Comparison of Cobalt and Nickel Complexes with Sterically Demanding Cyclic Diphosphine Ligands: Electrocatalytic H₂ Production by [Co(P\textsuperscript{Bu_2}N\textsubscript{Ph}_2)(CH\textsubscript{3}CN\textsubscript{3}][BF\textsubscript{4}]\textsubscript{2}]


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The cyclic diphosphine ligands P\textsuperscript{Bu_2}N\textsubscript{Ph}_2 and P\textsuperscript{Bu_2}N\textsubscript{Br}_2 have been synthesized and used to prepare new complexes of Co(II) and Ni(II) with the formula [M(P\textsuperscript{Bu_2}N\textsubscript{R}_2)(CH\textsubscript{3}CN\textsubscript{3}][BF\textsubscript{4}]\textsubscript{2} (n = 2, 3). The products have been characterized by variable-temperature NMR data, X-ray diffraction studies, and cyclic voltammetry, and properties of the new complexes have been compared with those of previously studied complexes containing P\textsuperscript{Ph}_2NR\textsubscript{2} ligands. The variation of either phosphorus or nitrogen substituents in these ligands can result in significant differences in the structure, electrochemistry, and reactivity of the metal complexes. [Co(P\textsuperscript{Bu_2}N\textsubscript{Ph}_2)(CH\textsubscript{3}CN\textsubscript{3}][BF\textsubscript{4}]\textsubscript{2} is found to be an effective electrocatalyst for the formation of hydrogen using bromoanilinium tetrafluoroborate as the acid, with a turnover frequency of 160 s\textsuperscript{-1} and an overpotential of 160 mV. These cobalt derivatives are a promising class of catalysts for further study and optimization.

Introduction

The electrocatalytic reduction of protons to produce hydrogen is the simplest fuel generation reaction. This reaction has potential technological importance in the storage of the electrical energy produced using renewable energy sources such as solar and wind, which exhibit significant temporal variations. Although platinum is an excellent catalyst for this reaction, its high cost and low abundance have limited the search for alternatives. The high catalytic activity of [NiFe] and [FeFe] hydrogenase enzymes clearly demonstrate that the use of noble metals is not required for H₂ production and oxidation.¹⁻⁶ These considerations have resulted in the development of a variety of molecular catalysts, including FeS dimers,⁷⁻¹¹ CpMoS₂ dimers,¹² and cobalt macrocycles.¹³⁻¹⁵ Efforts in our laboratories have focused primarily on the design of H₂ oxidation and production catalysts that involve first-row transition-metal complexes containing diphosphine ligands with pendant bases.¹⁶,¹⁷ In our comparisons of nickel and cobalt complexes with P\textsuperscript{Ph}_2NR\textsubscript{2} ligands, such as those shown in 1, we have found different and complementary structural requirements for catalytic activity. Nickel complexes incorporating two P\textsuperscript{Ph}_2NR\textsubscript{2} ligands are fast and efficient catalysts for H₂ production (1a) and for H₂ oxidation (1b).¹⁸,¹⁹ The studies showed that ligand substituents markedly alter the affinities of the complexes for H₂ addition and control the bias of the catalyst for oxidation or reduction.
The closely related nickel complex [Ni(PPh$_2$N$_2$Br$_2$)-
(dpdp)(BF$_4$)$_2$ (where dpdp is bis(diphenylphosphino)propane), which contains only one base positioned near the metal
center, is a much poorer catalyst for H$_2$ oxidation than 1b,
despite a stronger thermodynamic driving force for H$_2$
addition.\textsuperscript{20} We therefore concluded that two bases positioned near
the active metal site were important for catalytic activity in the
Ni bis(diphosphine) systems. However, in these previous studies
with P$_2$N$_2$Br$_2$ ligands, we were unable to examine the effect on catalytic activity of other ligands in nickel complexes of the type
[NI(P$_2$N$_2$Br$_2$)$_2$]$_n$(BF$_4$)$_2$ ($n$ = 2, 3) because of difficulties in their
synthesis. For example, the addition of 1 equiv of P$_2$N$_2$Br$_2$ to
[NI(CH$_3$CN)$_6$](BF$_4$)$_2$ resulted in the formation of 1/2 equiv of
the known bis(diphosphine) complex 1a rather than the desired
mixed ligand derivative.\textsuperscript{22}

In our studies of cobalt complexes with P$_2$N$_2$Br$_2$ ligands we
found that the syntheses of products containing either one or
two cyclic ligands were readily achieved by controlling ligand
stoichiometry in the syntheses.\textsuperscript{22} The complex [Co(P$_2$N$_2$Br$_2$)$_2$
(CH$_3$CN)](BF$_4$)$_2$ was isostructural with the active nickel cata-
lyst for H$_2$ formation because of the facile dissociation of
one P$_2$N$_2$Br$_2$ ligand in the presence of acid. In contrast,
[Co(P$_2$N$_2$Br$_2$)$_2$](CH$_3$CN)$_2$[BF$_4$]$_2$, with a single base positioned
near the cobalt center, was stable to excess acid and performed
as an effective electrocatalyst for hydrogen formation with a
rate and overpotential similar to those of 1a.

In this paper we describe the syntheses and characteriza-
tions of the new cyclic ligands P$_2$N$_2$Ph$_2$ and P$_2$Bu$_2$N$_2$Br$_2$ and
their nickel and cobalt complexes. Introduction of the steri-
cally demanding and electron-donating tert-butyl substituent
on phosphorus might be expected to affect the stoichiometry of
the ligand additions, cause structural distortions in the
resulting complexes, and influence the reduction potentials
at the metal centers. We report here how these effects are
manifested in the nickel and cobalt derivatives, and we
investigate the factors that promote high electrocatalytic
activity for one of the new cobalt derivatives, while the other
new complexes were found to be catalytically inactive.

## Results

### Synthesis and Characterization of Ligands

The two new cyclic diphosphine ligands P$_2$Bu$_2$N$_2$Ph$_2$ and P$_2$Bu$_2$N$_2$Br$_2$ were
prepared by first reacting tert-butylphosphine with parafor-
maldehyde to form bis(hydroxymethyl)-terti-butylphosphine
followed by reaction with 1 equiv of either aniline or
benzylamine in hot ethanol. The desired ligands precipitate
as white solids upon cooling, and subsequent workup
produces the desired ligands in reasonable yields and high
purity. An interesting feature of these new ligands is the
observation of conformational isomers in the variable-
temperature NMR spectra. Furthermore, the two ligands,
which differ only by the presence of phenyl or benzyl
substituents on the nitrogens, show significantly different
fluxional properties.

At room temperature P$_2$Bu$_2$N$_2$Ph$_2$ exists as two discrete
isomers which each display a pair of mutually coupled
methylene protons (NCH$_2$P) in the $^1$H NMR spectrum. The
two-bond proton–phosphorus coupling constant ($^2$J$_{HP}$)
for each NCH$_2$P resonance was determined through selective
homonuclear decoupling experiments. By comparison of
$^2$J$_{HP}$ with literature values,\textsuperscript{21} each isomer was determined to
possess both an axial P$_2$N$_2$Br$_2$ proton ($^2$J$_{HP}$ = 4.7 or
5.4 Hz) and an equatorial P$_2$N$_2$Br$_2$ proton ($^2$J$_{HP}$ =
14.8 Hz). In the 2D NOESY spectrum of P$_2$Bu$_2$N$_2$Br$_2$, both
isomers displayed a cross-peak between the resonance of the ortho
hydrogens of NPh (H$_{ortho}$) and the H$_{eq}$ resonances (see
Figure S1 in the Supporting Information). However, only
one isomer displayed a NOESY cross-peak between the
H$_{ortho}$ and H$_{ax}$ resonances. Therefore, the isomers were
assigned as “crown” and “saddle” conformers, with the
“saddle” conformer possessing a NOESY cross-peak
between H$_{ortho}$ and H$_{ax}$. This conformer assignment
was supported by MM2 calculations through determination of
the average H$_{ortho}$ and H$_{ax}$ distances, which were found to be
3.5 Å (“crown”) and 1.9 Å (“saddle”). No peak coalescence
was observed in the $^1$H NMR spectrum of P$_2$Bu$_2$N$_2$Ph$_2$ up to
80 °C in CD$_3$CN, indicating that conformational exchange is
slow for this molecule. Models indicate that the phenyl ring
is restricted in its orientation, resulting in a relatively high
energy barrier for rearrangement.

For the second ligand, P$_2$Bu$_2$N$_2$Br$_2$, the PCH$_2$N methylene
protons are equivalent on the NMR time scale at room
temperature, indicating fast exchange between conforma-
tions under these conditions. The benzyl and methylene
resonances begin to decoalesce at 0 °C in THF-$d_8$. At
−50 °C, two conformers of P$_2$Bu$_2$N$_2$Br$_2$ are observed clearly in

\textsuperscript{20} Wilson, A. D.; Newell, R. H.; McNevin, M. J.; Muckerman,
128, 358–366.

\textsuperscript{21} Wilson, A. D.; Miedaner, A.; Muckerman, J. T.; DuBois,
104, 6951–6956.

\textsuperscript{22} Fraze, K.; Wilson, A. D.; Appel, A. M.; Rakowski DuBois,

\textsuperscript{23} (a) Märkl, V. G.; Jin, G. Y.; Schoener, C. Tetrahedron Lett.
1980, 21, 1409–1412. (b) Albrand, J. P.; Gagnaire, D.; Robert, J. B.
a 4:1 ratio (Figure S4, Supporting Information). The major conformation is assigned as a “crown” isomer on the basis of NMR data similar to that described above for crown-
P_{Bu}^t_2NPh_2 (Figure S5, Supporting Information). For the minor conformation, two NCH_2Ph and three equal-intensity PCH_2N resonances are observed, while a fourth PCH_2N resonance appears to overlap with a resonance from the “crown” conformation, as determined by peak integration and a 1H–1H COSY spectrum (Figure S6, Supporting Information).

The low symmetry indicated for this isomer is consistent with its assignment as a “chair-boat” conformer. Isomers with tert-butylic substituents on opposite faces of the eight-membered ring are less consistent with observed spectral data.

**Synthesis and Characterization of Metal Complexes.** The addition of 1 equiv of a cyclic P_{Bu}^t_2NPh_2 ligand to an acetonitrile solution of [Co(CH_3CN)_6]^2+(BF_4)_2 or [Ni(CH_3CN)_6]^2+(BF_4)_2 followed by workup provides a convenient synthesis of [Co(P_{Bu}^t_2NPh_2)(CH_3CN)_3](BF_4)_2 (2-Ph), [Co(P_{Bu}^t_2NPh_2)(CH_3CN)_3](BF_4)_2 (2-Bz), [Ni(P_{Bu}^t_2NPh_2)(CH_3CN)_3](BF_4)_2 (3-Ph), and [Ni(P_{Bu}^t_2NPh_2)(CH_3CN)_3](BF_4)_2 (3-Bz) (Scheme 1). Elemental analyses of the products are consistent with these formulations. Magnetic moments of 1.81 and 1.95 μ_B were determined for 2-Ph and 2-Bz, respectively, using the Evans method. These values are consistent with low-spin Co(II) complexes with one unpaired spin. 24

The nickel complexes were further characterized by NMR spectroscopy. The NMR spectra of [Ni(P_{Bu}^t_2NPh_2)(CH_3CN)_3](BF_4)_2 (3-Ph) show an interesting solvent dependence. In CD_2Cl_2, the room-temperature ^1H NMR spectrum displays sharp resonances consistent with a diamagnetic, five-coordinate, square-pyramidal complex. A single AB pattern is observed for the methyl protons of the ligand (4.26, 3.64 ppm), indicating that the two chelate rings of the ligand are equivalent or are rapidly interconverting. In the room-temperature ^31P{^1H} NMR spectrum in CD_2Cl_2, a broad singlet is observed at 11.9 ppm.

In contrast, the room-temperature ^1H NMR spectrum of 3-Ph in CD_2CN displays a broad tert-butyl resonance at 3.5 ppm and a broad PCH_2N resonance at 8.1 ppm, both of which are shifted downfield from the typically observed

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Figure 1. Plots of μ_{eff} as a function of temperature for [Ni-(P_{Bu}^t_2NPh_2)(CH_3CN)_3](BF_4)_2 (3-Ph, blue trace) and [Ni(P_{Bu}^t_2NPh_2)(CH_3CN)_3](BF_4)_2 (3-Bz, red trace) in CD_2CN.

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normal ranges expected for a diamagnetic complex. However, at room temperature the NCH₃Ph resonance appears as a broad hump in the baseline at ca. 5.7 ppm. When the solution is warmed to 80 °C, this resonance sharpens and shifts upfield to 5.0 ppm (Δν₁/₂ ca. 72 Hz), while the remaining resonances remain unshifted (Figure S9, Supporting Information). Determination of the solution magnetic moment (Evans method) of 3-Bz in CD₃CN results in small values for μₑff at low temperatures (< 0.5 μB) and no observable paramagnetic character above 40 °C (Figure 1). As observed for 3-Ph, a 31P{¹H} NMR resonance for 3-Bz is not observed at or above room temperature but does appear as a broad singlet at ~2.5 ppm upon cooling the solution to −40 °C.

Complex 3-Bz was not soluble in the weakly coordinating solvents THF, acetone, and CH₂Cl₂; however, it is soluble in CD₃NO₂. In the latter solvent at room temperature, the ¹H NMR resonances for 3-Bz are broad but lie in the chemical shift range of a diamagnetic complex, and a broad 31P{¹H} NMR resonance appears at 5.3 ppm. A single NCH₃Ph resonance that integrates to 4H is observed at 2.42 ppm when the sample is cooled to ~20 °C, two equal-intensity NCH₃Ph resonances are observed at 5.08 and 3.91 ppm, with each resonance integrating to 2H (Figure S10, Supporting Information).

The NMR data for 3-Bz in CD₃NO₂ are interpreted in terms of a weak agostic interaction of the methylene protons of the benzyl group with Ni, as shown in Scheme 3. At low temperature, one of the benzyl hydrogens interacts with nickel, resulting in a boat conformation for that ring system, while the other six-membered ring has a chair conformation. At room temperature the benzyl hydrogen atoms of these two ring systems interchange, resulting in a single resonance for these protons. A weak agostic interaction is consistent with the X-ray diffraction study of this complex, discussed below. The value of the C−H coupling constant would provide additional support for an agostic hydrogen. However, no signals were observed for either NCH₃Ph group in the ¹H-coupled ¹³C NMR spectrum of 3-Bz recorded at ~20 °C; therefore, a value for ¹JCH could not be measured for this complex.

### Structural Studies

Vapor diffusion of Et₂O into an acetonitrile solution of [Co(P²Bu₂N²Ph₂)(CH₃CN)₃](BF₄)₂ (2-Ph) or [Co(P²Bu₂N²Bz₂)(CH₃CN)₃](BF₄)₂ (2-Bz) resulted in the formation of dark brown crystals that were suitable for an X-ray diffraction study. The crystals consist of discrete cations and BF₄⁻ anions. Drawings of the cations are shown in Figure 2, and selected bond lengths and angles are given in Tables 1 and 2, respectively. The structures are best described as square pyramids with acetonitrile ligands occupying the axial positions. These structures and the metric parameters of the cations are similar to those previously determined for [Co(P²Ph₃N²Ph₂)(CH₃CN)₃](BF₄)₂, and in Tables 1 and 2, the values for the latter complex are included for comparison.

In the structure of 2-Ph, the Co−N bond distance for the axial acetonitrile (2.08 Å) is significantly longer than those of the two basal acetonitrile ligands (1.94 and 1.96 Å). The small bite angle observed for the diphosphine ligand (83.60°) is typical for cyclic P₂R₂ ligands coordinated to divalent first-row transition metals. The N(3)−Co−N(4) angle of 85.50° between the two basal acetonitrile ligands is smaller than that observed for the analogous [Co(P²Ph₂N²Ph₂)(CH₃CN)₃]²⁺ cation (88.7°). This acute angle in 2-Ph is attributed to steric interactions between the tert-butyl groups on the diphosphine ligand and the two basal acetonitrile ligands. Consistent with this explanation, the C−N−Co angles of the basal acetonitrile ligands are less than 180° (164.40 and 174.35°) and bend away from the tert-butyl groups. The corresponding angles for [Co(P²Ph₂N²Ph₂)(CH₃CN)₃]²⁺ are 172.66 and 173.73°. In addition, the dihedral angle between the plane defined by the two N atoms of the basal acetonitrile ligands and cobalt and the plane defined by the two phosphorus atoms and cobalt is 18.98° for 2-Ph. The corresponding angle for [Co(P²PH₂N²PH₂)(CH₃CN)₃]²⁺ is 16.09°. Similar distortions are observed for the cation of 2-Bz as well. In short, a comparison of the metric data for 2-Ph and 2-Bz with that of [Co(P²Ph₂N²Ph₂)(CH₃CN)₃]²⁺ suggests that steric interactions between the bulky tert-butyl groups and the basal acetonitrile ligands result in small but notable distortions to relieve these interactions.

An examination of the diphosphine ligand conformations in 2-Ph and 2-Bz shows that each six-membered chelate ring adjacent to the axial acetonitrile ligand adopts a chair
conformation to minimize steric interactions with acetonitrile, and the second six-membered ring of each ligand has a boat conformation. As a result the nonbonding Co–N(2) distances are 3.27 and 3.53 Å for 2-Ph and 2-Bz, respectively. Additionally, in 2-Ph the N atom of the ring with the boat conformation is nearly planar and the attached phenyl ring folds over the cobalt atom, resulting in the close approach of the ipso (3.11 Å) and ortho (3.15 Å) carbon atoms to cobalt. For 2-Bz, one of the hydrogen atoms on the benzyl attached to the N atom of the ring in the boat conformation is in close contact with the Co atom in this complex (2.76 Å). The paramagnetism of these complexes prevented the use of NMR spectral data to provide evidence for or against significant interactions between Co and either the C atoms of the phenyl rings or the H atoms of the benzyl carbons.

Red crystals of [Ni(P₂Bu₂NPh₂)(CH₃CN)₂][BF₄]₂ (3-Bz) suitable for an X-ray diffraction study were grown by vapor diffusion of Et₂O into an acetonitrile solution of the complex. The crystal consists of discrete [Ni(P₂Bu₂NPh₂)(CH₃CN)₂][BF₄]₂ cations and BF₄⁻ anions. A drawing of the cation is shown in Figure 2, and selected bond lengths and angles are given in Tables 1 and 2, respectively. The structure of this nickel complex is very similar to that of the corresponding cobalt complex, 3-Ph, with the most notable difference being the longer Ni–N(5) distance (2.31 Å) for the apical acetonitrile compared to that of the Co–N(5) distance (2.08 Å). This is consistent with the addition of a second electron into the d₆ orbital that has antibonding character with respect to the σ orbital of the acetonitrile ligand. In addition, the Ni–C distances to the ipso (3.23 Å) and ortho (3.34 Å) carbon atoms of the phenyl ring folded over the Ni atom are slightly longer than the corresponding distances of 2-Ph, 3.11 and 3.15 Å, respectively.

Red crystals of [Ni(P₂Bu₂NPh₂)(CH₃CN)₂][BF₄]₂ (3-Bz) suitable for an X-ray diffraction study were grown by vapor diffusion of Et₂O into an acetonitrile solution of the complex. The crystal consists of discrete [Ni(P₂Bu₂NPh₂)(CH₃CN)₂][BF₄]₂ cations and BF₄⁻ anions. A drawing of the cation is shown in Figure 2, and selected bond lengths and angles are given in Tables 1 and 2, respectively. The nickel is coordinated

<table>
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<th>compd</th>
<th>M–P(1) Å</th>
<th>M–P(2) Å</th>
<th>M–N(3) Å</th>
<th>M–N(4) Å</th>
<th>M–N(5) Å</th>
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<tr>
<td>[Co(P₂Bu₂NPh₂)(CH₃CN)₃]²⁺</td>
<td>2.1918(5)</td>
<td>2.1978(5)</td>
<td>1.9516(15)</td>
<td>1.9427(15)</td>
<td>2.0776(15)</td>
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<tr>
<td>[Co(P₂Bu₂NPh₂)(CH₃CN)₃]²⁺</td>
<td>2.2242(5)</td>
<td>2.2504(5)</td>
<td>1.9386(13)</td>
<td>1.9647(13)</td>
<td>2.0766(13)</td>
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<tr>
<td>[Co(P₂Bu₂NPh₂)(CH₃CN)₃]²⁺</td>
<td>2.2239(4)</td>
<td>2.2419(4)</td>
<td>1.9607(12)</td>
<td>1.950(12)</td>
<td>2.0586(12)</td>
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<tr>
<td>[Ni(P₂Bu₂NPh₂)(CH₃CN)₂][BF₄]₂</td>
<td>2.1881(6)</td>
<td>2.2158(6)</td>
<td>1.9141(18)</td>
<td>1.9451(17)</td>
<td>2.3113(18)</td>
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<tr>
<td>[Ni(P₂Bu₂NPh₂)(CH₃CN)₂][BF₄]₂</td>
<td>2.1902(5)</td>
<td>2.1965(5)</td>
<td>1.9035(17)</td>
<td>1.9105(16)</td>
<td>2.116(16)</td>
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</table>
to the diphosphine ligand and two acetonitrile ligands in a planar arrangement. The acute N(3)−N(4) angle of 83.6° and the bending of the two acetonitrile ligands away from the tert-butyl groups on phosphorus, as indicated by Ni−N−C angles of 163.5 and 164.8°, are again consistent with significant steric interactions between the two acetonitrile ligands and the tert-butyl groups on phosphorus. The diphosphine ligands adopt chair/boat conformations, and the N atom of the ring with a boat conformation is 3.49 Å from the N atom. One of the methylene hydrogen atoms on the benzyl group in the boat chelate is in close contact with the Ni atom in this complex (2.56 Å). This Ni−H distance is also significantly shorter than the sum of the van der Waals radii of Ni and H (2.72 Å),20 suggesting that a weak agostic interaction is present. This Ni···H distance is also significantly shorter than the analogous Co···H distance in 2-Bz (2.76 Å).

**Electrochemical Studies.** As shown in Figure 3, a cyclic voltammogram of \([\text{Co(P}^{\text{Bu}2\text{NPh}2}\text{(CH}_3\text{CN)}_2]^{2+} \text{(2-Ph)}\) exhibits a single reversible reduction wave at \(E_{1/2} = -0.87 \text{ V} (\Delta E_p = 63 \text{ mV})\) and a quasi-reversible oxidation wave at \(E_{1/2} = +0.34 \text{ V} (\Delta E_p = 114 \text{ mV})\). A plot of the peak current \(i_p\) versus the square root of the scan rate for the wave at \(-0.87 \text{ V}\) is linear, indicating that this is a diffusion-controlled process. This wave is assigned to the Co(II/I) couple. The quasi-reversible oxidation wave at \(+0.34 \text{ V}\) is assigned to the Co(III/II) couple. Similar behavior is observed for 2-Bz. For this complex the Co(II/I) couple is slightly more negative than that of the corresponding phenyl derivative, as expected, and the Co(III/II) couple is somewhat less reversible. Data for these complexes and related cobalt complexes are summarized in Table 3.

Figure 4 shows the cyclic voltammogram recorded on an acetonitrile solution of \([\text{Ni(P}^{\text{Bu}2\text{NPh}2}\text{(CH}_3\text{CN)}_2]^{2+} \text{(3-Ph)}\) at a small reduction wave is observed consistently at −0.59 and −1.61 V. The first reversible reduction wave is assigned to the Ni(II/I) couple. A plot of the peak current \(i_p\) versus the square root of the scan rate for the wave at −0.59 V is linear and indicates that this is a diffusion-controlled process. The second large reduction wave at −1.61 V is assigned to an irreversible Ni(III)/Ni(II) couple. Similar results were obtained for \([\text{Ni(P}^{\text{Bu}2\text{NPh}2}\text{(CH}_3\text{CN)}_2]^{2+} \text{(3-Bz)}\), and these results are summarized in Table 3.

A small reduction wave is observed consistently at −1.0 V in the cyclic voltammogram of 3-Ph, and a small amount of free \(\text{P}^{\text{Bu}2\text{NPh}2}\) (crown isomer) also is observed in the \(^1\text{H}\) NMR spectrum of 3-Ph in CD$_2$CN (but not in CD$_2$Cl$_2$). The relative intensity of the wave at −1.0 V is similar to the relative intensity of the \(^1\text{H}\) NMR resonances observed for the free \(\text{P}^{\text{Bu}2\text{NPh}2}\). Addition of \(\text{P}^{\text{Bu}2\text{NPh}2}\) to acetonitrile solutions of 3-Ph leads to an increase in the intensity of the wave.

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**Table 2. Selected Bond Angles (deg)**

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<th>Bond</th>
<th>Angle (deg)</th>
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<tr>
<td>P(1)−Co(1)−P(2)</td>
<td>82.45(17)</td>
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<tr>
<td>P(1)−Co(1)−N(3)</td>
<td>95.08(4)</td>
</tr>
<tr>
<td>P(1)−Co(1)−N(4)</td>
<td>164.14(5)</td>
</tr>
<tr>
<td>P(1)−Co(1)−N(5)</td>
<td>98.58(4)</td>
</tr>
<tr>
<td>P(2)−Co(1)−N(3)</td>
<td>172.61(4)</td>
</tr>
<tr>
<td>N(3)−Co(1)−N(5)</td>
<td>88.69(6)</td>
</tr>
</tbody>
</table>

**Figure 3.** Cyclic voltammogram of a 2 × 10⁻³ M solution of \([\text{Co(P}^{\text{Bu}2\text{NPh}2}\text{(CH}_3\text{CN)}_2]^{2+} \text{(2-Ph)}\). Conditions: scan rate 100 mV/s, 0.2 M NEt$_4$BF$_4$ (supporting electrolyte) acetonitrile solution, glassy-carbon working electrode. The wave at 0.0 V is the ferrocenium/ferrocene couple, used as an internal standard.

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Organometallics, Vol. 29, No. 21, 2010

Wiedner et al.

Table 3. Cyclic Voltammetry Parameters for Cobalt and Nickel Complexes

<table>
<thead>
<tr>
<th>complex</th>
<th>$E_{1/2}(III/II)^{a}$ (Δ$E_p$) [i$<em>p$,i$</em>{cat}$]</th>
<th>$E_{1/2}(II/I)^{a}$ (Δ$E_p$) [i$<em>p$,i$</em>{cat}$]</th>
<th>$E_i(0)^{a}$ (i$<em>p^2$, $E</em>{1/2}(I/0)$)</th>
<th>ref</th>
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</thead>
<tbody>
<tr>
<td><a href="BF$_4$">Co(P$<em>{Bu_2}$N$</em>{Ph_2}$)(CH$_3$CN)$_2$</a>$_2$</td>
<td>+0.34 (114) [0.4]</td>
<td>−0.87 (63) [1.0]</td>
<td>this work</td>
<td></td>
</tr>
<tr>
<td><a href="BF$_4$">Co(P$<em>2$N$</em>{Ph_2}$)(CH$_3$CN)$_2$</a>$_2$</td>
<td>+0.26 (161) [2.2]</td>
<td>−0.94 (82) [1.1]</td>
<td>this work</td>
<td>22</td>
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<tr>
<td><a href="BF$_4$">Co(P$<em>{Bu_2}$N$</em>{Ph_2}$)(CH$_3$CN)$_2$</a>$_2$</td>
<td>−0.99 (70) [1.0]</td>
<td>−0.91 (72) [1.0]</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td><a href="dppp">Co</a>(CH$_3$CN)$_2$](BF$_4$)$_2$</td>
<td>−1.21 (95) [0.9]</td>
<td>−1.61 (irr)</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td><a href="BF$_4$">Co(P$<em>2$N$</em>{Ph_2}$)(CH$_3$CN)$_2$</a>$_2$</td>
<td>−0.58 (71) [1.0]</td>
<td>−0.69 (104) [1.0]</td>
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<td>−0.80</td>
<td>−1.28</td>
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$^{a}$Half-wave potential in volts versus the FeCp$_3^+/FeCp_3$ couple in 0.2 M NEt$_4$BF$_4$/CH$_3$CN solutions. $^{b}$Separation of cathodic and anodic peak potentials at a scan rate of 100 mV/s. Under these conditions ferrocene exhibited Δ$E_p$ values of 70 ± 5 mV. $^{c}$Ratio of anodic and cathodic peak currents at 100 mV/s. $^{d}$Peak potential of irreversible Ni(0) couple.

Figure 4. Cyclic voltammogram of a $2 \times 10^{-3}$ M solution of [Ni(P$_{Bu_2}$N$_{Ph_2}$)(CH$_3$CN)$_2$](BF$_4$)$_2$ (3-Ph). Conditions: scan rate 100 mV/s, 0.2 M NEt$_4$BF$_4$ (supporting electrolyte) acetonitrile solution, glassy-carbon working electrode. The wave at 0.0 V is the ferrocenium/ferrocene couple used as an internal standard.

Figure 5. Successive cyclic voltammograms of a 0.002 M solution of [Co(P$_{Bu_2}$N$_{Ph_2}$)(CH$_3$CN)$_2$](BF$_4$)$_2$ in acetonitrile at increasing concentrations of 4-bromoanilinium tetrafluoroborate. Conditions: scan rate 50 mV/s, 0.2 M NEt$_4$BF$_4$ (supporting electrolyte), glassy-carbon working electrode. Potentials are referenced to the ferrocenium/ferrocene couple at 0.0 V (not shown).

(top graph) is consistent with a second-order dependence of the overall catalytic rate on acid. At higher concentrations of acid (middle graph), no acid dependence is observed, and this is tentatively interpreted in terms of a rate-limiting elimination of H$_2$ under these conditions. Using the limiting current in this acid-independent region, a turnover frequency of 160 s$^{-1}$ can be calculated for 2-Ph using eq 1.$^{29,30}$ A linear relationship is observed between $i_{cat}$ and [2-Ph], which demonstrates a first-order dependence of the catalytic current on the concentration of catalyst at constant acid concentration (0.1 M, bottom graph in Figure 6) using eq 2.$^{29,30}$ A controlled-potential electrolysis experiment was performed on the complex at −1.11 V in the presence of 4-bromoanilinium tetrafluoroborate, and the evolution of H$_2$ was confirmed by gas chromatography (current efficiency 96 ± 5%).

\[
\frac{i_{cat}}{i_p} = \frac{2}{0.446}\sqrt{RTk \over Fv} \quad (1)
\]

\[
i_{cat} = nFA[\text{Cat}]T(Dk)^{1/2} \quad (2)
\]


at −1.0 V, while the intensity of the Ni(II/II) couple of 3-Ph remains unchanged. The free ligand P$_{Bu_2}$N$_{Ph_2}$ does not give an electrochemical response in this potential range, and so the wave at −1.0 V is attributed to the reduction of [Ni(P$_{Bu_2}$N$_{Ph_2}$)(CH$_3$CN)$_2$](BF$_4$)$_2$ formed from the reaction of the free ligand with electrochemically generated [Ni(P$_{Bu_2}$N$_{Ph_2}$)(CH$_3$CN)$_2$](BF$_4$)$_2$. Further studies of this bis(diphosphine) Ni complex are in progress. Spontaneous ligand dissociation and rearrangement are not observed for 3-Bz on the CV time scale.

Catalytic Hydrogen Production. Figure 5 shows successive cyclic voltammograms of [Co(P$_{Bu_2}$N$_{Ph_2}$)(CH$_3$CN)$_2$](BF$_4$)$_2$ (2-Ph) recorded in acetonitrile with increasing concentrations of 4-bromoanilinium tetrafluoroborate as the acid ($pK_a$ = 9.43). The cyclic voltammogram of 2-Ph exhibits a catalytic wave for the reduction of protons at a half-wave potential of −0.88 V in the presence of 0.03 M acid. This potential agrees well with the Co(II/I) potential of the catalyst and corresponds to an overpotential of approximately 160 mV using the method proposed by Evans et al. for determining overpotentials.$^{28}$

The two top graphs in Figure 6 show plots of $i_{cat}/i_p$ (where $i_{cat}$ is the peak current in the presence of acid and $i_p$ is the peak current in the absence of acid) versus acid concentration. The linear region of this plot at low acid concentrations...
Similar studies were attempted with 2-Ph using 4-cyanoanilinium tetrafluoroborate (pK$_a$ = 7.0 in acetonitrile)\textsuperscript{31} (Figure S11, Supporting Information) and 2,6-dichloroanilinium tetrafluoroborate (pK$_a$ = 5.1 in acetonitrile)\textsuperscript{27} (Figure S12, Supporting Information) as acids. Catalytic currents for each of these acids were observed to be higher than those with 4-bromoanilinium tetrafluoroborate. However, a negative shift in both the catalytic onset potential and half-peak potential was observed as the acid concentration was increased. The half-peak potential reached a maximum of $-1.1\, V$ for 4-cyanoanilinium tetrafluoroborate and $-1.3\, V$ for 2,6-dichloroanilinium tetrafluoroborate (Figure 7). Both of these potentials are near the half-wave potential of [Co(CH$_3$CN)$_6$]$^{2+}$ at $-1.21\, V$. In contrast, when using 4-bromoanilinium tetrafluoroborate at similar acid concentrations the observed half-peak potential reaches a maximum of $-0.92\, V$, which is close to the half-wave potential of $-0.87\, V$ for 2-Ph.

The UV–vis spectra of 0.001 M acetonitrile solutions of 2-Ph in the presence of 0.075 M solutions of each acid were monitored with time in order to determine the relative stability of 2-Ph (Figure S13, Supporting Information).

For a 75:1 ratio of acid to 2-Ph, the complex decomposes to form [Co(CH$_3$CN)$_6$]$^{2+}$ with a half-life of approximately 40 min for 4-cyanoanilinium tetrafluoroborate and 18 min for 2,6-dichloroanilinium tetrafluoroborate. In contrast, 2-Ph displays a half-life of 190 min in the presence of 4-bromoanilinium tetrafluoroborate. These data indicate that 2-Ph is significantly less stable in the presence of 4-cyanoanilinium or 2,6-dichloroanilinium salts; therefore, [Co(CH$_3$CN)$_6$]$^{2+}$ likely contributes significantly to the observed catalytic currents. As a result, meaningful comparisons of catalytic currents using these acids with those for 4-bromoanilinium tetrafluoroborate are not possible.

The complex [Co(P$_{3Bz}^+$N$_{Bz}^-$)(CH$_3$CN)$_3$](BF$_4$)$_2$ (2-Bz) has more basic N atoms than 2-Ph because the benzyl substituents are more electron-donating than phenyl groups. When 2-Bz is treated with small quantities of 4-bromoanilinium tetrafluoroborate (0.005 M), the Co(II/I) half-wave potential shifts from $-0.94$ to $-0.79\, V$, presumably as a result of protonation of a benzyl amine (Figure S17, Supporting Information). Additionally, a new irreversible reduction wave appears at a half-wave potential of $-1.08\, V$. At 0.030 M of 4-bromoanilinium tetrafluoroborate (a moderate acid concentration for catalytic studies) the half-wave potential of the catalytic wave has shifted to $-1.29\, V$, suggesting that the proton reduction is associated with [Co(CH$_3$CN)$_6$]$^{2+}$ formed through loss of the protonated P$_{3Bz}^+$N$_{Bz}^-$ ligand. The decomposition is even more rapid when using 4-cyanoanilinium tetrafluoroborate.

The nickel complexes 3-Ph and 3-Bz were also investigated for electrocatalytic proton reduction, but no catalytic activity was observed at the Ni(II/I) couple for either complex (Figure S18 and S19, Supporting Information). The complex 3-Ph shows some degradation in the presence of small amounts of 4-cyanoanilinium tetrafluoroborate (25 mM), while 3-Bz decomposes much more quickly (within 15 min) at similar concentrations of the same acid. When 2,6-dichloroanilinium tetrafluoroborate is used, 3-Ph also decomposes by ca. 60% within 35 min. Therefore, the [Ni(P$_{3Bz}^+$N$_{R}^-$)(CH$_3$CN)$_3$](BF$_4$)$_2$ ($n = 2, 3$) complexes show acid stability similar to that of [Co(P$_{3Bz}^+$N$_{R}^-$)(CH$_3$CN)$_3$](BF$_4$)$_2$ while displaying no catalytic activity at modest potentials.

Discussion

Complex Characterization. The cyclic PR₂N₂R₂ ligands with tert-butyl substituents on phosphorus favor the formation of monodentate (diphosphine) complexes with both cobalt and nickel. Five-coordinate, square-pyramidal products of the formula \([M(P^{Bu}_{2}N^{Bu}_{2})(CH\_3CN)]_{2}\) (2-Ph, 2-Bz, and 3-Ph) and the agostic complex \([Ni(P^{Bu}_{2}N^{Bu}_{2})(CH\_3CN)]_{2}\) (3-Bz) have been isolated and characterized. The formation of mononuclear bis(diphosphine) complexes of the type \([M(P^{Bu}_{2}N^{Bu}_{2})_{2}]^{2+}\) was not observed under conditions studied here, even for nickel, for which the quite sterically hindered analogue with cyclohexylphosphine donors has been prepared previously. Further evidence of the steric demands of these ligands was observed in the X-ray diffraction studies of the products. Complexes 2-Ph, 2-Bz, 3-Ph, and 3-Bz all display small N–M–N angles in the range of 82°–85°, and one or both of the basal acetonitrile ligands are bent away from the bulky phosphine substituents with M–N–C angles of 163°–165°. The basal planes of the molecules show small tetrahedral distortions with dihedral angles of ca. 18° between the P–M–P and N–M–N planes. These structural distortions have a marked effect on the reduction potentials of the complexes, which are discussed below.

For the cobalt complexes 2-Ph and 2-Bz, the structures observed in the solid state are likely preserved in solution with the exception of ring conformations. The solution magnetic moments of 1.8 with the exception of ring conformations. The solution observed in the solid state are likely preserved in solution. The basal planes of the molecules show small tetrahedral distortions with dihedral angles of ca. 18° between the P–M–P and N–M–N planes. These structural distortions have a marked effect on the reduction potentials of the complexes, which are discussed below.

Comparisons of Catalytic Properties. Our results indicate that \([Co(P^{Bu}_{2}N^{Bu}_{2})(CH\_3CN)]_{2}(BF\_4)_{2}\) is an effective catalyst for the electrochemical reduction of protons to \(H\_2\) using 4-bromoanilinium tetrafluoroborate as the acid, with the onset of the catalytic current occurring at the Co(II/I) couple. Kinetic studies of the catalytic reaction are consistent with pre-equilibrium steps involving the addition of two protons to a Co(I) complex, followed by a rate-determining step, which is the first order in catalyst. This rate-determining step could involve the cleavage of the Co–H bond, followed by an intramolecular proton transfer step. Similar kinetic behavior has been observed previously for \([Ni(P^{Bu}_{2}N^{Bu}_{2})(CH\_3CN)]_{2}(BF\_4)_{2}\) complexes. In those studies, \(H\_2\) loss was favored as the rate-determining step, because in most cases where we have been able to observe it spectroscopically, intramolecular proton transfer for complexes containing \(R^2-N^2R^2\) ligands has been fast.

As discussed above, the substitution of the tert-butyl substituent for phenyl on the cyclic phosphine ligand in these cobalt derivatives results in a positive shift in the potential of this couple by 0.12 V. The positive shift is surprising because tert-butyl groups are expected to be significantly better electron donors than phenyl substituents.

This shift is attributed to the steric interactions between the tert-butyl groups and the acetonitrile ligands, discussed above, that result in a distortion from the square-planar geometry in the basal plane of the structure. The antibonding overlap of the basal ligands with the dₓz orbital are reduced as a result of this distortion leading to more positive redox potentials. A similar positive shift in potential has been observed for the Ni(II/I) couples of \([Ni(P^{Bu}_{2}N^{Bu}_{2})(CH\_3CN)]_{2}(BF\_4)_{2}\) relative to that of \([Ni(P^{Bu}_{2}N^{Bu}_{2})(CH\_3CN)]_{2}(BF\_4)_{2}\) as shown in the last two entries of Table 3. The bulky cyclohexyl substituents on phosphorus also result in distortions from a square-planar structure and a resulting stabilization of the LUMO.

A second interesting feature of the electrochemical data is that replacement of a diphosphine ligand with acetonitrile ligands results in the redox potentials of the Co(II/I) couple becoming more negative: i.e., \([Co(P^{Bu}_{2}N^{Bu}_{2})(CH\_3CN)]_{2}(BF\_4)_{2}\) (–0.58 V), \([Co(P^{Bu}_{2}N^{Bu}_{2})(CH\_3CN)]_{2}(BF\_4)_{2}\) (–0.99 V), and \([Co(CH\_3CN)]_{2}(BF\_4)_{2}\) (–1.21 V). However, opposing trends are observed for the nickel complexes. For the last two entries in Table 3, replacing phosphine ligands with acetonitrile ligands result in positive potential shifts for the Ni(II/I) couple but negative shifts for the potentials of the Ni(I/0) couples. The origin of these differences between cobalt and nickel is not clear. It can also be seen from Table 3 that replacement of phenyl substituents on nitrogen with benzyl substituents results in a shift of the M(II/I) couple to more negative potentials by 0.07–0.10 V. This observation is also true for Ni(II/I) couples previously reported for \([Ni(P^{Bu}_{2}N^{Bu}_{2})(CH\_3CN)]_{2}(BF\_4)_{2}\) complexes. The potential shifts that are observed as a result of changing substituents on nitrogen indicate that there is effective electronic communication between the pendant base of these \(R^2-N^2R^2\) ligands and the metal.
90 s⁻¹ for [Co(PPh₂NPh₂)(CH₂CN)₃](BF₄)₂]. The catalytic rates and overpotentials for 2-Ph are quite comparable to those of several [Ni(PPh₂NPh₂)(CH₂CN)](BF₄)₂] catalysts reported previously by our group. For example, [Ni(PPh₂NPh₂)(CH₂CN)](BF₄)₂] (where R² = (thiophene-3-yl)phenyl) has a turnover frequency of 56 s⁻¹ and an estimated overpotential of 280 mV under similar conditions.

In contrast to 2-Ph, the corresponding benzyl derivative 2-Bz is not an effective catalyst for H₂ production. In this case protonation of the more basic amine in the ligand occurs before reduction of the complex to Co(I), and this protonation results in rapid loss of ligand. Similar decomposition of the catalyst 2-Ph is also observed when stronger acids such as 2,6-dichloroanilinium tetrafluoroborate are used. Our earlier observation that [Co(PPh₂NPh₂)(CH₂CN)](BF₄)₂] is an effective catalyst even in the presence of triflic acid suggests that the introduction of the tert-butyl substituent significantly reduces the overall stabilities of the complexes toward toward acid catalysis. The nickel complexes 3-Ph and 3-Bz were also found to be ineffective as catalysts for hydrogen formation. The relatively positive potentials observed for the Ni(II/I) couples in these complexes (see Table 3) require that somewhat stronger acids be used than in the cobalt systems, and under these conditions complex decomposition, via ligand protonation and dissociation, is relatively rapid. Again we note that previously studied [Ni(PPh₂NPh₂)(CH₂CN)](BF₄)₂] derivatives were significantly more stable in the presence of acid. Nevertheless, no evidence for a catalytic wave for hydrogen formation was observed in our studies of 3-Ph and 3-Bz, even at low acid concentrations when the complexes are still intact. The lack of activity is consistent with our earlier observations that two or more basic pyridine bases appear to be important for the catalytic activity of nickel diphosphine complexes.

In summary, our results indicate that cobalt complexes containing a single diphosphine ligand with a positioned pendant base constitute a promising class of catalysts for further study and optimization. The comparative studies reported here are relevant to further catalyst optimization, because they demonstrate that the variation of either the phosphorus or nitrogen substituent in the cyclic PPh₂NPh₂ ligands can result in significant consequences for the metal complex stoichiometry, structure, redox properties, and catalytic activity.

### Experimental Section

#### General Experimental Procedures.

1H and 31P{1H} NMR spectra were recorded on a Varian Inova spectrometer (500 MHz for 1H) at 20 °C unless otherwise noted. All 1H chemical shifts have been internally calibrated to the monoproton impurity of the deuterated solvent. The 31P{1H} NMR spectra were referenced to external phosphoric acid at 0 ppm. Magnetic moments were determined by the Evans method in CD₃CN solution containing SiMe₃. UV–vis spectra were recorded on a Shimadzu UV-2401 PC spectrometer using UV Probe (version 1.1.0) software. MM2 calculations were performed using the software embedded within ChemBio3D Ultra, version 12.0. Gas chromatograms were recorded on an Agilent Technologies 6890 Networks GC system equipped with an Agilent HP-1 column (30 m length x 0.530 mm i.d. x 2.65 μm film) and a thermal conductivity detector using argon as the carrier gas.

Electrochemical measurements were performed using a CH Instruments 660C potentiostat equipped with a standard three-electrode cell consisting of an oven-dried 4–5 mL conical vial fitted with a polysilicone cap having openings sized to closely accept each electrode. For each experiment, the cell was assembled and used under a flow of nitrogen that was bubbled through dry anhydrous. Immediately prior to each measurement, the working electrode (1 mm PEEK-encased glassy carbon, Cypress Systems EE040) was polished using grade 3 alumina polishing ginal (Fisher A446-100) and then rinsed with neat acetonitrile. A glassy-carbon rod (Structure Probe, Inc.) was used as the counter electrode, and a silver wire suspended in a solution of Et₄NBF₄ (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 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. Solvents were purified by passage through neutral alumina using an Innovative Technology, Inc., Pure Solv solvent purification system. NMR solvents were purchased from Cambridge Isotope and were dried, degassed, and distilled prior to use. Tetraethylammonium tetrafluoroborate was dried in vacuo at room temperature for 2 days. Anilinium salts were prepared by reaction of the parent aniline with 1.5 equiv of HBF₄·Et₂O, and then the crude salts were recrystallized from CH₃CN/Et₂O. tert-Butylphosphine was purchased from Strem Chemicals. [Co(CH₃CN)₆](BF₄)₂] and [Ni(CH₃CN)₆](BF₄)₂] were prepared according to literature procedures.

#### Syntheses.

P₂Bu₂NPh₂ tert-Butylphosphine (2.0 mL, 0.016 mol, 1.0 equiv) was measured into a two-neck 100 mL round-bottom flask, which was then fitted with a rubber septum and a gas adapter. Degassed absolute EtOH (ca. 25 mL) was transferred by cannula into the flask, and then solid paraformaldehyde (1.07 g, 0.036 mol, 2.3 equiv) was added. The reaction mixture was stirred in an oil bath at 65 °C for 16 h, resulting in a clear solution. The solution was cooled to room temperature, and then aniline (1.5 mL, 0.016 mol, 1.0 equiv) was added via syringe over 10 min. The reaction mixture was heated in an oil bath at 65 °C for 23 h, causing a white precipitate to form. When the mixture was lowered to room temperature, the volatiles were removed in vacuo. The crude solid was slurried in CH₂CN (25 mL), and then the white powder was collected by vacuum filtration and rinsed with CH₂CN (25 mL) and CH₂Cl₂ (5 × 10 mL). Upon drying in vacuo, P₂Bu₂NPh₂·(2.13 g, 0.005 mol, 63%) was obtained as a white powder. The product displayed a low solubility in both polar and nonpolar solvents. NMR analysis indicated the presence of two isomers in ca. 1:1 ratio in solution, with the observed ratio varying for different samples. 1H NMR integrations were determined individually for each isomer. Crown isomer: 1H NMR (acetonitrile-d₃) δ 7.09 (t, 4H, JHH = 8.1 Hz, Ar H), 6.71 (d, 4H, JHH = 8.1 Hz, Ar H), 6.52 (t, 2H, JHH = 8.1 Hz, Ar H), 4.35 (t, 4H, JHH = 14.8 Hz, PCHeqHaxN), 3.95 (dd, 4H, JHH = 14.8 Hz, JHp = 5.4 Hz, PCHeqHaxN), 1.28 (d, 18H, Jhp = 9.4 Hz, C(CH₃)₃), 31P{1H} NMR (acetonitrile-d₃) δ 27.87 (s). Saddle isomer: 1H NMR (acetonitrile-d₃) δ 7.14 (t, 4H, JHH = 8.1 Hz, Ar H), 6.71 (d, 4H, JHH = 8.1 Hz, Ar H), 6.63 (t, 2H, JHH = 6.7 Hz, Ar H), 4.08 (dd, 4H, JHH = 13.7 Hz, JHp = 4.7 Hz, PCHaxHeqN), 3.71 (t, 4H, JHH = 14.8 Hz, JHp = 4.7 Hz, PCHaxHeqN), 1.23 (d, 18H, Jhp = 10.8 Hz, C(CH₃)₃); 31P{1H} NMR (acetonitrile-d₃) δ −18.24. Anal. Calcd for C₂₆H₃₄N₆P₂: C, 69.54; H, 8.75; N, 6.76. Found: C, 69.63; H, 8.80; N, 6.71.

P₂Bu₂N₂Ph₂ tert-Butylphosphine (5.6 g, 0.062 mol), paraformaldehyde (3.7 g, 0.124 mol), and ethanol (100 mL) were combined in a Schlenk flask and heated to 60 °C for 12 h.

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Benzylamine (6.66 g, 0.062 mol) was then added to the solution dropwise, and the reaction was maintained at 60 °C for another 12 h. The solution was cooled to room temperature, and the solvent was reduced to about 20 mL under reduced pressure and then filtered to isolate the insoluble product. The white precipitate was washed with 3 × 15 mL of ethanol to give 13 g of \( \text{P}^{\text{Bu}}_{2} \text{N}^{\text{Bu}} \text{B}^2 \) (95% yield). \(^1\)H NMR (acetone-\(d_6\)) \(\delta\) 7.39 (d, 4H, \(J_{HH} = 7.0\) Hz, Ar, 7.31 (t, 4H, \(J_{HH} = 7.4\) Hz, Ar, 7.22 (t, 2H, \(J_{HH} = 7.3\) Hz, Ar, 7.39) (300 MHz) in 2.0H, NiCl\(\text{CH}_3\)CN, 3.20 (s, 8H, H\(_{CCH_3}\)). 24P \(^1\)P \(\text{Ni}^{1\text{H}}\) NMR (acetone-\(d_6\)) \(\delta\) -45.1 (br s). \(^1\)H NMR (THF-d\(_8\)) \(\delta\) 7.45–7.10 (12.2H, \(J_{HH} = 7.2\) Hz, Ar, crown + chair + boat), 4.07 (s, 4.0H, NH\(_{CH_3}\)CN, 0.75 (s, 0.5H, N\(_{CH_3}\)CN), 3.72 (s, 0.5H, N\(_{CH_3}\)CN, chair + boat), 3.46 (d, 4.5H, \(J_{HH} = 14.3\) Hz, P\(_{CH_3}\)N, crown + chair - boat), 3.20 (d, 4.0H, \(J_{HH} = 14.4\) Hz, P\(_{CH_3}\)N, crown), 2.87 (d, 0.5H, \(J_{HH} = 11.8\) Hz, P\(_{CH_3}\)N, chair - boat), 2.80 (d, 0.5H, \(J_{HH} = 13.9\) Hz, P\(_{CH_3}\)N, chair - boat), 2.42 (dd, 0.5H, \(J_{HH} = 11.8\) Hz, \(J_{HH} = 27.4\) Hz, P\(_{CH_3}\)N, chair - boat), 0.17 (s, 20.0P, chair - boat), 6.23 (s, 2.0P, crown). Anal. Calcd: C, 46.78; H, 5.89; N, 9.68. \(^{31}\)P \(\text{Ni}^{1\text{H}}\) NMR (CD\(_3\)CN, \(37.5\) (s, 0.5P, chair - boat), 3.31 (P\(_{CH_3}\)N, chair - boat), 3.53 (br s, 3.5H, P\(_{CH_3}\)N, chair - boat), 1.96 (s, 9H, C\(_{2}\)CN). \(^{31}\)P \(\text{Ni}^{1\text{H}}\) NMR (acetone-\(d_6\)) \(\delta\) 1.53 (irrev). Acid Dependence. General Procedure. A 1.5 mL portion of a 0.0020 M solution of catalyst in 0.2 M \(\text{NEt}_4\text{BF}_4/\text{CH}_3\)CN containing ferrocene as a reference was syringed into a CV cell. An initial CV was obtained with a scan rate of 50 mV/s. A 0.50 M solution of acid in 0.2 M \(\text{NEt}_4\text{BF}_4/\text{CH}_3\)CN was then added in sequential aliquots (20 × 15 μL, 3–4 × 150 μL) with a CV being obtained after each addition. The current intensity of the Fe anodic wave was used as an internal reference to adjust the values for \(i_0\) and [acid] to compensate for sample dilution; as the acid solution was introduced.

Acid-Independent Rate. A 1.0 mL portion of a 0.0010 M solution of catalyst in 0.2 M \(\text{NEt}_4\text{BF}_4/\text{CH}_3\)CN containing ferrocene as a reference was syringed into a CV cell. An initial CV was obtained with a scan rate of 50 mV/s. A 1.0 mL solution of 4-bromoanilinium tetrafluoroborate in 0.2 M \(\text{NEt}_4\text{BF}_4/\text{CH}_3\)CN was then added in sequential aliquots (20 × 15 μL, 3–4 × 150 μL) with a CV being obtained after each addition. The current intensity of the Fe anodic wave was used as an internal reference to adjust the values for \(i_0\) and [acid] to compensate for sample dilution; as the acid solution was introduced.

Catalyst Concentration Dependence for \([\text{Co}^{\text{Bu}}_{2}\text{N}^{\text{Bu}}_{2}]_{2}(\text{CH}_3\text{CN})_6][\text{B}^2\text{F}_4]\). A 1.5 mL portion of an acetonitrile solution that was 0.1 M in 4-bromoanilinium tetrafluoroborate and 0.2 M in \(\text{NEt}_4\text{BF}_4\) containing a ferrocene reference was syringed into a CV cell. Sequential aliquots from a solution that was 0.020 M in \([\text{Co}^{\text{Bu}}_{2}\text{N}^{\text{Bu}}_{2}]_{2}(\text{CH}_3\text{CN})_6][\text{B}^2\text{F}_4]\) in 0.2 M \(\text{NEt}_4\text{BF}_4/\text{CH}_3\)CN were syringed into the CV cell (6 × 20 μL), with a CV being recorded after each addition.

Bulk Electrolysis. A three-necked flask with a stirrer was used for a bulk electrolysis experiment. One neck was a 24/40 joint that accepted a rubber septum through which two lengths of copper wire were fed. One wire was attached to a 1 mm PEEK-encased glassy-carbon electrode for CV measurement, and the second wire was attached to a cylinder of reticulated vitreous carbon as a working electrode for bulk electrolysis. The other two necks of the flask were fed. Both were fitted with glass compartments with Vycor frits on the bottom. One was used as the reference electrode—it was filled with a 0.2 M \(\text{NEt}_4\text{BF}_4\) acetonitrile solution and a Ni–Cr wire. With these fittings attached, the cell had a total volume of 149 mL. The cell was filled from stock solutions to give 18 mL of an acetoniitrile solution that was 0.0010 M in \([\text{Co}^{\text{Bu}}_{2}\text{N}^{\text{Bu}}_{2}]_{2}(\text{CH}_3\text{CN})_6][\text{B}^2\text{F}_4]\), 0.230 M in 4-bromoanilinium tetrafluoroborate, and 0.20 M in \(\text{NEt}_4\text{BF}_4\).
The decay was first-order in time interval using the Beer–Lambert law. Assuming that the decay was first-order in time, the rate of decay \( k \) was determined from the slope of a plot of \( \ln(2-\Phi) \) vs time, and then the half-life was calculated as \( \ln 2/k \).

<table>
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<th>Reaction</th>
<th>([\text{Co}(\text{P}^\text{Bu}_2\text{N}^\text{Ph}_2)^2]_2(\text{CH}_3\text{CN})_3][\text{BF}_4]^2_2, [\text{Co}(\text{P}^\text{Bu}_2\text{N}^\text{Br}_2)^2]_2(\text{CH}_3\text{CN})_3][\text{BF}_4]^2_2, [\text{Ni}(\text{P}^\text{Bu}_2\text{N}^\text{Ph}_2)^2]_2(\text{CH}_3\text{CN})_3][\text{BF}_4]^2_2, )</th>
</tr>
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<tr>
<td>([\text{Co}(\text{P}^\text{Bu}_2\text{N}^\text{Ph}_2)^2]_2(\text{CH}_3\text{CN})_3][\text{BF}_4]^2_2)</td>
<td>([\text{Co}(\text{P}^\text{Bu}_2\text{N}^\text{Br}_2)^2]_2(\text{CH}_3\text{CN})_3][\text{BF}_4]^2_2)</td>
</tr>
<tr>
<td>([\text{Ni}(\text{P}^\text{Bu}_2\text{N}^\text{Ph}_2)^2]_2(\text{CH}_3\text{CN})_3][\text{BF}_4]^2_2)</td>
<td>([\text{Ni}(\text{P}^\text{Bu}_2\text{N}^\text{Br}_2)^2]_2(\text{CH}_3\text{CN})_3][\text{BF}_4]^2_2)</td>
</tr>
</tbody>
</table>

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**Supporting Information Available:** CIF files giving crystallographic data for complexes 2-Ph, 2-Bz, 3-Ph, and 3-Bz, figures giving 2D and variable-temperature NMR spectra, details of MM2 calculations and tables of XYZ coordinates for optimized \( \text{P}^\text{Bu}_2\text{N}^\text{Ph}_2 \) conformers, and additional cyclic voltammetry plots. This material is available free of charge via the Internet at http://pubs.acs.org.