sub>, the oxidation occurs from the endo-endo isomer 2A, which would be expected to be the kinetic isomer resulting from H-H bond cleavage, the overpotential would be approximately 0.5 V larger than if the oxidation occurs from the exo-exo isomer 2C. Thus, hydrogen bonding between the protonated pendant base in the second coordination sphere and the metal center can have important consequences in terms of catalytic rates and overpotentials.

#### SUMMARY AND CONCLUSIONS

A series of nickel complexes containing bulky  $P_{2}^{fBu}N_{2}^{R}$  (R = Ph, Bn) ligands was synthesized. The  $[Ni^{II}(P_{2}^{fBu}N_{2}^{R})_{2}]^{2+}$  state was shown to be high in energy as a result of the large *t*-Bu group on phosphorus. Therefore, the  $[Ni^{I}(P_{2}^{fBu}N_{2}^{R})_{2}]^{+}$  and  $[HNi^{II}-(P_{2}^{fBu}N_{2}^{R})_{2}]^{+}$  complexes could be isolated and characterized

without disproportionation to  $[Ni^{II}(P^{fBu}_2N^R_2)_2]^{2+}$ . Electrochemical investigations of  $[HNi^{II}(P^{fBu}_2N^R_2)_2]^+$  indicate that proton transfer from nickel to nitrogen is very rapid, indicating that this is not a rate-limiting process in corresponding catalytic systems.

Double protonation of Ni( $P^{fBu}_2N^{Bn}_2$ )<sub>2</sub> led to the formation of  $[Ni(P^{fBu}_2N^{Bn}HN^{Bn})_2]^{2+}$ , which can be observed as a mixture of endo-endo (**2A**), endo-exo (**2B**), and exo-exo (**2C**) isomers in analogy to related systems. Hydrogen release from  $[Ni-(P^{fBu}_2N^{Bn}HN^{Bn})_2]^{2+}$  is uphill due to the high energy of  $[Ni^{II}(P^{fBu}_2N^{R}_2)_2]^{2+}$ , and so this complex could be characterized electrochemically. The  $E_{1/2}(I/0)$  potentials of **2A**–**2C** were found to differ significantly as a result of Ni…HN bonding in the endo isomers, with the oxidation potential increasing with the number of Ni…HN bonds. From these potentials, the Ni…HN bond of **2B** was calculated to have a free energy of 7.4 kcal/mol, and the second Ni…HN bond of **2A** was calculated to have a free energy of 3.7 kcal/mol. These values correspond very well with those derived from computations.

These studies demonstrate the importance of hydrogen bonding in catalytic Ni systems for  $H_2$  oxidation and production, as Ni···HN bonding has been shown to significantly affect the I/0 half-wave potentials of species protonated at a pendant amine. These differences in potential can ultimately affect the observed overpotential, and so efficient proton movement between endo and exo sites of the pendant amines is likely important for minimizing catalytic overpotentials. In a more general sense, these studies provide insight into how hydrogen bonding between a metal center in a low oxidation state and an acid located in the second coordination sphere can influence catalytic reactions in synthetic homogeneous catalyst systems, and by extension they suggest the possibility of similar interactions in enzymes where measuring such interactions directly are likely to be more difficult.

#### EXPERIMENTAL SECTION

General Experimental Procedures. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Varian Inova spectrometer (500 MHz for <sup>1</sup>H) at 25 °C unless otherwise noted. All <sup>1</sup>H chemical shifts have been internally calibrated to the monoprotio impurity of the deuterated solvent. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced to external phosphoric acid at 0 ppm. Magnetic moments were determined by Evans method<sup>45–47</sup> in CD<sub>3</sub>CN solution. UV–vis spectra were recorded on a Shimadzu UV-2401 PC spectrometer using UV Probe (version 1.10) software. Elemental analyses were performed by Atlantic Microlab, Inc. Electrospray ionization (ESI) mass spectra were collected at the Indiana University Mass Spectrometry Facility on a Waters/Micromass LCT Classic using anhydrous solvents and inertatmosphere techniques.

Electrochemical measurements were performed using a CH Instruments 660C potentiostat equipped with a standard threeelectrode cell. Experiments were performed in a glovebox using a 4 mL glass vial as the cell, or on a Schlenk line using an oven-dried 4-5 mL conical vial fitted with a polysilicone cap having openings sized to closely accept each electrode. For each experiment performed on a Schlenk line, the cell was assembled and used under a flow of nitrogen that was bubbled through dry acetonitrile. The working electrode (1 mm PEEK-encased glassy carbon, Cypress Systems EE040) was polished using grade 3 alumina polishing gamal (Fisher A446-100) and then rinsed with neat acetonitrile. A glassy-carbon rod (Structure Probe, Inc.) was used as the counterelectrode, and a silver wire suspended in a solution of Et<sub>4</sub>NBF<sub>4</sub> (0.2 M) in acetonitrile and separated from the analyte solution by a Vycor frit (CH Instruments 112) was used as a pseudo reference electrode. Ferrocene, decamethylferrocene ( $E_{1/2}$  = -0.50 V in CH<sub>3</sub>CN, -0.55 V in PhCN), or cobaltocenium hexafluorophosphate ( $E_{1/2} = -1.33$  V) was used as an internal standard, and all potentials are referenced to the ferrocenium/ferrocene couple at 0 V.

Methods and Materials. All manipulations were carried out under N2 using standard vacuum-line, Schlenk, and inert-atmosphere glovebox techniques. Benzonitrile was degassed and dried over 5 Å molecular sieves. All other solvents were purified by passage through neutral alumina using an Innovative Technology, Inc., Pure Solv solvent purification system. NMR solvents were purchased from Cambridge Isotopes and were dried, degassed, and distilled prior to use. Tetraethylammonium tetrafluoroborate was twice recrystallized from CH<sub>3</sub>CN/Et<sub>2</sub>O and dried in vacuo at room temperature. Tetra-nbutylammonium triflate was recrystallized from CH2Cl2/hexane at -30 °C and dried in vacuo at room temperature. Anilinium and pyridinium salts were prepared by reaction of the parent base with 1.5 equiv of  $HBF_4$ ·Et<sub>2</sub>O, and then the crude salts were recrystallized from CH<sub>3</sub>CN/Et<sub>2</sub>O. Benzylamine was degassed via four consecutive freeze-pump-thaw cycles. Pyrrolidine was dried over CaH2 and distilled prior to use.  $[Fe(C_5Me_5)_2]BF_4$  was prepared by oxidation of  $Fe(C_5Me_5)_2$  with AgBF<sub>4</sub> in toluene. Zinc dust (<10  $\mu$ m) was purchased from Aldrich, and Ni(COD)<sub>2</sub> was purchased from Strem Chemicals.  $P^{tBu}_{2}N^{Ph}_{2}$ ,  $P^{tBu}_{2}N^{Bn}_{2}$ , and  $[Co(\hat{P}^{tBu}_{2}N^{Ph}_{2})(CH_{3}CN)_{3}]$ - $(BF_4)_2$  were prepared according to literature procedures.

**Computational Details.** All structures were optimized without symmetry constraints using the B3P86<sup>48,49</sup> functional. The Stuttgart basis set with effective core potential (ECP)<sup>50</sup> was used for the Ni atom, whereas the 6-31G\* basis set<sup>51,52</sup> was used for all of the other atoms with one additional p polarization funtion ( $\xi(p) = 1.1$ ) for the proton on pendant amines. The optimized structures were confirmed by frequency calculations. For each species, the gas-phase free energy was calculated at 298 K in the harmonic approximation. Solvation free energy in acetonitrile was calculated by using the polarizable continuum model C-PCM model<sup>53,54</sup> using Bondi<sup>55</sup> atomic radii. Intramolecular interactions were analyzed in terms of natural bond orbitals (NBO).<sup>32–39</sup> This computational setup has been shown to describe well the H<sub>2</sub> chemistry of the Ni(P<sub>2</sub>N<sub>2</sub>)<sub>2</sub> complexes.<sup>56</sup> All of the calculations were carried out with the program Gaussian 09.<sup>57</sup> **Syntheses.**  $Ni(P^{Bu}_2N^{Ph}_2)_2$ . In the dark, solid Ni(COD)<sub>2</sub> (101.5 mg.

**Syntheses.**  $Ni(P^{tBu}_2N^{pn}_2)_2$ . In the dark, solid Ni(COD)<sub>2</sub> (101.5 mg, 0.37 mmol) was added to a cold (ca. -35 °C) suspension of  $P^{tBu}_2N^{Ph}_2$  (431.0 mg, 1.0 mmol) in THF (16 mL). After it was stirred overnight at ambient temperature, the mixture was heated in a 60 °C oil bath for 24 h in the dark. Upon cooling, the mixture was filtered and the filtrate was concentrated to dryness. The residue was rinsed with CH<sub>3</sub>CN (3 × 5 mL) and dried in vacuo to afford Ni( $P^{tBu}_2N^{Ph}_2$ )<sub>2</sub> (274.2 mg, 0.31 mmol, 84%) as a yellow powder. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.22 (t, 8H, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, ArH), 7.06 (d, 8H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, ArH), 6.84 (t, 4H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, ArH), 3.46 (d, 8H, <sup>2</sup>J<sub>HH</sub> = 12.6 Hz, PCH<sub>A</sub>H<sub>B</sub>N), 3.36 (d, 8H, <sup>2</sup>J<sub>HH</sub> = 12.6 Hz, PCH<sub>A</sub>H<sub>B</sub>N), 1.06 (d, 36H, <sup>3</sup>J<sub>HP</sub> = 11.5 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  20.11 (s). Anal. Calcd for C<sub>48</sub>H<sub>72</sub>N<sub>4</sub>NiP<sub>4</sub>: C, 64.94; H, 8.18; N, 6.31. Found: C, 65.04; H, 8.15; N, 6.37.

The complex Ni(COD)( $P^{Hu}_2N^{Ph}_2$ ) could be identified by NMR spectroscopy as the major product if the reaction was conducted at room temperature. <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ): 4.11 (br s, 4H, C= CH-C), 3.41 (m, 4H, PCH<sub>A</sub>H<sub>B</sub>N), 3.21 (m, 4H, PCH<sub>A</sub>H<sub>B</sub>N), 2.45 (m, 4H, COD), 2.20 (m, 4H, COD), 1,12 (m, 18H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR ( $C_6D_6$ ):  $\delta$  21.03 (s).

Ni( $P^{Bu}_2 N^{Bn}_2$ )<sub>2</sub>. In the dark, solid Ni(COD)<sub>2</sub> (0.4071 g, 1.48 mmol) was added to a cold (ca. -35 °C) solution of  $P^{fBu}_2 N^{Bn}_2$  (1.3099 g, 2.96 mmol) in THF (20 mL). The solution was stirred for 4 days at ambient temperature, and then the solution was concentrated to dryness. The residue was rinsed with CH<sub>3</sub>CN (2 × 10 mL) and dried in vacuo to afford Ni( $P^{fBu}_2 N^{Bn}_2$ )<sub>2</sub> (1.2746 g, 1.35 mmol, 91%) as a yellow powder. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): 7.24–7.09 (m, 20H, ArH), 3.58 (s, 8H, NCH<sub>2</sub>Ph), 2.83 (dd, 8H, <sup>2</sup>J<sub>HH</sub> = 11.3 Hz, <sup>2</sup>J<sub>HP</sub> = 3.2 Hz, PCH<sub>A</sub>H<sub>B</sub>N), 2.41 (d, 8H, <sup>2</sup>J<sub>HH</sub> = 11.3 Hz, PCH<sub>A</sub>H<sub>B</sub>N), 1.07 (d, 36H, <sup>3</sup>J<sub>HP</sub> = 11.4 Hz, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 15.45 (s). Anal. Calcd for C<sub>52</sub>H<sub>80</sub>N<sub>4</sub>NiP<sub>4</sub>: C, 66.17; H, 8.54; N, 5.94. Found: C, 66.89; H, 8.57; N, 5.86.

 $[Ni(P^{IBu}_2N^{Ph}_2)_2]BF_4$ . In the dark, solid  $[Fe(C_5Me_5)_2]BF_4$  (106.6 mg, 0.256 mmol, 1.0 equiv) was added to a solution of Ni $(P^{IBu}_2N^{Ph}_2)_2$ 

(257.6 mg, 0.290 mmol, 1.1 equiv) in toluene (10 mL). THF (1 mL) was added to the mixture, which was stirred until there was not any visible ferrocenium salt present (ca. 1 day). The solvent was removed in vacuo and the solid rinsed with toluene (3 × 3 mL). The remaining solid was crystallized by vapor diffusion of Et<sub>2</sub>O into CH<sub>2</sub>Cl<sub>2</sub> to afford  $[Ni(P^{tBu}_2N^{Ph}_2)_2]BF_4$  (197.9 mg, 0.203 mmol, 79%) as purple-red crystals. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  62.48 (br s,  $\Delta \nu_{1/2} = 265$  Hz, 8H, PCH<sub>A</sub>H<sub>X</sub>N), 13.43 (br s,  $\Delta \nu_{1/2} = 92$  Hz, 8H, PCH<sub>A</sub>H<sub>X</sub>N), 9.10 (br s,  $\Delta \nu_{1/2} = 77$  Hz, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 7.48 (t, 8H, J = 5.7 Hz, ArH), 6.80 (d, 8H, J = 8.1 Hz, ArH), 6.51 (td, 4H, J = 7.2 Hz, 2.2 Hz, ArH).  $\mu_{\rm eff}$  (CD<sub>3</sub>CN) = 1.71  $\mu_{\rm B}$ . Anal. Calcd for C<sub>48</sub>H<sub>72</sub>BF<sub>4</sub>N<sub>4</sub>NiP<sub>4</sub>: C, 59.16; H, 7.45; N, 5.75. Found: C, 59.17; H, 7.61; N, 5.73.

[*Ni*( $P^{tBu}_2 N^{Bn}_2$ )<sub>2</sub>]*B*F<sub>4</sub>. In the dark, a solution of Ni( $P^{tBu}_2 N^{Bn}_2$ )<sub>2</sub> (501.4 mg, 0.531 mmol, 1.1 equiv) in toluene (15 mL) was added to solid [Fe(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]BF<sub>4</sub> (200.0 mg, 0.484 mmol, 1.0 equiv). THF (3 mL) was added to the mixture, which was stirred until there was not any visible ferrocenium salt present (ca. 2 days). The mixture was concentrated slightly to remove THF, and then the mixture was filtered and the solid rinsed with toluene (2 × 3 mL). The remaining solid was dissolved in a 3:1 mixture of Et<sub>2</sub>O and MeCN, and then the solution was cooled to -35 °C. The orange crystals that formed were rinsed with ether and dried in vacuo to afford [Ni( $P^{tBu}_2 N^{Bn}_2$ )<sub>2</sub>]BF<sub>4</sub> (428.3 mg, 0.416 mmol, 86%). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  8.11 (br s,  $\Delta \nu_{1/2}$  = 133 Hz, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 7.25 (t, 8H, *J* = 7.0 Hz, ArH), 7.20 (t, 4H, *J* = 7.1 Hz, ArH), 7.01 (d, 8H, *J* = 7.0 Hz, ArH), 4.58 (br s,  $\Delta \nu_{1/2}$  = 79 Hz, 8H).  $\mu_{\text{eff}}$  (CD<sub>3</sub>CN) = 1.78  $\mu_{\text{B}}$  Anal. Calcd for C<sub>52</sub>H<sub>80</sub>BF<sub>4</sub>N<sub>4</sub>NiP<sub>4</sub>: C, 60.60; H, 7.82; N, 5.44. Found: C, 60.66; H, 7.97; N, 5.49.

 $[Co(P^{tBu}_2N^{ph}_2)_2]BF_4$ . Solid zinc dust (307 mg, 4.7 mmol, 23 equiv) was added to a brown solution of  $[Co(P^{tBu}_2N^{ph}_2)(CH_3CN)_3](BF_4)_2$ (154.8 mg, 0.201 mmol) in CH<sub>3</sub>CN (8 mL). After it was stirred for 21 h, the mixture was filtered and the green filtrate was added to solid P<sup>tBu</sup><sub>2</sub>N<sup>Ph</sup><sub>2</sub> (80.6 mg, 0.194 mmol, 1 equiv). The green mixture was stirred for 45 min, during which time the added ligand dissolved completely. The solvent was removed in vacuo, and then the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and passed through a small plug of Celite inside of a glass pipet. After the Celite was rinsed with additional CH<sub>2</sub>Cl<sub>2</sub> (2 mL), the combined filtrate was concentrated to a volume of ca. 4 mL. To this solution was added hexane (15 mL), and then the precipitate was collected by filtration and dried in vacuo to afford  $[\tilde{Co}(P^{t\tilde{Bu}}_{2}N^{Ph}_{2})_{2}]BF_{4}$  (184.4 mg, 0.189 mmol, 97%) as a green powder. The <sup>1</sup>H NMR spectrum was analyzed using the line-fitting feature of MestReNova (version 6.0.4), and the listed peak integrations were obtained directly from the areas of the best-fit lines. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  78.49 (br s,  $\Delta \nu_{1/2}$  = 314 Hz, 8H PCH<sub>A</sub>H<sub>X</sub>N), 9.28 (br s,  $\Delta \nu_{1/2}$  = 315 Hz, 6H, PCH<sub>A</sub>H<sub>X</sub>N), 8.06 (s, 9H, ArH), 7.99 (br s,  $\Delta \nu_{1/2}$  = 188 Hz, 34H, C(CH<sub>3</sub>)<sub>3</sub>), 7.17 (s, 8H, ArH), 6.00 (s, 4H, ArH).  $\mu_{\text{eff}}$  (CD<sub>3</sub>CN) = 2.85  $\mu_{\text{B}}$ . ESI-MS: obsd  $\{[Co(P_2N_2)_2] - 2H\}^+$  at m/z 885.3890, predicted 885.3883.  $[HNi(P^{tBu}_2N^{Ph}_2)_2]BF_4$ . In the dark, a solution of pyridinium

[*HNi*(*P*<sup>16*u*</sup><sub>2</sub>*N*<sup>*rn*</sup><sub>2</sub>)<sub>2</sub>]*BF*<sub>4</sub>. In the dark, a solution of pyridinium tetrafluoroborate (25.0 mg, 0.150 mmol) in CH<sub>3</sub>CN (2 mL) was added to a stirred solution of Ni( $P^{16u}_2N^{Ph}_2$ )<sub>2</sub> (160.8 mg, 0.181 mmol, 1.2 equiv) in THF (6 mL). After 1.5 h, the mixture was concentrated to dryness. The residue was washed with Et<sub>2</sub>O (1 × 10 mL, 3 × 4 mL) to afford [HNi( $P^{16u}_2N^{Ph}_2$ )<sub>2</sub>]BF<sub>4</sub> (110.9 mg, 0.114 mmol, 76%) as a yellow powder. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  7.93 (m, 8H, ArH), 7.15 (m, 8H, ArH), 6.95 (m, 4H, ArH), 3.68 (d, 8H, <sup>2</sup>J<sub>HH</sub> = 13.7 Hz, PCH<sub>A</sub>H<sub>B</sub>N), 3.58 (d, 8H, <sup>2</sup>J<sub>HH</sub> = 13.7 Hz, PCH<sub>A</sub>H<sub>B</sub>N), 3.58 (d, 8H, <sup>2</sup>J<sub>HH</sub> = 13.7 Hz, PCH<sub>A</sub>H<sub>B</sub>N), 3.58 (d, 8H, <sup>2</sup>J<sub>HH</sub> = 13.7 Hz, PCH<sub>A</sub>H<sub>B</sub>N), 1.20 (d, 36H, <sup>3</sup>J<sub>HP</sub> = 12.3 Hz, C(CH<sub>3</sub>)<sub>3</sub>), -12.46 (quintet, 1H, <sup>2</sup>J<sub>HP</sub> = 12.8 Hz, NiH). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN):  $\delta$  26.64 (s). Anal. Calcd for C<sub>48</sub>H<sub>73</sub>BF<sub>4</sub>N<sub>4</sub>NiP<sub>4</sub>: C, S9.10; H, 7.54; N, 5.74. Found: C, 59.38; H, 7.73; N, 5.74.

[*HNi*( $P^{tBu}_2 N^{Bn}_2$ )<sub>2</sub>]*BF*<sub>4</sub>. In the dark, a solution of 2,6-lutidinium tetrafluoroborate (28.2 mg, 0.145 mmol) in CH<sub>3</sub>CN (2 mL) was added to a stirred solution of Ni( $P^{tBu}_2 N^{Bn}_2$ )<sub>2</sub> (165.4 mg, 0.175 mmol, 1.2 equiv) in THF (6 mL). After it was stirred for 45 min, the mixture was concentrated to dryness. The residue was washed with Et<sub>2</sub>O (4 × 2 mL) to afford [HNi( $P^{tBu}_2 N^{Bn}_2$ )<sub>2</sub>]*B*F<sub>4</sub> (113.4 mg, 0.110 mmol, 76%) as a yellow powder. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  7.35 (m, 12H, ArH), 7.15 (m, 8H, ArH), 3.73 (s, 8H, NCH<sub>2</sub>Ph), 2.80 (d, 8H, <sup>2</sup>J<sub>HH</sub> = 12.4 Hz, PCH<sub>A</sub>H<sub>B</sub>N), 2.61 (d, 8H, <sup>2</sup>J<sub>HH</sub> = 12.4 Hz, PCH<sub>A</sub>H<sub>B</sub>N), 1.00

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# Table 4. Crystallographic Data for Ni $(P^{tBu}_2N^{Bn}_2)_2$ , [Ni $(P^{tBu}_2N^{Bn}_2)_2$ ]BF<sub>4</sub>, and [Co $(P^{tBu}_2N^{Ph}_2)_2$ ]BF<sub>4</sub>

	$Ni(P^{tBu}_2N^{Bn}_2)_2$	$[\mathrm{Ni}(\mathrm{P^{tBu}}_{2}\mathrm{N^{Bn}}_{2})_{2}]\mathrm{BF}_{4}{\cdot}2\mathrm{CH}_{3}\mathrm{CN}$	$1.5[Co(P_{2}^{tBu}N_{2}^{Ph})_{2}]BF_{4}\cdot CH_{3}CN$
emp formula	$C_{52}H_{80}N_4NiP_4$	C <sub>56</sub> H <sub>86</sub> BF <sub>4</sub> N <sub>6</sub> NiP <sub>4</sub>	$C_{74}H_{111}B_{1.50}Co_{1.50}F_6N_7P_6$
mass (amu)	943.79	1112.71	1503.13
temp (K)	100(2)	100(2)	100(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	triclinic	monoclinic
space group	C2/c	$P\overline{1}$	P2/n
a (Å)	38.5337(7)	13.4155(15)	14.876(4)
b (Å)	12.8379(2)	13.7624(15)	11.517(3)
c (Å)	20.9599(4)	19.175(2)	43.545(12)
$\alpha$ (deg)	90	86.220(3)	90
$\beta$ (deg)	97.2350(10)	70.099(3)	91.718(7)
γ (deg)	90	77.714(3)	90
V (Å <sup>3</sup> )	10286.1(3)	3252.6(6)	7457(4)
Ζ	8	2	4
calcd density (Mg/m <sup>3</sup> )	1.219	1.136	1.339
abs coeff (mm <sup>-1</sup> )	0.539	0.445	0.528
F(000)	4064	1186	3184
cryst size (mm <sup>3</sup> )	$0.10 \times 0.05 \times 0.03$	$0.17\times0.08\times0.06$	$0.20 \times 0.16 \times 0.02$
color and morphology	yellow block	orange block	green plate
$\theta$ range (deg)	1.67-33.22	1.65-25.35	1.46-33.34
no. of rflns collected	72 824	58 463	99 242
no. of indep rflns	$19636\ (R(int) = 0.1838)$	11 914 $(R(int) = 0.0688)$	28678(R(int) = 0.1168)
$T_{\rm max}/T_{\rm min}$	1.04	1.05	1.10
no. of data/restraints/params	19 636/0/562	11 914/48/730	28 678/0/885
$GOF^a$ on $F^2$	1.039	1.048	1.016
$R \operatorname{index}^{b} (I > 2\sigma(I))$			
R1	0.0701	0.0942	0.0666
wR2	0.0845	0.2735	0.1093
R index <sup>b</sup> (all data)			
R1	0.2493	0.1207	0.1575
wR2	0.1286	0.2999	0.1339
weighting coeff <sup>c</sup>			
а	0.0248	0.1741	0.0419
Ь	0	15.7368	0
largest diff peak, hole (e Å <sup>-3</sup> )	0.539, -0.579	2.548, -0.714	3.066, -2.518

 ${}^{a}\text{GOF} = S = \left[\sum_{v} w(F_{o}^{2} - F_{c}^{2})/(M - N)\right]^{1/2}, \text{ where } M \text{ is the number of reflections and } N \text{ is the number of parameters refined. } {}^{b}\text{R1} = \sum_{v} ||F_{o}| - |F_{c}||/\sum_{v} |F_{o}|^{2}, w(F_{o}^{2} - F_{c}^{2})/\sum_{v} w(F_{o}^{2})^{2}|^{1/2}. } {}^{c}w^{-1} = \left[\sigma^{2}(F_{o}^{2}) + (ap)^{2} + bp\right], \text{ where } p = (F_{o}^{2} + 2F_{c}^{2})/3.$ 

(d, 36H,  ${}^{3}J_{HP} = 11.7$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), -11.63 (quintet, 1H,  ${}^{3}J_{HP} = 11.3$  Hz, NiH).  ${}^{31}P{}^{1}H{}$  NMR (CD<sub>3</sub>CN):  $\delta$  21.78 (s). Anal. Calcd for C<sub>52</sub>H<sub>81</sub>BF<sub>4</sub>N<sub>4</sub>NiP<sub>4</sub>: C, 60.54; H, 7.91; N, 5.43. Found: C, 60.24; H, 8.09; N, 5.49.

Protonation of  $Ni(P^{tBu}_2N^{Bn}_2)_2$  with p-Cyanoanilinium To form  $[Ni(P^{tBu}_2N^{Bn}HN^{Bn})_2](BF_4)_2$  (2A–2C). A solution of p-cyanoanilinium tetrafluoroborate (6.6 mg, 0.032 mmol, 2.1 equiv) in ca. 0.7 mL of CD<sub>3</sub>CN was added to solid Ni $(P^{tBu}_2N^{Bn}_2)_2$  (14.4 mg, 0.015 mmol, 1.0 equiv) in a J. Young NMR tube, resulting in a clear yellow solution upon mixing. The solution was degassed by three consecutive freeze–pump–thaw cycles, and the reaction was monitored by NMR spectroscopy. <sup>31</sup>P{<sup>1</sup>H} NMR: δ 29.53 (s, 2A, endo-endo), 25.91 (s, 2B, endo-exo), 2.59 (s, 2B, endo-exo), -1.51 (s, 2C, exo-exo).

**p** $K_a$  **Measurements.** Using solutions of known concentrations, aliquots of the analyte and the acid or base reference were combined in an NMR tube to produce a total volume of 0.7 mL with analyte concentrations of <15 mM and reference concentrations of <50 mM. The samples were analyzed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy after 1 h, and the ratios of the nickel species present were determined by integration. The NMR spectra were recorded again 1 h later, and the ratios were the same within experimental error. The ratios of acid and base were determined by mass balance after taking into account the self-association of the acid–base pair.<sup>58</sup> Each measurement was performed twice to verify consistency, and equilibrium constants ( $K_{eq}$ ) were determined from these measurements. The p $K_a$  value of each

analyte was determined from the measured  $K_{\rm eq}$  and the  $pK_{\rm a}$  of the reference. The listed error is three times the standard deviation for all of the measurements. [HNi(P<sup>fBu</sup>2N<sup>Ph</sup>2)<sub>2</sub>]BF<sub>4</sub>: [HNi(P<sup>fBu</sup>2N<sup>Ph</sup>2)<sub>2</sub>]BF<sub>4</sub> was combined with 0.8, 1.0, and 1.3 equiv of benzylamine to give  $K_{\rm eq} = 1.5 \pm 0.3$  and  $pK_{\rm a} = 16.7 \pm 0.4$ . [HNi(P<sup>fBu</sup>2N<sup>Bn</sup>2)<sub>2</sub>]BF<sub>4</sub>: [HNi-(P<sup>fBu</sup>2N<sup>Bn</sup>2)<sub>2</sub>]BF<sub>4</sub> was combined with 3.3, 6.1, and 14.7 equiv of pyrrolidine to give  $K_{\rm eq} = 0.028 \pm 0.005$  and  $pK_{\rm a} = 21.1 \pm 0.4$ . Ni(P<sup>fBu</sup>2N<sup>Bn</sup>HN<sup>Bn</sup>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**2A**): Ni(P<sup>fBu</sup>2N<sup>Bn</sup>2)<sub>2</sub> was combined with 1.3 and 2.5 equiv of pyridinium tetrafluoroborate to give  $K_{\rm eq} = 0.50 \pm 0.10$  and  $pK_{\rm a} = 21.1 \pm 0.4$ .

**X-ray Diffraction Studies.** For each of the crystal structure studies, a single crystal was mounted using NVH immersion oil onto a nylon fiber and cooled to the data collection temperature of 100(2) K. Data were collected on a Brüker-AXS Kappa APEX II CCD diffractometer with 0.710 73 Å Mo K $\alpha$  radiation. Unit cell parameters were obtained from 90 data frames at  $0.3^{\circ} \phi$  (Ni(P<sup>fBu</sup>2N<sup>Bn</sup>2)<sub>2</sub> and [Co(P<sup>fBu</sup>2N<sup>Ph</sup>2)<sub>2</sub>]BF<sub>4</sub>) or 36 data frames at  $0.5^{\circ} \phi$  ([Ni(P<sup>fBu</sup>2N<sup>Bn</sup>2)<sub>2</sub>]-BF<sub>4</sub>) from three different sections of the Ewald sphere. The data sets were treated with SADABS absorption corrections based on redundant multiscan data (G. Sheldrick, Bruker-AXS, 2001). All non-hydrogen atoms were treated as idealized contributions. Additional details of the structural studies are given in Table 4.

Crystals of  $Ni(P^{\ell Bu}_2 N^{Bn}_2)_2$  suitable for an X-ray diffraction study were grown from slow evaporation of a pentane solution at room

temperature. The systematic absences in the diffraction data were consistent with the centrosymmetric, monoclinic space group C2/c. The molecule is located on a general position, yielding Z = 8 and Z' = 1.

Crystals of  $[Ni(P^{tBu}_2N^{Bn}_2)_2]BF_4$  suitable for an X-ray diffraction study were grown from a CH<sub>3</sub>CN/Et<sub>2</sub>O solution at -35 °C. The systematic absences in the diffraction data were consistent with the triclinic space group  $P\overline{1}$ . The asymmetric unit contains one  $[Ni(P^{tBu}_2N^{Bn}_2)_2]^+$  cation, one  $BF_4^-$  anion, and two molecules of acetonitrile solvent located on general positions, yielding Z = 2 and Z' = 1. The  $BF_4^-$  anion and one molecule of acetonitrile solvent were each disordered over two positions. These positions were located from the difference map and restrained to be equivalent using SADI and EADP commands to stabilize the refinement.

Crystals of  $[Co(P^{Hb_2}N^{Ph_2})_2]BF_4$  suitable for an X-ray diffraction study were grown from vapor diffusion of Et<sub>2</sub>O into CH<sub>3</sub>CN. The systematic absences in the diffraction data were consistent with the centrosymmetric, monoclinic space group P2/n. The asymmetric unit contains 1.5  $[Co(P^{Hb_2}N^{Ph_2})_2]^+$  cations, 1.5  $BF_4^-$  anions, and one molecule of acetonitrile solvent, yielding Z = 4 and Z' = 1.5. There is some residual density around the cobalt that sits on the special position. This is likely an artifact of some disorder about the symmetry element and does not appear to be related to any accuracy issues with the model.

# ASSOCIATED CONTENT

# **Supporting Information**

CIF files giving crystallographic data for Ni( $P^{tBu}_2N^{Bn}_2$ )<sub>2</sub>, [Ni( $P^{tBu}_2N^{Bn}_2$ )<sub>2</sub>]BF<sub>4</sub>, and [Co( $P^{tBu}_2N^{Ph}_2$ )<sub>2</sub>]BF<sub>4</sub> and figures giving the UV–vis spectrum for [Co( $P^{tBu}_2N^{Ph}_2$ )<sub>2</sub>]BF<sub>4</sub>, kinetic plots for the decomposition of [HNi( $P^{tBu}_2N^{Ph}_2$ )<sub>2</sub>]BF<sub>4</sub> and [HNi( $P^{tBu}_2N^{Bn}_2$ )<sub>2</sub>]BF<sub>4</sub>, NMR spectra of **2A**–**2C**, and additional cyclic voltammetry plots of [HNi( $P^{tBu}_2N^{Ph}_2$ )<sub>2</sub>]BF<sub>4</sub> and [HNi-( $P^{tBu}_2N^{Bn}_2$ )<sub>2</sub>]BF<sub>4</sub>. This material is available free of charge via the Internet at http://pubs.acs.org.

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## Notes

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