Title
Reactivity of a series of isostructural cobalt pincer complexes with CO2, CO, and H+

Permalink
https://escholarship.org/uc/item/1mz2t2fb

Journal
Inorganic Chemistry, 53(24)

ISSN
0020-1669

Authors
Shaffer, DW
Johnson, SI
Rheingold, AL
et al.

Publication Date
2014-12-15

DOI
10.1021/ic5021725

Peer reviewed
Reactivity of a Series of Isostructural Cobalt Pincer Complexes with CO₂, CO, and H⁺


†Department of Chemistry, University of California, Irvine, 1102 Natural Sciences 2, Irvine, California 92697, United States
‡Joint Center for Artificial Photosynthesis, California Institute of Technology, Pasadena, California 91125, United States
§Department of Chemistry, California Institute of Technology, Pasadena, California 91125, United States
∥Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093, United States

Supporting Information

ABSTRACT: The preparation and characterization of a series of isostructural cobalt complexes \([\text{Co}(\text{t}-\text{Bu})_2\text{P}^\text{III}\text{Py}^\text{II}(\text{t}-\text{Bu})_2(\text{CH}_3\text{CN})_2]^{-}[\text{BF}_4]_2\) (Py = pyridine, E = CH₃, NH, O, and X = BF₄ (1a−c)) and the corresponding one-electron reduced analogues \([\text{Co}(\text{t}-\text{Bu})_2\text{P}^\text{III}\text{Py}^\text{II}(\text{t}-\text{Bu})_2(\text{CH}_3\text{CN})_2][\text{BF}_4]_2\) (2a−c) are reported. The reactivity of the reduced cobalt complexes with CO₂, CO, and H⁺ to generate intermediates in a CO₂ to CO and H₂O reduction cycle are described. The reduction of 1a−c and subsequent reactivity with CO₂ was investigated by cyclic voltammetry, and for 1a also by infrared spectroelectrochemistry. The corresponding CO complexes of (2a−c) were prepared, and the Co−CO bond strengths were characterized by IR spectroscopy. Quantum mechanical methods (B3LYP-d3 with solvation) were used to characterize the competitive reactivity of the reduced cobalt centers with H⁺ versus CO₂. By investigating a series of isostructural complexes, correlations in reactivity with ligand electron withdrawing effects are made.

INTRODUCTION

There is great interest in using CO₂ as a feedstock for generating chemical fuels from renewable energy sources.¹ A potential high-value transformation is the two electron reduction of CO₂ to produce CO, which can be combined with H₂ generated from renewable sources⁵ to produce liquid hydrocarbon fuels through industrial Fischer–Tropsch processes.³ However, fast and efficient catalysts composed of abundant metals are still needed for the selective reduction of CO₂ to CO.¹⁻⁵

The Sabatier principle is effective at describing catalytic activity to guide the development of new catalysts.⁵ This concept illustrates the importance of balancing substrate and product interaction at a catalyst active site in order to achieve high efficiency and reaction rate. The effect of maximizing substrate interaction while minimizing product interaction is often depicted as a volcano plot. We are interested in applying this principle, commonly used to describe catalytic activity relationships in heterogeneous systems, to the design of molecular transition metal catalysts for CO₂ reduction to CO. By adjusting the ligand properties, we can modify the energy of CO₂ binding and CO release at a single metal site.

For this study, a series of isostructural cobalt complexes using pincer ligands of varying electron withdrawing character was synthesized and studied. The complexes are shown in Chart 1. Cobalt complexes with these pincer ligands have been previously studied for their physical properties,⁶ and recent work has focused on catalytic applications such as C−H activation,⁷ borylation,⁸ and olefin polymerization.⁹ The combination of the pyridine backbone and phosphine arms provides stability toward reducing conditions. The meridional tridentate ligand scaffold leaves an open coordination site trans to the pyridine for CO₂ binding, which is reminiscent of triphosphine complexes that show catalytic activity for reduction of CO₂ to CO.¹⁰ Additionally, the ligand variants with CH₃, NH, and O bridges between the pyridine and phosphine are readily synthesized and represent a stepwise increase in the electron withdrawing nature of the ligand without altering the primary coordination sphere. Although there are several examples of molecular cobalt complexes that have activity toward CO₂ reduction,¹¹ the use of these ligand environments has been minimally explored.¹²

Received: September 8, 2014
Published: December 3, 2014
Reduction of CO₂ to CO requires formal loss of an O²⁻ dianion. In other examples of catalytic reduction, stoichiometric amounts of oxygen atom acceptors (i.e., diboron, borane, hydrosilane, or anhydrides) have been used to close the catalytic cycle. However, the formation of strong bonds with oxygen acceptors precludes an efficient energy-storing catalytic cycle. An ideal scenario would utilize protons as a stoichiometric O atom acceptor to generate water, as shown in eq 1. However, this adds the complication of competitive proton binding at the reduced metal center and can result in reduction of protons instead of CO₂. Therefore, we also examined the relationship between the redox properties of the complexes and pKₐ of the reduced metal centers. The thermodynamic and kinetic parameters for CO₂, CO, and H⁺ binding are all important considerations for selective catalyst design for the reaction shown in eq 1.

\[
\text{CO}_2 + 2e^- + 2H^+ \rightarrow \text{CO} + \text{H}_2\text{O}
\]

\[
E^{\circ}_{\text{red}} = -0.53 \text{ V at pH 7 vs NHE}
\]

## RESULTS AND DISCUSSION

**Synthesis, Characterization, and Structural Studies of [(P[N^N][P]Co(NCCCH₃)](BF₄)] (1a–c).** The series of [(P[N^N][P]Co(NCCCH₃)](BF₄)] (E = C, 1a; N, 1b; O, 1c) complexes were prepared by addition of the free ligands to [Co(NCCCH₃)](BF₄)]. For all three ligands, addition of solid P[N^N][P] to an acetonitrile solution of [Co(NCCCH₃)](BF₄)] produced a dark orange solution. Removal of solvent in vacuo resulted in dark orange oils that precipitated the products as orange powders upon stirring in THF or benzene.

Two variations of the Co(II)–P[N^N][P] tetrafluoroborurate salt were obtained using different methods of recrystallization. Diffusion of pentane into a saturated dichloromethane solution produced orange crystals of the 5-coordinate cobalt complex with one acetonitrile ligand in the plane of the P[N^N][P] ligand and an axial BF₄⁻ with a Co−F distance of 2.3446(9) Å. The structure for this complex with the formula [(P[N^N][P]Co(NCCCH₃)](BF₄)](BF₄)] is shown in Figure S1 in the Supporting Information. The value of τ₅ is 0.18, and the sum of the angles around the basal plane is 358.7°. However, elemental analysis of crystals grown from acetonitrile/toluene solution was indicative of low-spin, cis Co coordination centers being a bending of the apical NCCH₃ ligand (Figure 1). The dibromide (P[N^N][P]CoBr₂) was also synthesized using CoBr₂ but isolated as the BPh₄⁺ salt by treating it with 2 equiv of NaBPh₄ in CH₂CN, forming the analogous complex [(P[N^N][P]Co(NCCCH₃)](BPh₄)] (1a'). The structure for this complex is shown in Figure 1. The metrical parameters of the BPh₄⁺ salt, which are listed in Table 1, are similar to those of the BF₄⁻-bound salt, with the obvious exception of those involving the pseudoaxial ligand.

X-ray quality crystals of 1b were grown by slow evaporation of acetonitrile from an acetonitrile/toluene solution. The structure of the cationic cobalt complex of 1b, which is shown in Figure 2, is similar to that of 1a', with the most notable difference being a bending of the apical NCCH₃ ligand away from the pyridine that is manifested in a larger Npy−Co−Npydial angle. The τ₅ value for 1b is 0.08. The reaction between P[N^N][P] and [Co(NCCCH₃)](BF₄)] (1c) proceeded similarly; however, attempts at growing X-ray quality crystals resulted in oils and decomposition products. One attempt resulted in a crystallographically characterized macrocyclic (P,N₂)Co complex, possibly formed by nucleophilic attack of a (O-py-O)²⁻ fragment on a (P[N^N][P]Co complex. An analogous nickel example of the same decomposition pathway has been described.

**Magnetic Properties of [(P[N^N][P]Co(NCCCH₃)](BF₄)] (1a–c).** The spin states of the complexes were experimentally determined to facilitate the computational studies. EPR spectra at 77 K for 1a–c are indicative of low-spin, S = 1/2 systems (shown in Figure 3). EPR spectra 1a and 1b were taken in frozen EtOH solutions; 1c is unstable in EtOH, so its spectrum was collected in 1:1 CH₂CN/THF. The signals for 1a–c were centered at g = 2.28, 2.26, and 2.24, respectively, with hyperfine coupling to the cobalt center of 94, 91, and 85 G, respectively. The same spin state is observed at room temperature using the Evans method measurements for complexes 1a–c.

<table>
<thead>
<tr>
<th>Bond</th>
<th>1a</th>
<th>1b</th>
<th>2b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–Npy</td>
<td>1.9632(15)</td>
<td>1.9480(13)</td>
<td>1.925(3)</td>
</tr>
<tr>
<td>Co–P₁</td>
<td>2.2761(6)</td>
<td>2.2625(4)</td>
<td>2.1854(7)</td>
</tr>
<tr>
<td>Co–P₂</td>
<td>2.3030(6)</td>
<td>2.2893(4)</td>
<td>2.1854(7)</td>
</tr>
<tr>
<td>Co–L₅</td>
<td>1.9002(16)</td>
<td>1.8963(13)</td>
<td>1.834(3)</td>
</tr>
<tr>
<td>Co–L₆</td>
<td>2.0868(17)</td>
<td>2.0720(14)</td>
<td></td>
</tr>
<tr>
<td>Npy−Co−L₅</td>
<td>176.97(7)</td>
<td>168.5(5)</td>
<td>177.68(13)</td>
</tr>
<tr>
<td>P−Co−P</td>
<td>160.17(2)</td>
<td>163.41(17)</td>
<td>168.47(4)</td>
</tr>
<tr>
<td>τ₅</td>
<td>0.28</td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>

*In Figure 3, the ORTEP diagram of [(P[N^N][P]Co(NCCCH₃)](BPh₄)] (1'). Ellipsoids are shown at 50% probability. Hydrogen atoms (except –CH₂–), a molecule of CH₃CN, and two BPh₄⁻ ions have been omitted for clarity.*
Figure 2. ORTEP diagram of [(P^N^P)^Co(NCCH_3)_2][BF_4]_2 (1b). Ellipsoids are shown at 50% probability. Hydrogen atoms (except N-H), a molecule of CH_3CN, and BF_4^- ions have been omitted for clarity.

Figure 3. EPR spectra for [(P^N^P)^Co(NCCH_3)_2][BF_4]_2 (E = C, 1a, top/black; N, 1b, middle/blue) in EtOH at 77 K and [(P^N^P)^Co(NCCH_3)_2][BF_4]_2 (1c, bottom/red) in 1:1 CH_3CN/THF.

Electrochemical Studies of (P^N^P)^Co(NCCH_3)_2][BF_4]_2 (1a–c). Cyclic voltammetry of 1a–c (shown in Figure 4) reveals two reduction events. The first reduction, assigned to the Co(II/I) couple (vide infra), is reversible (E_1/2 values are listed in Table 2). This couple becomes more positive from 1a, 1b, to 1c, which is the expected trend as the pincer ligand becomes more electron withdrawing (E = CH_2, NH, O) in this isostructural series. The first reductions of 1a–c display diffusion-controlled behavior (linear relationship between \(i_p\) vs \(\nu^{1/2}\), \(\nu =\) scan rate) for scan rates from 0.025 V/s to 1.60 V/s (see Figure S2 in the Supporting Information).

In the same range of scan rates, the second reduction for 1a–c is completely irreversible (see Supporting Information Figure S3). Although reduced P^N^P cobalt complexes are known to exhibit ligand noninnocence, no redox potential shifts are observed in the reduction of 1a–c for the scan rates investigated (25–1600 mV/s), indicating no chemical change on the electrochemical time scale. However, because of the possibility of ligand redox noninnocence, we have not formally assigned the reduction to a metal centered Co(I/0) event. No trend correlates these reduction potentials with the electronic nature of the ligand; however, as the reduction is not reversible, the observed onset potential may not accurately reflect E_1/2.

Complexes 1a and 1b have irreversible oxidations at 1.33 and 1.20 V, respectively, but 1c displays no oxidation within the limits of the solvent window.

Synthesis and Characterization of [(P^N^P)^Co(NCCH_3)_2][BF_4]_2 (2a–c). The reversible nature of the Co(II/I) couples indicates that the corresponding Co(I) complexes should be stable and isolable. Chemical reductions were carried out to isolate the [(P^N^P)^Co]^+ complexes. Treatment of [(P^N^P)^Co(NCCH_3)_2][BF_4]_2 (1a) with 1 equiv of KC_8 in THF/CH_3CN at ca. 200 K produced a dark green solution. Filtration, solvent removal, and washing the resulting solid with diethyl ether gives [(PCNCP)^Co(NCCH_3)][BF_4]_2 (2a) in 89% yield. Complex 2a is diamagnetic and displays a ^1H NMR spectrum in CD_3CN with resonances at 7.46 ppm (triplet) and 3.11 ppm (singlet) corresponding to the methylene groups, and 7.08 ppm (doublet) corresponding to the aromatic protons. The infrared absorption spectrum of solid 2a reveals an absorption feature at 2229 cm^-1, attributed to the coordinated acetonitrile. Single crystals of 2a were grown by evaporation of CH_3CN from a CH_3CN/toluene solution and evaluated by X-ray crystallography. The resulting structure confirmed the connectivity as 4-coordinate [(P^N^P)^Co(NCCH_3)][BF_4]_2 and is shown in Supporting Information Figure S10; however, the data was not of high enough quality for a refined structure. The formulation was also supported by atmospheric-pressure chemical ionization mass spectrometry (APCI-MS), which displayed peaks at m/z of 495.4 and 454.4, corresponding to

Table 2. Redox Potentials versus Fe(Cp)_2^{+/0} for [(P^N^P)^Co(NCCH_3)_2][BF_4]_2 (E = C, 1a; N, 1b; O, 1c)

<table>
<thead>
<tr>
<th>compd</th>
<th>(E_{pa})(red1)</th>
<th>(E_{pa})(red2)</th>
<th>(E_{pa})(ox)</th>
<th>(E_{pa})(red1)</th>
<th>(E_{pa})(red2)</th>
<th>(E_{pa})(ox)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>-2.83</td>
<td>-2.45</td>
<td>-1.03</td>
<td>1.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>-2.56</td>
<td>-0.88</td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>-2.27</td>
<td>-0.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
[(P^6N^3P)Co(NCCH_3)]^+ and [(P^6N^3P)Co]^+, respectively, and no peak corresponding to [(P^6N^3P)Co(NCCH_3)]^2^+. [(P^6N^3P)Co(NCCH_3)][BF_4] (2b) was obtained in a procedure similar to that of 2a. Treatment of a solution of 1b in THF/CH_3CN with 1 equiv of KC_8 caused a color change from dark orange to dark purple. Filtration, removal of solvent, and washing with diethyl ether provides 2b in 93% yield. The ^1H NMR of 2b in CD_3CN contains peaks at 7.16 ppm (triplet) and 6.01 ppm (doublet) corresponding to the aromatic protons and a broad singlet at 1.47 ppm corresponding to the tert-butyl group. The N–H protons appear as a broad singlet at 6.48 ppm. The ^31P NMR spectrum displays a broad peak at 121.0 ppm. The IR absorption spectrum of solid 2b displays a clear N–H stretch at 3322 cm^−1 and a peak at 2213 cm^−1 attributed to the coordinated acetonitrile. APCI-MS verified the formulation of 2b, exhibiting peaks at 497.4 and 456.3, corresponding to [(P^6N^3P)Co(NCCH_3)]^+ and [(P^6N^3P)-Co]^+, respectively. No significant peak was observed corresponding to [(P^6N^3P)Co(NCCH_3)]^2^+. Crystals of sufficient quality for analysis by X-ray diffraction were grown by cooling a saturated CH_3CN/toluene solution to 238 K. The structure, shown in Figure 5, reveals a square-planar geometry around the cobalt(I) center, with the angles around the metal center summing to 360.2°. Shorter metal–ligand bond distances relative to 1b are consistent with stronger σ-bonding for the more electron-rich metal center. Elemental analysis of these crystals confirmed the formulation as [(P^6N^3P)Co(NCCH_3)]; [BF_4].

Complex 2c was synthesized by stirring the free P^6N^3P ligand with [Co(NCCH_3)]_4[BF_4]_2 in THF/CH_3CN, followed by cooling to 238 K and addition of an equivalent of KC_8. The dark purple product, 2c, was filtered, washed with diethyl ether, and isolated in 72% yield. The ^1H NMR spectrum displayed aromatic peaks at 7.67 ppm (triplet) and 6.55 ppm (doublet) and a tert-butyl resonance at 1.56 ppm. The solid state IR spectrum exhibits a peak at 2250 cm^−1. The formulation of 2c was also supported by APCI-MS, which contained peaks at m/z of 499.3 and 458.3, corresponding to [(P^6N^3P)Co(NCCH_3)]^+ and [(P^6N^3P)Co]^+, respectively, and no peak corresponding to [(P^6N^3P)Co(NCCH_3)]^2^+.

Electrochemical Reduction of [(P^6N^3P)Co(NCCH_3)]^2^−-[BF_4]_2 (1a–c) under 1 atm CO_2. The reactivity of CO_2 with the reduced forms of 1a–c was examined by cyclic voltammetry in CO_2-saturated acetonitrile. Figure 6 displays voltammograms of 1a–b and 2c under nitrogen (dotted lines) and carbon dioxide (solid lines). Due to the instability of 1c (which slowly decomposed in solution), 2c was used in its place for electrochemical reactivity experiments. For all three compounds there is no difference in the Co(II/I) couple between the voltammograms under CO_2 versus N_2, remaining fully reversible at scan rates from 0.0125 to 1.6 V/s (shown in Figure S4 in the Supporting Information), indicating the Co(I) complexes are unreactive to CO_2. This was confirmed by adding CO_2 to 2a; after 10 min, the ^1H and ^31P NMR spectra exhibited no observable change.

The second reduction for 1a–c, on the other hand, exhibits significantly different behavior in the presence of CO_2, displaying a positive shift in the reduction potential that varies with scan rate and ligand substituent. For 1a, at slower scan rates, the second reductive wave under CO_2 appears positive relative to that under N_2. Figure 7, left, shows cyclic voltammograms of 1a under CO_2 at different scan rates (ν), normalized by dividing the current by ν^−1/2. Two peaks in the cathodic current are observed (in addition to the reversible first reduction): the first at approximately −2.2 V, and the second at approximately −2.5 V (similar to the potential under N_2). At scan rates ≤125 mV/s, the former shows some reversibility, whereas the more negative reduction is irreversible at all scan rates. The shift in reduction potential relative to the reduction under N_2 reaches a maximum of 300 mV at the slowest scan rate. The second reductive wave under CO_2 appears positive relative to CO_2 at different scan rates (ν) normalized by ν^−1/2. At scan rates ≤25 mV/s, the second reduction of 1b under CO_2 at different scan rates (ν) normalized by ν^−1/2. At scan rates ≤25 mV/s, the second reduction of 1b under CO_2 at different scan rates (ν) normalized by ν^−1/2.

Figure 6. Cyclic voltammograms of [(P^6N^3P)Co(NCCH_3)]_2[BF_4]_2 (E = C, 1a, top; N, 1b, middle, blue) and [(P^6N^3P)Co-(NCCH_3)][BF_4]_2 (2c, bottom, red) under N_2 (dotted lines) and CO_2 (solid lines). 1.0 mM analyte in CH_3CN with 0.20 M Bu_4NBF_4 at 100 mV/s. Arrows indicate the scan direction and the resting potential. Figure 7, middle, shows cyclic voltammograms of 1b at different scan rates (ν), normalized by dividing the current by ν^−1/2. Two peaks in the cathodic current are observed (in addition to the irreversible first reduction): the first at approximately −2.2 V, and the second at approximately −2.5 V (similar to the potential under N_2). At scan rates ≤125 mV/s, the former shows some reversibility, whereas the more negative reduction is irreversible at all scan rates. The shift in reduction potential relative to the reduction under N_2 reaches a maximum of 300 mV at the slowest scan rate. The second reduction of 1b at different scan rates (ν) normalized by ν^−1/2.
mV/s, no distinct shift was observed. The cyclic voltammograms for 2c do not show any scan rate dependent reactivity under CO2 at scan rates as low as 12.5 mV/s, shown in Figure 7, right.

Unlike other molecular cobalt-based CO2 reduction catalysts, the Co(I) complexes display no reactivity with CO2.11f This was observed electrochemically for all of the complexes, and confirmed by NMR for 2a. However, reactivity with CO2 is observed at the second reduction event, and was examined in more detail using scan rate dependent cyclic voltammetry. The positive potential shift with decreasing scan rate is consistent with a fast following reaction after the second reduction (kinetic potential shift). Since the concentration of saturated CO2 in acetonitrile19 is over 100-fold higher than the complex in our experimental conditions, the reaction was modeled using pseudo-first-order kinetics. We attempted to model the potential shift to obtain exact kinetic parameters for the reaction with CO2 using DigiElch software. However, the added complication of the irreversible electron transfer step with an irreversible chemical step made extraction of exact kinetic information difficult. Using eq 220 for a first order chemical step following an electron transfer, we have estimated $k_f$ to be about $10^2 - 3$ s$^{-1}$ for the reaction of reduced 1a and 1b with CO2 ($\Delta E$ = potential shift, $\nu$ = scan rate).

$$\Delta E = -\frac{RT}{nF} \left[ 0.780 + \frac{1}{2} \ln \left( \frac{nF\nu}{(kf)RT} \right) \right]$$

(2)

Notably, 1c, with the most positive reduction potential, does not give a discernible kinetic potential shift with CO2, even at the slowest scan rates. Prior analysis of single metal site reactivity toward CO2 points toward a correlation between reduction potential and activation of CO2.14,21 The complexes support this trend since the complex with the most positive reduction potential (1c) shows slow or no reaction with CO2, and the more negative reduction potentials in 1a and 1b are concomitant with more favorable reactivity toward CO2.

**Spectroelectrochemical Investigation of the CO2 Activation Product.** The reaction of the reduced complex 1a with CO2 was investigated by infrared spectroelectrochemistry. A $-2.20$ V potential was applied to a CO2-saturated acetonitrile solution of 1.0 mM 1a containing 0.20 M Bu4NPF6 and 1.0 mM ferrocene, and the difference infrared absorption spectra was measured over 12 min. Figure 8 shows the C–O double- and triple-bond region of the spectra over the course of the experiment. As the sample was electrolyzed, a peak grew in at 1921 cm$^{-1}$. Isotopically labeled 13CO2 was used to authenticate that the observed stretch is a result of CO2 reduction. When the identical experiment was performed with 13CO2, the observed peak shifted to 1876 cm$^{-1}$. This is consistent with the value predicted for a CO bond based on a simple harmonic oscillator.

The CO adduct of 2a, [(P6^3^N^3^P)Co(NCCH3)][BF4], was independently prepared, and solution based IR measurements matched the stretch observed in the spectroelectrochemical experiment (*vide infra*). The initial product for the reaction of CO2 with the two-electron reduced complex is expected to be a metal carboxylate. However, metal carboxylates at basic metal centers can reductively disproportionate to CO and CO3$^{2-}$.22 In essence, a second equivalent of CO2 is acting as the oxygen atom acceptor for the initial CO2 reduction to CO. This would result in the Co(II) carbonyl complex, which is easily reducible under the experimental conditions to the experimentally observed Co(I) carbonyl.
The Sabatier principle describes the importance of both substrate activation and product release for catalysis. This is particularly important as CO is a much better ligand than CO$_2$ for most metal complexes, but must dissociate for the catalyst to turn over. To investigate the CO binding interaction, the cobalt(I) complexes [(P$^\text{N}^\text{P}$)Co(NCC$_3$H$_7$)$_2$][BF$_4$] (2a–c) were treated with CO and the resulting products characterized by $^1$H NMR, $^{31}$P NMR, and IR spectroscopies. In CD$_3$CN, solutions of 2a–c were bubbled with CO under 1 atm to produce new diamagnetic products. Only 2a produced a single product, assigned as [(P$^\text{N}^\text{P}$)Co(CO)][BF$_4$]. For 2a, the $^1$H NMR spectrum of the resulting orange solution indicates clean conversion to a new product with aromatic peaks at 7.72 ppm (doublet). The methylene and conversion to a new product with aromatic peaks at 7.72 ppm NMR spectrum of the resulting orange solution indicates clean conversion to a new product with aromatic peaks at 7.72 ppm CO infrared stretch increases from E = CH$_2$ (1911 cm$^{-1}$) and a weak but sharp signal at 1901 cm$^{-1}$. When taken as a solution droplet with 0.2 M Bu$_4$NBF$_4$ in CH$_3$CN, the carbonyl absorption was observed at 1920 cm$^{-1}$, consistent with the product in the IR spectroelectrochemical experiment described above.

Unlike 2a, treatment of CD$_3$CN solutions of 2b and 2c with CO produced mixtures of two products which were observed by $^1$H and $^{31}$P NMR spectroscopy. Bubbling CO through a dark purple solution of 2b in CD$_3$CN in a septum-capped NMR tube produced a green solution. The $^1$H NMR spectrum of this solution appears to contain a single set of resonances analogous to those obtained from 2a. A broad triplet at 7.45 ppm and a doublet at 6.35 ppm are consistent with the aromatic backbone protons, a broad singlet at 6.99 ppm is consistent with the N–H resonance, and the tert-butyl resonance appears as a virtual triplet at 1.44 ppm. The $^{31}$P NMR spectrum, however, contains two broad peaks at 158.9 and 142.2 ppm, suggesting the presence of two species with overlapping $^1$H NMR signals. No remaining 2b was detected.

The infrared absorption spectrum of this solution taken as an evaporated thin film displays a single strong absorption in the carbonyl region at 1923 cm$^{-1}$ consistent with a cobalt(I)–carbonyl stretch, a very weak additional absorption at 1877 cm$^{-1}$, and a single broad N–H stretch at 3303 cm$^{-1}$. Analogous treatment of a CD$_3$CN solution of 2c with CO resulted in an immediate color change from dark purple to green, and like 2b, the starting material was completely consumed. The resulting $^1$H and $^{31}$P NMR spectra contained resonances corresponding to two different products. In the $^1$H NMR spectrum, two sets of P$^\text{N}^\text{P}$ resonances are clearly represented by two broad triplets at 8.10 and 7.95 ppm, overlapping doublets at 7.0 ppm, and a distorted broad virtual triplet at 1.54 ppm. The products appear in a ratio of approximately 0.6:1.0. The $^{31}$P NMR spectrum contains broad peaks at 238.1 and 229.7 ppm. Thin film IR absorption reveals a single strong absorption in the carbonyl region at 1936 cm$^{-1}$ and a weak but sharp signal at 1901 cm$^{-1}$.

On the basis of the major carbonyl stretch, the Co–CO bond varies in strength by $2a > 2b > 2c$. The increasing electron-withdrawing character of the ligands from CH$_2$ to NH to O substitution is manifested in the CO stretching frequency in addition to the potential of the cobalt(I/II) couple. The major CO infrared stretch increases from E = CH$_2$ (1911 cm$^{-1}$) to E = NH (1923 cm$^{-1}$) to E = O (1936 cm$^{-1}$). The increase in CO bond strength indicates less electron density at the metal for π-backbonding and a more weakly bound M–CO. This presents a dichotomy where metal centers with more negative reduction potentials are more favorable toward CO$_2$ activation, but in turn also have a stronger association with the product. This relationship has also been observed in heterogeneous systems by Norskov et al., where the scaling relationships for CO$_2$ activation and CO release are directly correlated, making catalyst optimization at single metal sites difficult.$^{23}$

**Electrocatalytic Studies.** To test for electrocatalytic activity, 1a was titrated with proton sources and studied by cyclic voltammetry and controlled-potential electrolysies. Cyclic voltammetry during titration of 1a with triethylammonium tetrafluoroborate (pK$_a$ = 18.8 in CH$_3$CN)$^{24}$ resulted in a minor increase in current relative to the acid without complex (see Figure S5 in the Supporting Information). The much weaker acid [HDBU][BF$_4$] was then used (DBU = 1,8-diazabicyclo[5,4,0]undec-7-ene, pK$_a$ = 24.3 in CH$_3$CN)$^{24}$ in an attempt to avoid protonation of the reduced cobalt complex.$^{25}$ This resulted in a current enhancement under N$_2$, which increased under 1 atm of CO$_2$, as shown in Figure 9.

![Figure 9](https://example.com/figure9.png)

Bulk electrolysis was performed with 1a (1.0 mM) and [HDBU][BF$_4$] (50 mM) in CO$_2$-saturated CH$_3$CN solution at $-2.15$ V versus Fe(Cp)$_2$ for 1 h. During electrolysis, the orange solution changed to dark blue-green (consistent with 2a). GC–MS analysis of the headspace detected H$_2$, but no reduced carbon-containing products.

**Competitive Protonation of Reduced [(P$^\text{N}^\text{P}$)Co(NCC$_3$H$_7$)$_2$][BF$_4$] (1a–c).** An external proton source is necessary to complete CO$_2$ reduction to CO and H$_2$. However, addition of protons provides a competitive pathway for proton reduction to generate hydrogen. The expected pathway for the latter would involve protonation at the reduced metal center to give a metal hydride intermediate.$^{26}$

The basicity of cobalt(I) complex 2a was estimated using cyclic voltammetry. The reversibility of the cobalt(II/I) couple ($\approx \approx 1$) was observed as sequentially stronger acids were added (see Supporting Information Figure S6). The reduction remains reversible after the addition of 1 equiv of [HDMF]-[OTf] (DMF = dimethylformamide, OTf = trifluoromethanesulfonate, pK$_a$ = 6.1 in CH$_3$CN).$^{27}$ These results suggest that the pK$_a$ of a protonated [(P$^\text{N}^\text{P}$)CoH] is less than ~6. An NMR scale experiment in which slightly less than 1 equiv of HBF$_4$-OEt$_2$ (pK$_a$ = 1.8 ± 1.5 in CH$_3$CN)$^{28}$ was added to 2a in CD$_3$CN cleanly produced peaks consistent with a [(P$^\text{N}^\text{P}$)-CoH]$_2^+$, placing a lower bound on the pK$_a$ of ~3.$^{29}$

Inorganic Chemistry

**Article**
Overall, the pKₐ of the reduced cobalt complexes was difficult to experimentally measure due to complex instability. Therefore, quantum mechanical methods (B3LYP-d3 including PBF continuum solvation) were employed to gauge the relative energies of intermediates involved with CO₂ and H⁺ reduction pathways for the most electron donating and withdrawing ligands, P⁶N⁰P and P⁶N⁰P. Free energies for the reaction of solvent complexes with CO₂ and protons can be seen in Scheme 1. For both ligands, the Co(I) and Co(II) complexes

![Scheme 1. Calculated pKₐ Values and CO₂ Binding Energies for the Reduction of 1a and 1c](image)

lowest in free energy contain two acetonitrile molecules. The second solvent molecule is weakly bound by 2.2 kcal/mol for the P⁶N⁰P complex. It is thermodynamically unfavorable by >20 kcal/mol for the Co(II) complexes (1a and 1c) to lose one acetonitrile ligand and react with CO₂. The high-energy complex loosely binds CO₂ at the equatorial position through ligands, PCNCP and PONOP. Free energies for the reaction of pathways for the most electron donating and withdrawing ligands, P⁶N⁰P and P⁶N⁰P. Free energies for the reaction of solvent complexes with CO₂ and protons can be seen in Scheme 1. For both ligands, the Co(I) and Co(II) complexes

in 1 M DBU. ΔG in 1 M H⁺, both in CH₃CN. Potentials reported with respect to FeCp₂⁺/0.

The quantum mechanical studies suggest that the neutral complexes should favorably react with CO₂ by 7.1 and 12.9 kcal/mol for the P⁶N⁰P and P⁶N⁰P complexes, respectively. This mirrors the experimental findings which indicate reactivity with CO₂ after reducing the Co(I) complex. In contrast to 2a, the cyclic voltammogram of 2c did not exhibit a kinetic potential shift with low scan rates upon reduction of 2c, indicating a slower reaction with CO₂. However, an increase in current is observed under CO₂, indicating the reaction does proceed, to an extent, on the electrochemical time scale.

With the extra electron density provided by the second reduction, the lone pair from Co is donated into the π* orbital of the CO₂, bending the C-bound CO₂ adduct. This is similar to the bonding that occurs with the bent CH₃CN adduct. The competing reaction with protons is also favorable. At pH ≈ 24.3, reaction with protons is exergonic by 7.0 kcal/mol for the P⁶N⁰P complex, and 10.6 kcal/mol for the P⁶N⁰P complex.

**CONCLUSION**

The reduction and reactivity with CO₂, CO, and H⁺ were examined using experimental and quantum mechanical methods for a series of isomeric cobalt complexes with stepwise changes in the electronic structure. These substrates are important because the design of selective CO₂ to CO and H₂O reduction catalysts involves the competitive reaction of CO₂ over H⁺ at reduced metal centers and facile removal of the CO product.

Previous experimental studies have indicated that both CO₂ binding and protonation become more energetically favorable with increasing metal basicity, which is also observed with these complexes. An important result is that while the free energy of protonation can be tuned by adjusting the pKₐ of the acid, this has only a minimal effect on the free energy of CO₂ binding.

In the case of these complexes, the acid used in the electrolysis studies, [HDBU][BF₄] (pKₐ = 24.3), was insufficiently weak to prevent protonation at the metal centers. A much weaker acid (pKₐ > 36 in CH₃CN) would be necessary to avoid competitive hydrogen formation. However, metal centers with lower pKₐ values would allow the use of
weaker acids to circumvent a hydrogen production pathway, a strategy that has been demonstrated for another transition metal electrocatalyst.25

**EXPERIMENTAL SECTION**

**Synthetic Methods and Materials.** The complexes described below are air- and moisture-sensitive, and must be handled under an inert atmosphere of nitrogen using standard glovebox and Schlenk techniques. Unless otherwise noted, all procedures were performed at ambient temperature (21–24 °C). All solvents were sparged with argon and dried using a solvent purification system. Halocarbon solvents were passed through packed columns of neutral alumina and Q5 Reactant. Acetonitrile, ethereal, and halogenated solvents were passed through two columns of neutral alumina. DMF and alcohol solvents were passed through columns of activated molecular sieves.

The ligands P3N2P, P3N2P, and P3N2P and the cobalt starting material [Co(NCCH3)6][BF4]2 were synthesized according to established procedures.23 Potassium graphite (KC6) was synthesized by heating stoichiometric amounts of potassium and graphite in a sealed, evacuated Schlenk flask until a homogeneous bronze-colored powder was obtained. Triethylamine was freeze-thawed three times and dried over molecular sieves. Graphite was dried under vacuum at 150 °C. All other materials, including CO2 (99.999%) and CO (99.5%), were purchased from commercial sources and used without further purification.

**Physical Methods.** Elemental analyses (EA) were performed by Robertson Microlit Laboratories or on a PerkinElmer 2400 Series II CHNS/O analyzer. Electrospray ionization mass spectrometry (ESI-MS) and atmospheric-pressure chemical ionization mass spectrometry (APCI-MS) were performed with a JEOL JMR-600H mass spectrometer or a Waters LCT Premier mass spectrometer. Gas chromatography (GC) was performed on an Agilent Technologies 7890A GC system with front and back TCD channels. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX500 spectrometer with a TCI cryoprobe (400 MHz or 293 °C or 600 MHz) and a Bruker DRX400 with a switchable QNP probe (400 MHz or 140 °C) in dry, degassed solvents.1H NMR spectra were referenced to TMS using the residual proton impurities of the solvent, 13C NMR spectra were referenced to TMS using the natural abundance 13C of the solvent, and 31P NMR spectra were referenced to H3PO4 using the δ scale with the corresponding 1H spectrum. All chemical shifts are reported in the standard δ notation in parts per million; positive chemical shifts are a higher frequency than the reference. Solution magnetic moments were determined by Evans Method using a sealed capillary containing either 5% CHCl3/CDCl3 or 5% CH2Cl2/CD3CN as internal reference. Perpendicular-mode X-band electron paramagnetic resonance (EPR) spectra were collected using a Bruker EMX spectrometer. Infrared (IR) absorption measurements were taken as thin films or compressed solids on a Thermo Scientific Nicolet iS5 spectrophotometer with an iD5 ATR attachment. Spectroelectrochemical experiments were performed using a 3-electrode cell with platinum working, silver reference, and platinum counter electrodes. Background spectra were taken before electrolysis, and difference spectra were collected while applying a controlled potential. For each experiment, potentials were measured and applied relative to an internal ferrocene reference. Electrochemical experiments were carried out with a Biologic VSP-300 potentiostat or a Pine Wavedriver 10 potentiostat. Electrochemical experiments were carried out in acetonitrile solutions with 1.0 M electrolyte and 0.20 M Bu4NPF6 or Bu4NBF4. The working electrode was a glassy carbon disc with a diameter of 3 mm or 1 mm, the counter electrode was a glassy carbon rod, and the reference electrode was a silver wire in 0.20 M Bu4NPF6 or Bu4NBF4 in CH3CN separated from the bulk solution by a Vycor frit. Potentials were referenced at 100 mV/s (unless otherwise noted) to the ferrocene/ferrocenium couple at 0 V using ferrocene as an internal reference. Bulk electrolysis was carried out in a 2-compartment cell separated by a fine frit, with the working electrode (vitreous carbon) and reference electrode (silver wire in 0.2 M Bu4NPF6 in CH3CN separated by Vycor frit) in one compartment and the counter electrode (nichrome wire) in the other.

The working compartment contained 1.0 mM 2a, 1.0 mM ferrocene, 0.20 M Bu4NHCO2 and 50 mM [HDBU][BF4] in acetonitrile. The counter compartment contained 1.0 mM ferrocene and 0.20 M Bu4NPF6. The headspace of the working compartment was sampled by syringe.

**Syntheses.** [P3N2P]Co(NCCH3)6[BF4]2 (1a). Solid P3N2P (149.4 mg, 577.7 μmol) was added to a solution of [Co(NCCH3)6][BF4]2 (178.3 mg, 372.4 μmol) in 5 mL of CH3CN. The dark orange solution was stirred at 25 °C for 15 h, and then the solvent was removed in vacuo. The resulting crude product was redissolved in ca. 1 mL of CH2Cl2 with 5 drops of CH3CN and layered with 4 mL of Et2O. After 1 d, the resulting red-colored solid was isolated by filtration and washed with 2 × 4 mL THF (yield 424.2 mg, 92%). Anal. Calcld (Found) for C27H49N3B2F8P2Co (%): C 45.66 (45.91), H 6.95 (6.89), N 11.16 (10.90). μeff (5% CH2Cl2/CD3CN, Evans method, 298 K): 2.0 μB. EPR (EtOH, 77 K): g1 = 2.28, g2 = 2.02, A1 = 94 G.

[4(P3N2P)Co(NCCH3)6][BF4]2 (1b). A stirred orange solution of [Co(NCCH3)6][BF4]2 (143.4 mg, 299.5 μmol) in 8 mL of CH3CN was added solid P3N2P (19.4 mg, 360.4 μmol) resulting in a dark orange solution. After stirring for 12 h at 25 °C, the solvent was removed in vacuo, leaving a sticky dark orange residue. The residue was dissolved in 10 mL of 1:1 toluene/CH3CN, and the vial was placed in a larger container containing ca. 20 mL of toluene. After 2 days, the resulting dark orange crystals were decanted, washed with 2 × 2 mL THF, and dried in vacuo (yield 209.7 mg, 98%). Anal. Calcld (Found) for C27H50N6B2F8P2Co (%): C 45.05 (45.20), H 6.69 (6.56), N 11.16 (10.90). μeff (5% CH2Cl2/CD3CN, Evans method, 298 K): 2.0 μB. EPR (EtOH, 77 K): g1 = 2.26, g2 = 2.01, A1 = 91 G.

[4(P3N2P)Co(NCCH3)6][BF4]2 (1c). A solution of [Co(NCCH3)6][BF4]2 (90.9 mg, 190 μmol) in 7 mL of THF with 1 mL of CH3CN was added solid P3N2P (58.9 mg, 360.4 μmol) resulting in a dark orange solution. After stirring at 25 °C for 1 h, the dark orange solution was evaporated in vacuo to provide crude 2c (yield 134.7 μmol, 99%). All attempts to recrystallize 1c resulted in partial decomposition. EPR (THF/CH3CN, 77 K): g1 = 2.25, g2 = 2.00, A1 = 85 G.

[4(P3N2P)Co(NCCH3)6][BF4]2 (1a′). A colorless solution of P3N2P (200 mg, 506.9 μmol) in 5 mL of CH2Cl2 was added slowly to a 5 mL blue solution of CoBr2 (110.8 mg, 506.9 μmol) in CH3CN. The solution developed a dark purple color immediately upon contact. The crude product (53.6 mg) was dissolved in 5 mL of CH2Cl2 and 1 mL of CH3CN and treated with NaBP3A (59.9 mg, 175 μmol). After stirring for 1 d, 15 drops of CH3CN and 5 drops of toluene were added, and the suspension was filtered. The orange filtrate was dried in vacuo, producing an orange powder which was recrystallized by slow evaporation of a toluene/acetitrile solution. This material was characterized by crystallography only.

[4(P3N2P)Co(NCCH3)6][BF4]2 (2a). A dark orange solution of 1a (123.9 mg, 174.5 μmol) in 2 mL of THF and 2 mL of CH3CN was frozen in a cold well and then allowed to thaw. The just-thawed solution was added solid K6C6 (243.4 mg, 178 μmol), resulting in an immediate color change to dark green. After stirring at room temperature for 4 h, the solution was filtered, and the solvent was removed from the filtrate affording dark green residue. The sticky solid was suspended in 6 mL of Et2O, filtered, and washed with 4 mL of CH2Cl2 and 4 mL of Et2O. The solid was then extracted with 2 × 5 mL 4:1 CH3OH/CH3CN. Removal of solvent from the filtrate provided a dark green residue. Suspend in 4 mL of Et2O and removing the solvent again provided pure 2a as a dark green powder (yield 90.3 mg, 89%). APCI-MS (CH3CN) m/z: 495.4 ([M – BF4]–), 454.4 ([M – CH3CN]BF4)–.) 1H NMR (CD3CN) δ/ppm: 7.46 (d, J = 7.7 Hz, 2H, aryl –H), 6.99 (d, J = 7.7 Hz, 2H, aryl –H), 3.11 (s, 4H, –CH2–), 1.48 (s, 36H, –Bu). 13C(CH3) NMR (126 MHz, CD3CN) δ/ppm: 165.0 (s), 124.4 (t, J = 7.7 Hz, 1H, aryl –H), 120.2 (t, J = 7.7 Hz, 2H, aryl –H), 118.3 (t, J = 7.7 Hz, 2H, aryl –H), 30.5 (t, J = 7.7 Hz, 2H, aryl –H), 28.6 (d, J = 7.7 Hz, 2H, aryl –H), 26.2 (d, J = 7.7 Hz, 2H, aryl –H), 25.6 (d, J = 7.7 Hz, 2H, aryl –H), 22.7 (d, J = 7.7 Hz, 2H, aryl –H), 14.8 (s, 36H, –Bu).
A dark orange solution of 1b (110.1 mg, 155.3 μmol, 1 equiv.) in 4 mL of THF and 1.5 mL of CH₂CN was frozen in a cold well and then allowed to thaw. To the just-thawed solution was added solid KC₈ (21.2 mg, 155 μmol, 1 equiv.), resulting in an immediate color change to dark purple. After stirring at room temperature for 1.5 h, 2 mL of toluene was added, and the solution was filtered. Removal of solvent from the filtrate provided 2b (yield 84.4 mg, 93%). Anal. Calc. (Found) for C₂₂H₂₉NF₆P₆Co: C, 47.28 (47.50); H, 7.59 (7.39); N, 9.59 (9.56). APCI-MS (CH₃CN) m/z: 497.4 ([M – BF₄⁻]) , 456.3 ([M – CH₂CN,BF₄⁻]). ¹H NMR (CD₂CN) δ/ppm: 7.16 (t, J_HH = 8.0 Hz, 1H, aryl–H), 6.48 (br s, 2H, -NH), 6.01 (d, J_HH = 8.0 Hz, 2H, aryl–H), 1.47 (br t, 36H, Bu). IR (solid) ν/cm⁻¹: 3324 (N–H), 2213 (C≡N).

The formally Co(0) solvent complexes are best described as high spin, cationic Co(II) centers antiferromagnetically coupled to radical anionic pyridine ligands. The approximate scheme proposed by Yamaguchi was applied (using the large basis, unsolvated wave functions) to correct electronic energies of the unrestricted doublets for spin-contamination from the higher-energy quartet state. Values of the broken-symmetry doublets ranged from 1.50 to 1.65, leading to corrections of up to 3.2 kcal/mol. Wave functions for Co(II) and (Co) states did not suffer spin contamination.

**ASSOCIATED CONTENT**

Supporting Information CIF files (CCDC deposition numbers) for 1a (1022629), 1a’ (1022631), 1b (1022633), 2a (1022630), and 2b (1022632).

Additional crystallographic data, cyclic voltammograms, ¹H NMR spectra, and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

**Corresponding Author**
E-mail: j.yang@uci.edu.

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This material was based upon work performed at the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993, and additional support from the School of Physical Sciences at the University of California, Irvine. S.I.J. would like to acknowledge support from the National Science Foundation Graduate Research Fellowship under Grant DGE# 1144469. The authors thank C. Tsay and L. Henling for helpful discussions and assistance.

**REFERENCES**


