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### Journal

Inorganic Chemistry, 53(24)

### ISSN

0020-1669

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### Publication Date

2014-12-15

### DOI

10.1021/ic5021725

Peer reviewed

# Reactivity of a Series of Isostructural Cobalt Pincer Complexes with CO<sub>2</sub>, CO, and H<sup>+</sup>

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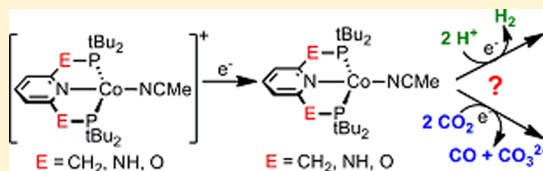
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## Supporting Information

**ABSTRACT:** The preparation and characterization of a series of isostructural cobalt complexes [Co(*t*-Bu)<sub>2</sub>P<sup>E</sup>Py<sup>E</sup>P(*t*-Bu)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (Py = pyridine, E = CH<sub>2</sub>, NH, O, and X = BF<sub>4</sub> (1a–c)) and the corresponding one-electron reduced analogues [Co(*t*-Bu)<sub>2</sub>P<sup>E</sup>Py<sup>E</sup>P(*t*-Bu)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (2a–c) are reported. The reactivity of the reduced cobalt complexes with CO<sub>2</sub>, CO, and H<sup>+</sup> to generate intermediates in a CO<sub>2</sub> to CO and H<sub>2</sub>O reduction cycle are described.

The reduction of 1a–c and subsequent reactivity with CO<sub>2</sub> 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<sup>+</sup> versus CO<sub>2</sub>. By investigating a series of isostructural complexes, correlations in reactivity with ligand electron withdrawing effects are made.



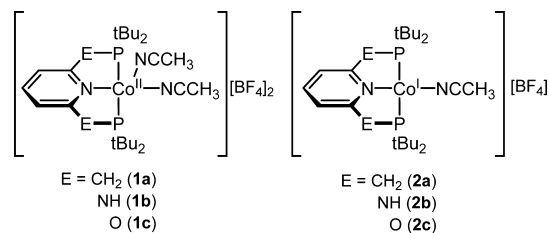
## INTRODUCTION

There is great interest in using CO<sub>2</sub> as a feedstock for generating chemical fuels from renewable energy sources.<sup>1</sup> A potential high-value transformation is the two electron reduction of CO<sub>2</sub> to produce CO, which can be combined with H<sub>2</sub> generated from renewable sources<sup>2</sup> to produce liquid hydrocarbon fuels through industrial Fischer–Tropsch processes.<sup>3</sup> However, fast and efficient catalysts composed of abundant metals are still needed for the selective reduction of CO<sub>2</sub> to CO.<sup>1f–k,4</sup>

The Sabatier principle is effective at describing catalytic activity to guide the development of new catalysts.<sup>5</sup> 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 CO<sub>2</sub> reduction to CO. By adjusting the ligand properties, we can modify the energy of CO<sub>2</sub> 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,<sup>6</sup> and recent work has focused on catalytic applications such as C–H

Chart 1

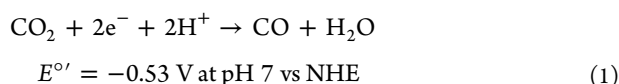


activation,<sup>7</sup> borylation,<sup>8</sup> and olefin polymerization.<sup>9</sup> The combination of the pyridine backbone and phosphine arms provides stability toward reducing conditions. The meridional tridentate ligand scaffold leaves an open coordination site *trans* to the pyridine for CO<sub>2</sub> binding, which is reminiscent of triphosphine complexes that show catalytic activity for reduction of CO<sub>2</sub> to CO.<sup>10</sup> Additionally, the ligand variants with CH<sub>2</sub>, 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 CO<sub>2</sub> reduction,<sup>11</sup> the use of these ligand environments has been minimally explored.<sup>12</sup>

Received: September 8, 2014

Published: December 3, 2014

Reduction of CO<sub>2</sub> to CO requires formal loss of an O<sup>2-</sup> 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.<sup>13</sup> 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 CO<sub>2</sub>.<sup>14</sup> Therefore, we also examined the relationship between the redox properties of the complexes and pK<sub>a</sub> of the reduced metal centers. The thermodynamic and kinetic parameters for CO<sub>2</sub>, CO, and H<sup>+</sup> binding are all important considerations for selective catalyst design for the reaction shown in eq 1.

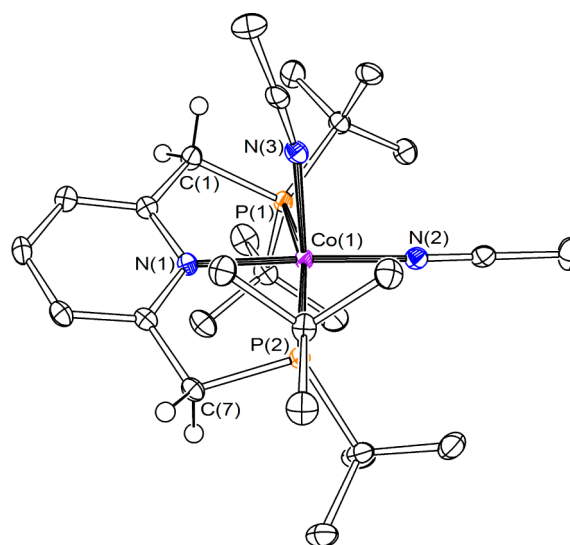


## RESULTS AND DISCUSSION

**Synthesis, Characterization, and Structural Studies of [(P<sup>E</sup>N<sup>E</sup>P)Co(NCCH<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (1a–c).** The series of [(P<sup>E</sup>N<sup>E</sup>P)Co(NCCH<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (E = C, 1a; N, 1b; O, 1c) complexes were prepared by addition of the free ligands to [Co(NCCH<sub>3</sub>)<sub>6</sub>][BF<sub>4</sub>]<sub>2</sub>. For all three ligands, addition of solid P<sup>E</sup>N<sup>E</sup>P to an acetonitrile solution of [Co(NCCH<sub>3</sub>)<sub>6</sub>][BF<sub>4</sub>]<sub>2</sub> 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<sup>C</sup>N<sup>C</sup>P tetrafluoroborate 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<sup>C</sup>N<sup>C</sup>P ligand and an axial BF<sub>4</sub> with a Co–F distance of 2.3446(9) Å. The structure for this complex with the formula [(P<sup>C</sup>N<sup>C</sup>P)Co(NCCH<sub>3</sub>)(BF<sub>4</sub>)]<sub>2</sub> is shown in Figure S1 in the Supporting Information. The value of τ<sub>5</sub> 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 consistent with the formulation [(P<sup>C</sup>N<sup>C</sup>P)Co(NCCH<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (1a). The dibromide (P<sup>C</sup>N<sup>C</sup>P)CoBr<sub>2</sub> was also synthesized using CoBr<sub>2</sub> but isolated as the BPh<sub>4</sub> salt by treating it with 2 equiv of NaBPh<sub>4</sub> in CH<sub>3</sub>CN, forming the analogous complex [(P<sup>C</sup>N<sup>C</sup>P)Co(NCCH<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>]<sub>2</sub> (1a'). The structure for this complex is shown in Figure 1. The metrical parameters of the BPh<sub>4</sub> salt, which are listed in Table 1, are similar to those of the BF<sub>4</sub>-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 NCCH<sub>3</sub> ligand away from the pyridine that is manifested in a larger N<sub>py</sub>–Co–N<sub>axial</sub> angle. The τ<sub>5</sub> value for 1b is 0.08.<sup>15</sup> The reaction between P<sup>O</sup>N<sup>O</sup>P and [Co(NCCH<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (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<sub>2</sub>N<sub>2</sub>)Co complex, possibly formed by nucleophilic attack of a (O-py-O)<sup>2-</sup>



**Figure 1.** ORTEP diagram of [(P<sup>C</sup>N<sup>C</sup>P)Co(NCCH<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>]<sub>2</sub> (1a'). Ellipsoids are shown at 50% probability. Hydrogen atoms (except –CH<sub>2</sub>–), a molecule of CH<sub>3</sub>CN, and two BPh<sub>4</sub><sup>–</sup> ions have been omitted for clarity.

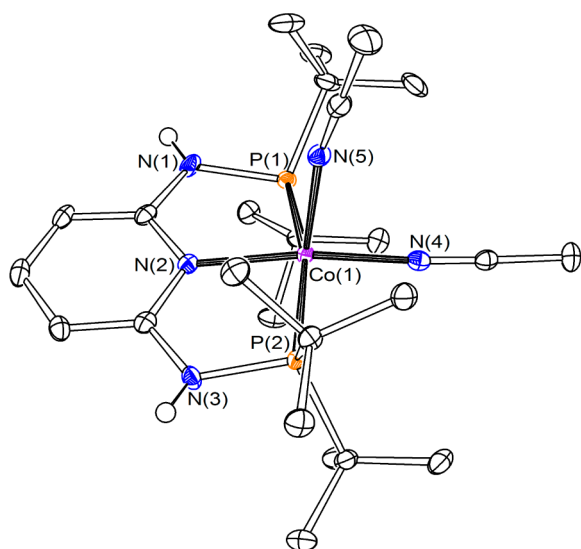
**Table 1.** Selected Bond Distances (Å), Angles (deg), and τ<sub>5</sub> for [(P<sup>C</sup>N<sup>C</sup>P)Co(NCCH<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>]<sub>2</sub> (1a'), [(P<sup>N</sup>N<sup>N</sup>P)Co(NCCH<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (1b), and [(P<sup>N</sup>N<sup>N</sup>P)Co(NCCH<sub>3</sub>)][BF<sub>4</sub>]<sub>2</sub> (2b)<sup>a</sup>

	1a'	1b	2b
Co–N <sub>py</sub>	1.9632(15)	1.9480(13)	1.925(3)
Co–P <sub>1</sub>	2.2761(6)	2.2623(4)	2.1844(7)
Co–P <sub>2</sub>	2.3030(6)	2.2893(4)	2.1843(7)
Co–L <sub>eq</sub>	1.9002(16)	1.8963(13)	1.834(3)
Co–L <sub>ax</sub>	2.0868(17)	2.0720(14)	
N <sub>py</sub> –Co–L <sub>eq</sub>	176.97(7)	168.50(5)	177.68(13)
P–Co–P	160.17(2)	163.416(17)	168.67(4)
τ <sub>5</sub>	0.28	0.08	

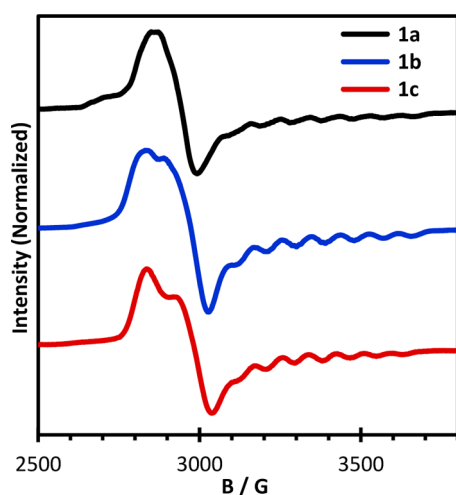
<sup>a</sup>L<sub>eq</sub> and L<sub>ax</sub> indicate the donor atoms of the ligands best described as *trans* and *cis*, respectively, from the pyridine donor N. 2b contains 4 cobalt molecules in the asymmetric unit. Parameters listed above are for a representative molecule in the asymmetric unit cell.

fragment on a (P<sup>O</sup>N<sup>O</sup>P)Co complex. An analogous nickel example of the same decomposition pathway has been described.<sup>16</sup>

**Magnetic Properties of [(P<sup>E</sup>N<sup>E</sup>P)Co(NCCH<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (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 CH<sub>3</sub>CN/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–b in CD<sub>3</sub>CN (5% C<sub>6</sub>H<sub>6</sub> as an internal reference). The magnetic moments (2.0 μ<sub>B</sub>) contrast with the high spin S = 3/2 systems observed for (Ph-P<sup>C</sup>N<sup>C</sup>P)CoX<sub>2</sub> salts (X = Cl, Br, NO<sub>3</sub>; 4.3–4.7 μ<sub>B</sub>), reflecting the stronger field nature of the acetonitrile ligands.<sup>6a,17</sup>



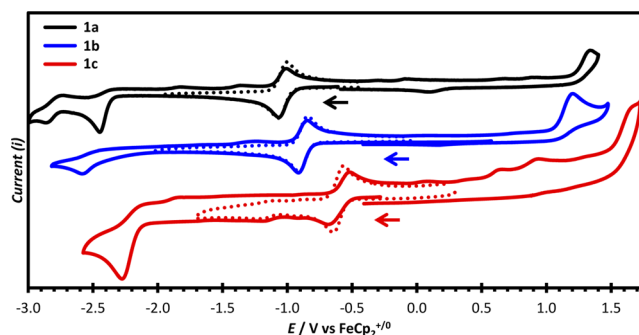
**Figure 2.** ORTEP diagram of  $[(P^{N^N^P})Co(NCCH_3)_2][BF_4]_2$  (**1b**). Ellipsoids are shown at 50% probability. Hydrogen atoms (except N–H), a molecule of  $CH_3CN$ , and  $BF_4^-$  ions have been omitted for clarity.



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

**Electrochemical Studies of  $(P^{E^N^E^P})Co(NCCH_3)_2[BF_4]_2$  (**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  $P^C N^C P$  cobalt complexes are known to exhibit ligand noninnocence,<sup>6d,18</sup> 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



**Figure 4.** Cyclic voltammograms of  $[(P^{E^N^E^P})Co(NCCH_3)_2][BF_4]_2$  ( $E = C$ , **1a**, top, black;  $N$ , **1b**, middle, blue;  $O$ , **1c**, bottom, red). 1.0 mM analyte in  $CH_3CN$  with 0.20 M  $Bu_4NPF_6$  at 100 mV/s. Isolation of the first reduction event is indicated by dotted lines. Arrows indicate scan direction and resting potential.

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

compd	$E_{pc}(\text{red3})$	$E_{pc}(\text{red2})$	$E_{1/2}(\text{red1})$	$E_{pa}(\text{ox})$
<b>1a</b>	−2.83	−2.45	−1.03	1.33
<b>1b</b>		−2.56	−0.88	1.20
<b>1c</b>		−2.27	−0.61	

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  $E_{1/2}$ .

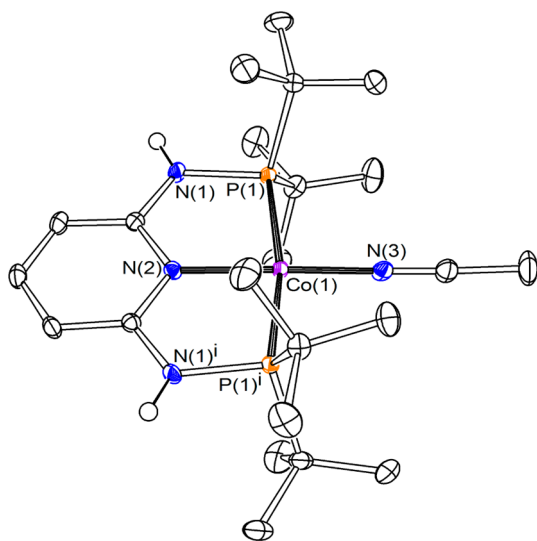
Complexes **1a** and **1b** have irreversible oxidations at 1.33 and 1.20 V, respectively, but **1c** displays no oxidation within the limits of the solvent window.

**Synthesis and Characterization of  $[(P^{E^N^E^P})Co(NCCH_3)] [BF_4]$  (**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  $[(P^{E^N^E^P})Co]^+$  complexes. Treatment of  $[(P^{C^N^C^P})Co(NCCH_3)_2][BF_4]_2$  (**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  $[(P^{C^N^C^P})Co(NCCH_3)][BF_4]$  (**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 7.08 ppm (doublet) corresponding to the aromatic protons, 3.11 ppm (singlet) corresponding to the methylene groups, and 1.48 ppm (broad singlet) corresponding to the *tert*-butyl groups. A peak for the coordinated acetonitrile ligand is not observed presumably due to exchange with the deuterated solvent. A very broad resonance at 103.0 ppm in the  $^{31}P$  NMR spectrum is assigned to the phosphorus atom in the ligand. The infrared absorption spectrum of solid **2a** reveals an absorption feature at  $2229\text{ cm}^{-1}$ , 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  $[(P^{C^N^C^P})Co(NCCH_3)][BF_4]$  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



$[(P^CN^CP)Co(NCCH_3)]^+$  and  $[(P^CN^CP)Co]^+$ , respectively, and no peak corresponding to  $[(P^CN^CP)Co(NCCH_3)_2]^+$ .

$[(P^NN^NP)Co-(NCCH_3)]_2[BF_4]$  (**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  $^{31}P$  NMR spectrum displays a broad peak at 121.0 ppm. The IR absorption spectrum of solid **2b** displays a clear N–H stretch at  $3322\text{ cm}^{-1}$  and a peak at  $2213\text{ cm}^{-1}$  attributed to the coordinated acetonitrile. APCI-MS verified the formulation of **2b**, exhibiting peaks at 497.4 and 456.3, corresponding to  $[(P^NN^NP)Co(NCCH_3)]^+$  and  $[(P^NN^NP)Co]^+$ , respectively. No significant peak was observed corresponding to  $[(P^NN^NP)Co(NCCH_3)_2]^+$ . 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



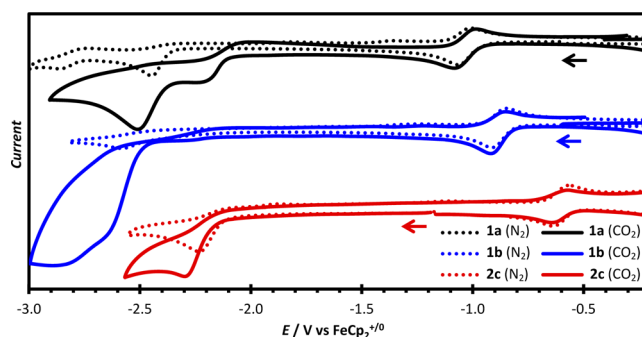
**Figure 5.** ORTEP diagram of one of four molecules in the asymmetric unit  $[(P^NN^NP)Co(NCCH_3)]_2[BF_4]$  (**2b**). Ellipsoids are shown at 50% probability. Hydrogen atoms (except N–H) and a  $BF_4^-$  ion have been omitted for clarity.

cobalt(I) center, with the angles around the metal center summing to  $360.2^\circ$ . Shorter metal–ligand bond distances relative to **1b** are consistent with stronger  $\pi$ -bonding for the more electron-rich metal center. Elemental analysis of these crystals confirmed the formulation as  $[(P^NN^NP)Co(NCCH_3)]_2[BF_4]$ .

Complex **2c** was synthesized by stirring the free  $P^ON^OP$  ligand with  $[Co(NCCH_3)_6][BF_4]_2$  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  $2250\text{ cm}^{-1}$ . The formulation of **2c** was also supported by APCI-MS, which contained peaks at  $m/z$  of 499.3 and 458.3, corresponding to  $[(P^ON^OP)Co(NCCH_3)]^+$

and  $[(P^ON^OP)Co]^+$ , respectively, and no peak corresponding to  $[(P^ON^OP)Co(NCCH_3)_2]^+$ .

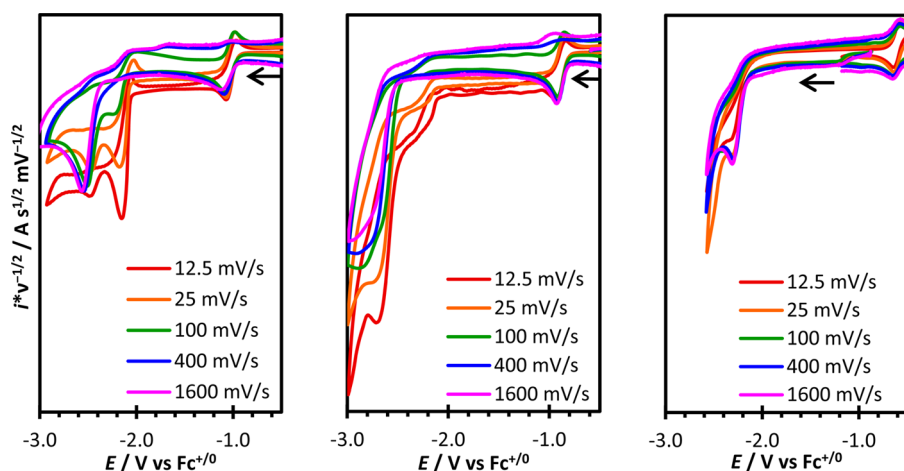
**Electrochemical Reduction of  $[(P^EN^EP)Co(NCCH_3)_2][BF_4]_2$  (**1a–c**) under 1 atm  $CO_2$ .** The reactivity of  $CO_2$  with the reduced forms of **1a–c** was examined by cyclic voltammetry in  $CO_2$ -saturated acetonitrile. Figure 6 displays



**Figure 6.** Cyclic voltammograms of  $[(P^EN^EP)Co(NCCH_3)_2][BF_4]_2$  ( $E = C$ , **1a**, top, black;  $N$ , **1b**, middle, blue) and  $[(P^ON^OP)Co(NCCH_3)]_2[BF_4]$  (**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.

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  $^{31}P$  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 ( $\nu$ ), normalized by dividing the current by  $\nu^{-1/2}$ . Two peaks in the cathodic current are observed (in addition to the reversible first reduction): the first at approximately  $-2.2\text{ V}$ , and the second at approximately  $-2.5\text{ V}$  (similar to the potential under  $N_2$ ). At scan rates  $\leq 125\text{ mV/s}$ , 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 of 12.5 mV/s. At sufficiently fast scan rates ( $\geq 800\text{ mV/s}$ ), no significant shift in potential is observed, though the magnitude of the wave at  $-2.5\text{ V}$  is greater. For **1b**, a similar positive shift is observed in the presence of  $CO_2$ , but without a distinct maximum in  $i_{pc}$  even at scan rates as slow as 12.5 mV/s. Figure 7, middle, shows cyclic voltammograms of **1b** under  $CO_2$  at different scan rates ( $\nu$ ) normalized by  $\nu^{-1/2}$ . At slow scan rates ( $\leq 25\text{ mV/s}$ ), the second reduction of **1b** contains a feature with an onset potential of approximately  $-2.2\text{ V}$  and an irreversible peak at  $-2.7\text{ V}$ . At 12.5 mV/s, a maximum shift of approximately 200 mV was observed for the new feature relative to the reduction under  $N_2$ . At scan rates faster than 200



**Figure 7.** Cyclic voltammograms of  $[(P^E N^E P)Co(NCCH_3)_2][BF_4]_2$  ( $E = C$ , **1a**, left;  $N$ , **1b**, middle) and  $[(P^O N^O P)Co(NCCH_3)_2][BF_4]$  (**2c**, right) at varying scan rates under  $CO_2$ , normalized by dividing the current by  $\nu^{1/2}$ . 1.0 mM analyte in  $CH_3CN$  with 0.20 M  $Bu_4NBF_4$ . Arrows indicate the scan direction and the position of the bulk material.

mV/s, no distinct shift was observed. The cyclic voltammograms for **2c** do not show any scan rate dependent reactivity under  $CO_2$  at scan rates as low as 12.5 mV/s, shown in Figure 7, right.

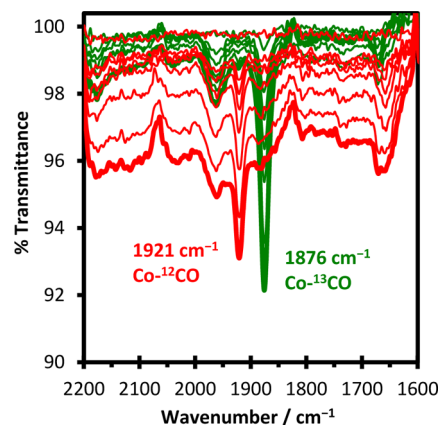
Unlike other molecular cobalt-based  $CO_2$  reduction catalysts, the Co(I) complexes display no reactivity with  $CO_2$ .<sup>11f-i</sup> This was observed electrochemically for all of the complexes, and confirmed by NMR for **2a**. However, reactivity with  $CO_2$  is observed at the second reduction 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  $CO_2$  in acetonitrile<sup>19</sup> 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  $CO_2$  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 2<sup>20</sup> 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  $CO_2$  ( $\Delta E =$  potential shift,  $\nu =$  scan rate).

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

Notably, **1c**, with the most positive reduction potential, does not give a discernible kinetic potential shift with  $CO_2$ , even at the slowest scan rates. Prior analysis of single metal site reactivity toward  $CO_2$  points toward a correlation between reduction potential and activation of  $CO_2$ .<sup>14,21</sup> The complexes support this trend since the complex with the most positive reduction potential (**1c**) shows slow or no reaction with  $CO_2$ , and the more negative reduction potentials in **1a** and **1b** are concomitant with more favorable reactivity toward  $CO_2$ .

**Spectroelectrochemical Investigation of the  $CO_2$  Activation Product.** The reaction of the reduced complex **1a** with  $CO_2$  was investigated by infrared spectroelectrochemistry. A  $-2.20$  V potential was applied to a  $CO_2$ -saturated acetonitrile solution of 1.0 mM **1a** containing 0.20 M  $Bu_4NPF_6$ , 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



**Figure 8.** Spectroelectrochemical infrared difference spectra of  $[(P^C N^C P)Co(NCCH_3)_2][BF_4]_2$  (**1a**) under natural abundance  $CO_2$  (red lines) and  $^{13}CO_2$  (green lines). 1.0 mM analyte in  $CH_3CN$  with 0.20 M  $Bu_4NPF_6$ .

the experiment. As the sample was electrolyzed, a peak grew in at  $1921 cm^{-1}$ . Isotopically labeled  $^{13}CO_2$  was used to authenticate that the observed stretch is a result of  $CO_2$  reduction. When the identical experiment was performed with  $^{13}CO_2$ , 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**,  $[(P^C N^C P)Co(CO)][BF_4]$ , 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  $CO_2$  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  $CO_3^{2-}$ .<sup>22</sup> In essence, a second equivalent of  $CO_2$  is acting as the oxygen atom acceptor for the initial  $CO_2$  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.

### Reaction of $[(P^E N^E P)Co(NCCH_3)]_2[BF_4]_2$ (**2a–c**) with CO.

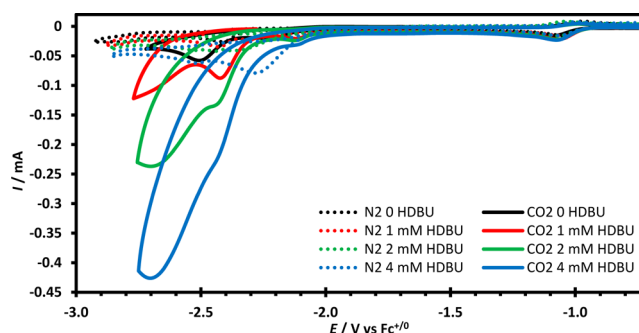
The Sabatier principle describes the importance of both substrate activation and product release for catalysis. This is particularly important as CO is a much better ligand than CO<sub>2</sub> for most metal complexes, but must dissociate for the catalyst to turn over. To investigate the CO binding interaction, the cobalt(I) complexes  $[(P^E N^E P)Co(NCCH_3)]_2[BF_4]_2$  (**2a–c**) were treated with CO and the resulting products characterized by <sup>1</sup>H NMR, <sup>31</sup>P NMR, and IR spectroscopies. In CD<sub>3</sub>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  $[(P^C N^C P)Co(CO)]_2[BF_4]_2$ . For **2a**, the <sup>1</sup>H NMR spectrum of the resulting orange solution indicates clean conversion to a new product with aromatic peaks at 7.72 ppm (triplet) and 7.36 ppm (doublet). The methylene and *tert*-butyl peaks both appear as virtual triplets at 3.86 and 1.42 ppm. The <sup>31</sup>P NMR spectrum displays a single peak at 106.3 ppm. The thin film IR absorption spectrum of  $[(P^C N^C P)Co(CO)]_2[BF_4]_2$  displayed a carbonyl absorption at 1911 cm<sup>-1</sup>. When taken as a solution droplet with 0.2 M Bu<sub>4</sub>NBF<sub>4</sub> in CH<sub>3</sub>CN, the carbonyl absorption was observed at 1920 cm<sup>-1</sup>, consistent with the product in the IR spectroelectrochemical experiment described above.

Unlike **2a**, treatment of CD<sub>3</sub>CN solutions of **2b** and **2c** with CO produced mixtures of two products which were observed by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. Bubbling CO through a dark purple solution of **2b** in CD<sub>3</sub>CN in a septum-capped NMR tube produced a green solution. The <sup>1</sup>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 <sup>31</sup>P NMR spectrum, however, contains two broad peaks at 158.9 and 142.2 ppm, suggesting the presence of two species with overlapping <sup>1</sup>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<sup>-1</sup> consistent with a cobalt(I)–carbonyl stretch, a very weak additional absorption at 1877 cm<sup>-1</sup>, and a single broad N–H stretch at 3303 cm<sup>-1</sup>. Analogous treatment of a CD<sub>3</sub>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 <sup>1</sup>H and <sup>31</sup>P NMR spectra contained resonances corresponding to two different products. In the <sup>1</sup>H NMR spectrum, two sets of P<sup>O</sup>N<sup>O</sup>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 <sup>31</sup>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<sup>-1</sup> and a weak but sharp signal at 1901 cm<sup>-1</sup>.

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<sub>2</sub> to NH to O substitution is manifested in the CO stretching frequency in addition to the potential of the cobalt(II/I) couple. The major CO infrared stretch increases from E = CH<sub>2</sub> (1911 cm<sup>-1</sup>) to E = NH (1923 cm<sup>-1</sup>) to E = O (1936 cm<sup>-1</sup>). The increase in CO bond strength indicates less electron density at the metal for  $\pi$ -back bonding and a more weakly bound M–CO. This presents

a dichotomy where metal centers with more negative reduction potentials are more favorable toward CO<sub>2</sub> 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<sub>2</sub> activation and CO release are directly correlated, making catalyst optimization at single metal sites difficult.<sup>23</sup>

**Electrocatalytic Studies.** To test for electrocatalytic activity, **1a** was titrated with proton sources and studied by cyclic voltammetry and controlled-potential electrolysis. Cyclic voltammetry during titration of **1a** with triethylammonium tetrafluoroborate (pK<sub>a</sub> = 18.8 in CH<sub>3</sub>CN)<sup>24</sup> 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<sub>4</sub>] was then used (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, pK<sub>a</sub> = 24.3 in CH<sub>3</sub>CN)<sup>24</sup> in an attempt to avoid protonation of the reduced cobalt complex.<sup>25</sup> This resulted in a current enhancement under N<sub>2</sub>, which increased under 1 atm of CO<sub>2</sub>, as shown in Figure 9.



**Figure 9.** Cyclic voltammograms of  $[(P^C N^C P)Co(NCCH_3)_2]_2[BF_4]_2$  (**1a**) titrated with  $[HDBU][BF_4]$  (0 mM, black; 1 mM, red; 2 mM, green; 4 mM, blue) under N<sub>2</sub> (dotted lines) and CO<sub>2</sub> (solid lines). 1.0 mM analyte and FeCp<sub>2</sub> internal reference in CH<sub>3</sub>CN with 0.20 M Bu<sub>4</sub>NPF<sub>6</sub> at 100 mV/s.

Bulk electrolysis was performed with **1a** (1.0 mM) and  $[HDBU][BF_4]$  (50 mM) in CO<sub>2</sub>-saturated CH<sub>3</sub>CN solution at -2.15 V versus Fe(Cp)<sub>2</sub><sup>+0</sup> for 1 h. During electrolysis the orange solution changed to dark blue-green (consistent with **2a**). GC–MS analysis of the headspace detected H<sub>2</sub>, but no reduced carbon-containing products.

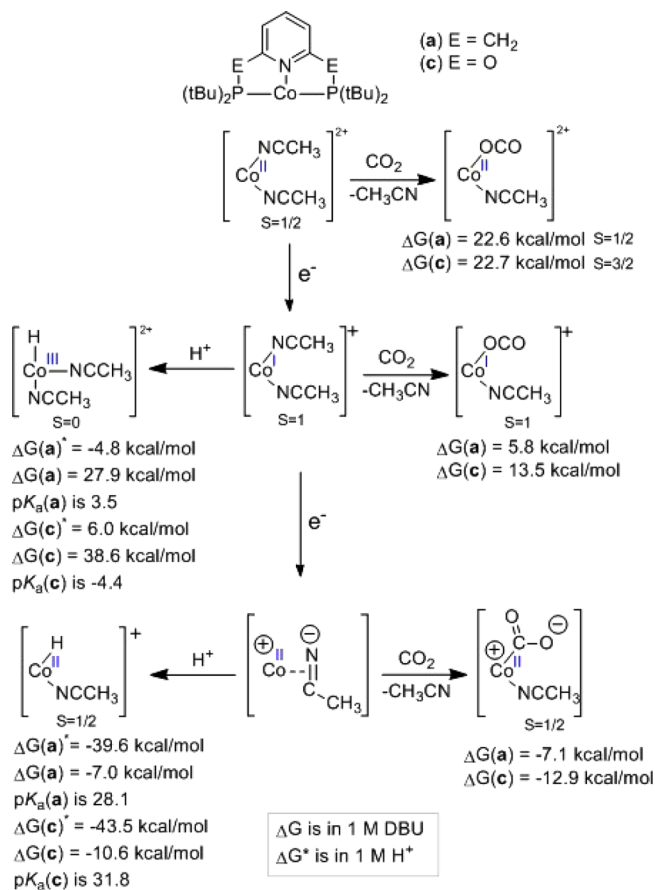
**Competitive Protonation of Reduced  $[(P^E N^E P)Co(NCCH_3)_2]_2[BF_4]_2$  (**1a–c**).** An external proton source is necessary to complete CO<sub>2</sub> reduction to CO and H<sub>2</sub>O. However, addition of protons provides a competitive pathway for proton reduction to generate hydrogen. The expected pathway for the latter would involve protonation at the reduced metal center to give a metal hydride intermediate.<sup>26</sup>

The basicity of cobalt(I) complex **2a** was estimated using cyclic voltammetry. The reversibility of the cobalt(II/I) couple (*i*<sub>pc</sub>/*i*<sub>pa</sub> ≈ 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<sub>a</sub> = 6.1 in CH<sub>3</sub>CN).<sup>27</sup> These results suggest that the pK<sub>a</sub> of a protonated  $[(P^C N^C P)Co^{III}H]^{+2}$  is less than ~6. An NMR scale experiment in which slightly less than 1 equiv of HBF<sub>4</sub>·OEt<sub>2</sub> (pK<sub>a</sub> = 1.8 ± 1.5 in CH<sub>3</sub>CN)<sup>28</sup> was added to **2a** in CD<sub>3</sub>CN cleanly produced peaks consistent with a  $[(P^C N^C P)Co^{III}H]^{+2}$ , placing a lower bound on the pK<sub>a</sub> of ~3.<sup>29</sup>



Overall, the  $pK_a$  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  $\text{CO}_2$  and  $\text{H}^+$  reduction pathways for the most electron donating and withdrawing ligands,  $\text{P}^{\text{CNC}}\text{P}$  and  $\text{P}^{\text{ON}}\text{OP}$ . Free energies for the reaction of solvento complexes with  $\text{CO}_2$  and protons can be seen in Scheme 1. For both ligands, the Co(I) and Co(II) complexes

**Scheme 1.** Calculated  $pK_a$  Values and  $\text{CO}_2$  Binding Energies for the Reduction of **1a** and **1c**<sup>a</sup>



<sup>a</sup> $\Delta G$  energies are calculated in 1 M DBU,  $\Delta G^*$  in 1 M H<sup>+</sup>, both in  $\text{CH}_3\text{CN}$ . Potentials reported with respect to  $\text{FeCp}_2^{+/0}$ .

lowest in free energy contain two acetonitrile molecules. The second solvent molecule is weakly bound by 2.2 kcal/mol for the  $\text{P}^{\text{ON}}\text{OP}$  (**2c**) 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  $\text{CO}_2$ . The high-energy complex loosely binds  $\text{CO}_2$  at the equatorial position through the oxygen. In the  $\text{P}^{\text{CNC}}\text{P}$  complex, the Co–O bond length is calculated to be 2.10 Å, and in  $\text{P}^{\text{ON}}\text{OP}$  complex the bond length is 2.12 Å.

It is also unfavorable for Co(I) (**2a** and **2c**) to react with  $\text{CO}_2$ , and only weakly coordinated complexes form, similar to the Co(II) case. Protonation of Co(I) by  $\text{HDBU}^+$  is also highly endergonic. However, protonation to form  $[(\text{P}^{\text{CNC}}\text{P})\text{Co}^{\text{III}}\text{H}(\text{NCCH}_3)_2]^{+2}$  from **2a** is accessible with strong acids, giving a calculated  $pK_a$  of 3.5, close to the value experimentally measured above. However, **2c** is calculated to be much less

basic, and protonation is not possible in  $\text{CH}_3\text{CN}$ . These results are consistent with our experimental observations.

At more negative potentials, the Co(I) cations can be further reduced, as seen experimentally. In both  $\text{P}^{\text{CNC}}\text{P}$  and  $\text{P}^{\text{ON}}\text{OP}$  complexes, two kinds of low-energy, formally Co(0) structures were identified. When zero, one, or two acetonitrile molecules are coordinated to a neutral  $(\text{P}^{\text{CNC}}\text{P})\text{Co}$  moiety through nitrogen, the wavefunction consists of a triplet Co(I) cation antiferromagnetically coupled to a radical anion ligand with spin distributed around the pyridine ring. The  $\text{P}^{\text{CNC}}\text{P}$  ligands can thus become “redox active”,<sup>6d,18</sup> but not under conditions for neutral-pH, low-overpotential  $\text{CO}_2$  reduction. A few kcal/mol lower in free energy, however, lie neutral  $(\text{P}^{\text{CNC}}\text{P})\text{Co}(\eta^2\text{-NCCH}_3)$  complexes incorporating a  $\pi$ -bound acetonitrile molecule. The Mulliken population on bound  $\text{CH}_3\text{CN}$  ( $-0.75 e^-$ ) and C–N and Co–C bond lengths (1.23 and 1.95 Å, respectively) suggest the description of a  $\eta^2 \pi$ -bound Co(II) metallacycle. Preference for this mode of acetonitrile binding has been observed on other reducing (low oxidation state) metal centers.<sup>30</sup> The existence of isomers with various modes of solvent coordination within 8 kcal/mol of this ground state underscores the fluxional coordination at the reduced metal.

The quantum mechanical studies suggest that the neutral complexes should favorably react with  $\text{CO}_2$  by 7.1 and 12.9 kcal/mol for the  $\text{P}^{\text{CNC}}\text{P}$  and  $\text{P}^{\text{ON}}\text{OP}$  complexes, respectively. This mirrors the experimental findings which indicate reactivity with  $\text{CO}_2$  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  $\text{CO}_2$ . However, an increase in current is observed under  $\text{CO}_2$ , 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  $\pi^*$  orbital of the  $\text{CO}_2$ , bending the C-bound  $\text{CO}_2$  adduct. This is similar to the bonding that occurs with the bent  $\text{CH}_3\text{CN}$  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  $\text{P}^{\text{CNC}}\text{P}$  complex, and 10.6 kcal/mol for the  $\text{P}^{\text{ON}}\text{OP}$  complex.

## CONCLUSION

The reduction and reactivity with  $\text{CO}_2$ , CO, and  $\text{H}^+$  were examined using experimental and quantum mechanical methods for a series of isostructural cobalt complexes with stepwise changes in the electronic structure. These substrates are important because the design of selective  $\text{CO}_2$  to CO and  $\text{H}_2\text{O}$  reduction catalysts involves the competitive reaction of  $\text{CO}_2$  over  $\text{H}^+$  at reduced metal centers and facile removal of the CO product.

Previous experimental studies have indicated that both  $\text{CO}_2$  binding and protonation become more energetically favorable with increasing metal basicity, which is also observed with these complexes.<sup>22d,31</sup> An important result is that while the free energy of protonation can be tuned by adjusting the  $pK_a$  of the acid, this has only a minimal effect on the free energy of  $\text{CO}_2$  binding.

In the case of these complexes, the acid used in the electrolysis studies,  $[\text{HDBU}][\text{BF}_4]$  ( $pK_a = 24.3$ <sup>24</sup> in  $\text{CH}_3\text{CN}$ ), was insufficiently weak to prevent protonation at the metal centers. A much weaker acid ( $pK_a > 36$  in  $\text{CH}_3\text{CN}$ ) would be necessary to avoid competitive hydrogen formation. However, metal centers with lower  $pK_a$  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.<sup>25</sup>

## 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  $P^CN^CP$ ,  $P^NN^NP$ , and  $P^ON^OP$  and the cobalt starting material  $[Co(NCCH_3)_6][BF_4]$  were synthesized according to established procedures.<sup>32</sup> Potassium graphite ( $KC_8$ ) 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–pump–thawed three times and dried over molecular sieves. Graphite was dried under vacuum at 150 °C. All other materials, including  $CO_2$  (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 ( $^1H$  and  $^{13}C$ ) or a DRX400 with a switchable QNP probe ( $^1H$  and  $^{31}P$ ) in dry, degassed solvents.  $^1H$  NMR spectra were referenced to TMS using the residual proteo impurities of the solvent,  $^{13}C$  NMR spectra were referenced to TMS using the natural abundance  $^{13}C$  of the solvent, and  $^{31}P$  NMR spectra were referenced to  $H_3PO_4$  using the  $\Xi$  scale with the corresponding  $^1H$  spectra.<sup>33</sup> All chemical shifts are reported in the standard  $\delta$  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%  $CHCl_3/CDCl_3$  or 5%  $C_6H_6/CD_3CN$  as internal reference.<sup>34</sup> 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 iSS spectrophotometer with an iD5 ATR attachment. Spectroelectrochemical experiments were performed using a 3-electrode cell with platinum working, silver reference, and platinum counter electrodes.<sup>35</sup> 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 mM analyte and 0.20 M  $Bu_4NPF_6$  or  $Bu_4NBF_4$ . 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  $Bu_4NPF_6$  or  $Bu_4NBF_4$  in  $CH_3CN$  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 (vitroous carbon) and reference electrode (silver wire in 0.2 M  $Bu_4NPF_6$  in  $CH_3CN$  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  $Bu_4NPF_6$ , and 50 mM  $[HDBU][BF_4]$  in acetonitrile. The counter compartment contained 1.0 mM ferrocene and 0.20 M  $Bu_4NPF_6$ . The headspace of the working compartment was sampled by syringe.

**Syntheses.**  $[(P^CN^CP)Co(NCCH_3)_2][BF_4]_2$  (**1a**). Solid  $P^CN^CP$  (149.4 mg, 377.7  $\mu$ mol) was added to a solution of  $[Co(NCCH_3)_6][BF_4]_2$  (178.3 mg, 372.4  $\mu$ mol) in 5 mL of  $CH_3CN$ . 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  $CH_2Cl_2$  with 5 drops of  $CH_3CN$  and layered with 4 mL of  $Et_2O$ . After 1 d, the resulting rust-colored solid was isolated by filtration and washed with 2  $\times$  4 mL THF (yield 244.2 mg, 92%). Anal. Calcd (Found) for  $C_{27}H_{46}N_3B_2F_8P_2Co$  (%): C 45.66 (45.91), H 6.95 (6.89), N 5.92 (6.18).  $\mu_{eff}$  (5%  $C_6H_6/CD_3CN$ , Evans method, 298 K): 2.0  $\mu_B$ . EPR (EtOH, 77 K):  $g_1 = 2.28$ ,  $g_2 = 2.02$ ,  $A_2 = 94$  G.

$[(P^NN^NP)Co(NCCH_3)_2][BF_4]_2$  (**1b**). To a stirred orange solution of  $[Co(NCCH_3)_6][BF_4]_2$  (143.4 mg, 299.5  $\mu$ mol) in 8 mL of  $CH_3CN$  was added solid  $P^NN^NP$  (119.4 mg, 360.4  $\mu$ mol) 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/ $CH_3CN$ , 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  $\times$  2 mL THF, and dried *in vacuo* (yield 209.7 mg, 98%). Anal. Calcd (Found) for  $C_{27}H_{50}N_6B_2F_8P_2Co$  (**1b-CH<sub>3</sub>CN**) (%): C 43.05 (43.20), H 6.69 (6.56), N 11.16 (10.90).  $\mu_{eff}$  (5%  $C_6H_6/CD_3CN$ , Evans method, 298 K): 2.0  $\mu_B$ . EPR (EtOH, 77 K):  $g_1 = 2.26$ ,  $g_2 = 2.01$ ,  $A_2 = 91$  G.

$[(P^ON^OP)Co(NCCH_3)_2][BF_4]_2$  (**1c**). To a solution of  $[Co(NCCH_3)_6][BF_4]_2$  (90.9 mg, 190  $\mu$ mol) in 7 mL of THF with 1 mL of  $CH_3CN$  was added solid  $P^ON^OP$  (75.8 mg, 190  $\mu$ mol). After stirring at 25 °C for 1 h, the dark orange solution was evaporated *in vacuo* to provide crude **2c** (yield 134.7 mg, 99%). All attempts to recrystallize **1c** resulted in partial decomposition. EPR (THF/ $CH_3CN$ , 77 K):  $g_1 = 2.24$ ,  $g_2 = 2.00$ ,  $A_2 = 85$  G.

$[(P^CN^CP)Co(NCCH_3)_2][BPh_4]_2$  (**1a'**). A colorless solution of  $P^CN^CP$  (200.5 mg, 506.9  $\mu$ mol) in 5 mL of  $CH_2Cl_2$  was added slowly to a 5 mL blue solution of  $CoBr_2$  (110.8 mg, 506.5  $\mu$ mol) in  $CH_3CN$ . The solution developed a dark purple color and was stirred for 12 h. The solvent was then removed *in vacuo*. The crude product (53.6 mg) was dissolved in 5 mL of  $CH_2Cl_2$  and 1 mL of  $CH_3CN$  and treated with  $NaBPh_4$  (59.9 mg, 175  $\mu$ mol). After stirring for 1 d, 15 drops of  $CH_3CN$  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/acetonitrile solution. This material was characterized by crystallography only.

$[(P^CN^CP)Co(NCCH_3)_2][BF_4]_2$  (**2a**). A dark orange solution of **1a** (123.9 mg, 174.5  $\mu$ mol) in 2 mL of THF and 2 mL of  $CH_3CN$  was frozen in a cold well and then allowed to thaw. To the just-thawed solution was added solid  $KC_8$  (24.3 mg, 178  $\mu$ mol), 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  $Et_2O$ , filtered, and washed with 4 mL of  $C_6H_6$  and 4 mL of  $Et_2O$ . The solid was then extracted with 2  $\times$  5 mL 4:1  $C_6H_6/CH_3CN$ . Removal of solvent from the filtrate provided a dark green residue. Suspending in 4 mL of  $Et_2O$  and removing the solvent again provided pure **2a** as a dark green powder (yield 90.3 mg, 89%). APCI-MS ( $CH_3CN$ )  $m/z$ : 495.4 ( $[M - BF_4]^+$ ), 454.4 ( $[M - CH_3CN, BF_4]^+$ ).  $^1H$  NMR ( $CD_3CN$ )  $\delta$ /ppm: 7.46 (t,  $^3J_{HH} = 7.7$  Hz, 1H, aryl-H), 6.99 (d,  $^3J_{HH} = 7.7$  Hz, 2H, aryl-H), 3.11 (s, 4H,  $-CH_2-$ ), 1.48 (s, 36H,  $^tBu$ ).  $^1H$  NMR ( $d_6$ -acetone)  $\delta$ /ppm: 7.55 (t,  $^3J_{HH} = 7.6$  Hz, 1H, aryl-H), 7.08 (d,  $^3J_{HH} = 7.5$  Hz, 2H, aryl-H), 3.31 (s, 4H,  $-CH_2-$ ), 1.55 (s, 36H,  $^tBu$ ).  $^{13}C\{^1H\}$  NMR (126 MHz,  $CD_3CN$ )  $\delta$ /ppm: 165.0, 134.1, 122.0, 35.8, 32.7, 30.0.  $^{31}P\{^1H\}$  NMR (162 MHz,  $CD_3CN$ )  $\delta$ /ppm: 103.0 (br s,  $P^tBu_2$ ).  $^{31}P\{^1H\}$  NMR (162 MHz,  $d_6$ -acetone)  $\delta$ /ppm: 69.3 (br s,  $P^tBu_2$ ). IR (solid)  $\bar{\nu}_{max}/cm^{-1}$ : 2229 ( $C\equiv N$ ).

$[(P^N N^P)Co(NCCH_3)]_2[BF_4]_2$  (**2b**). A dark orange solution of **1b** (110.1 mg, 155.3  $\mu$ mol) in 4 mL of THF and 1.5 mL of  $CH_3CN$  was frozen in a cold well and then allowed to thaw. To the just-thawed solution was added solid  $KC_8$  (21.2 mg, 155  $\mu$ mol, 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. Calcd (Found) for  $C_{23}H_{44}N_4BF_4P_2Co$  (%): C 47.28 (47.50), H 7.59 (7.39), N 9.59 (9.36). APCI-MS ( $CH_3CN$ )  $m/z$ : 497.4 ( $[M - BF_4]^+$ ), 456.3 ( $[M - CH_3CN, BF_4]^+$ ).  $^1H$  NMR ( $CD_3CN$ )  $\delta$ /ppm: 7.16 (t,  $^3J_{HH} = 8.0$  Hz, 1H, aryl-H), 6.48 (br s, 2H, -NH-), 6.01 (d,  $^3J_{HH} = 8.0$  Hz, 2H, aryl-H), 1.47 (br vt, 36H,  $^tBu$ ).  $^{13}C\{^1H\}$  NMR (126 MHz,  $CD_3CN$ )  $\delta$ /ppm: 165.0, 138.1, 97.7, 38.8, 28.8.  $^{31}P\{^1H\}$  NMR (162 MHz,  $CD_3CN$ )  $\delta$ /ppm: 121.0 (br s,  $P^tBu_2$ ). IR (solid)  $\bar{\nu}_{max}/cm^{-1}$ : 3324 (N-H), 2213 ( $C\equiv N$ ).

$[(P^O N^O P)Co(NCCH_3)]_2[BF_4]_2$  (**2c**).  $[Co(NCCH_3)_6][BF_4]_2$  (192.8 mg, 402.6  $\mu$ mol) was dissolved in 2 mL of  $CH_3CN$ . To this solution was added  $P^O N^O P$  (160.8 mg, 402.5  $\mu$ mol) as a 4 mL THF solution. After stirring at ambient temperature for 70 min, the dark orange reaction was frozen in a cold well. Immediately upon thawing, solid  $KC_8$  (57.8 mg, 423  $\mu$ mol) was added, causing an immediate color change to dark purple. After stirring at ambient temperature for 2.5 h, the reaction was filtered, separating a gray solid which was extracted with  $2 \times 1$  mL of THF. Removal of the solvent *in vacuo* provided a sticky dark purple solid, which was suspended in 4 mL of  $C_6H_6$  and dried again. The product was then isolated by suspending in 4 mL of  $C_6H_6$ , filtering, and drying the solid under vacuum (yield 170.2 mg, 72%). APCI-MS ( $CH_3CN$ )  $m/z$ : 499.3 ( $[M - BF_4]^+$ ), 458.3 ( $[M - CH_3CN, BF_4]^+$ ).  $^1H$  NMR ( $CD_3CN$ )  $\delta$ /ppm: 7.67 (t,  $^3J_{HH} = 8.1$  Hz, 1H, aryl-H), 6.55 (d,  $^3J_{HH} = 8.1$  Hz, 2H, aryl-H), 1.56 (s, 36H,  $^tBu$ ).  $^{13}C\{^1H\}$  NMR (126 MHz,  $CD_3CN$ )  $\delta$ /ppm: 167.8, 140.9, 102.9, 40.9, 28.0.  $^{31}P\{^1H\}$  NMR (162 MHz,  $CD_3CN$ )  $\delta$ /ppm: 214.2 (br s,  $P^tBu_2$ ). IR (solid)  $\bar{\nu}_{max}/cm^{-1}$ : 2250 ( $C\equiv N$ ).

**Reaction of  $[(P^C N^P)Co(NCCH_3)]_2[BF_4]_2$  (**2a**) with CO.** In an NMR tube capped with a septum, a  $CD_3CN$  solution of **2a** was bubbled with CO gas for 2 min resulting in a color change from dark green to orange.  $^1H$  NMR ( $CD_3CN$ )  $\delta$ /ppm: 7.72 (t,  $^3J_{HH} = 7.8$  Hz, 1H, aryl-H), 7.36 (d,  $^3J_{HH} = 7.8$  Hz, 2H, aryl-H), 3.86 (vt, 4H,  $-CH_2-$ ), 1.42 (vt, 36H,  $^tBu$ ).  $^{13}C\{^1H\}$  NMR (126 MHz,  $CD_3CN$ )  $\delta$ /ppm: 202.6, 162.3, 139.4, 122.4 (t,  $J = 5.0$  Hz), 38.8 (t,  $J = 8.3$  Hz), 37.8 (t,  $J = 9.8$  Hz), 29.5.  $^{31}P\{^1H\}$  NMR (162 MHz,  $CD_3CN$ )  $\delta$ /ppm: 106.3 (br s,  $P^tBu_2$ ). IR (thin film)  $\bar{\nu}_{max}/cm^{-1}$ : 1911 ( $C\equiv O$ ). IR ( $CH_3CN$  solution, 0.2 M  $Bu_4NBF_4$ )  $\bar{\nu}_{max}/cm^{-1}$ : 1920 ( $C\equiv O$ ).

**Reaction of  $[(P^N N^P)Co(NCCH_3)]_2[BF_4]_2$  (**2b**) with CO.** In an NMR tube capped with a septum, a  $CD_3CN$  solution of **2b** was bubbled with CO gas for 2 min resulting in a color change from dark purple to green.  $^1H$  NMR ( $CD_3CN$ )  $\delta$ /ppm: 7.45 (br t, 1H, aryl-H), 6.92 (br s, 2H, -NH-), 6.35 (d,  $^3J_{HH} = 8.1$  Hz, 2H, aryl-H), 1.44 (vt, 36H,  $^tBu$ ).  $^{31}P\{^1H\}$  NMR (162 MHz,  $CD_3CN$ )  $\delta$ /ppm: 158.9 (br s), 142.2 (br s). IR (thin film)  $\bar{\nu}_{max}/cm^{-1}$ : 3303 (N-H), 1923 ( $C\equiv O$ ), 1877 (weak).

**Reaction of  $[(P^O N^O P)Co(NCCH_3)]_2[BF_4]_2$  (**2c**) with CO.** In an NMR tube capped with a septum, a  $CD_3CN$  solution of **2c** was bubbled with CO gas for 2 min resulting in a color change from dark purple to dark yellow-green.  $^1H$  NMR ( $CD_3CN$ )  $\delta$ /ppm: 8.10 (br t, aryl-H), 7.95 (br t, aryl-H), 6.99 (m, aryl-H), 1.54 (br,  $^tBu$ ).  $^{31}P\{^1H\}$  NMR (162 MHz,  $CD_3CN$ )  $\delta$ /ppm: 238.1 (br s), 229.7 (br s). IR (thin film)  $\bar{\nu}_{max}/cm^{-1}$ : 1936 ( $C\equiv O$ ), 1901 (weak).

**Computational Methods.** The free energies of organometallic species were calculated using

$$G_{298K} = E_{elec} + G_{solv} + ZPE + H_{vib} + nkT/2 - T(S_{elec} + S_{vib})$$

where  $G_{solv}$  is the free energy of solvation, ZPE is the zero point energy correction,  $S_{vib}$  and  $S_{elec}$  are the vibrational and electronic entropies, and  $n = 12$  accounts for the potential and kinetic energies of the translational and rotational modes. Geometry optimization and frequency calculations were performed using the B3LYP-d3 dispersion-corrected hybrid density functional<sup>36</sup> with the Los Alamos small core potential<sup>37</sup> and 3- $\zeta$  valence functions on cobalt (augmented with diffuse functions and additional  $s$  ( $\alpha = 0.28$ ) and  $p$  ( $\alpha = 0.25$ )

functions) and 6-31G\*\* on organics.<sup>38</sup> (The single d-function on phosphorus was replaced by two uncontracted gaussians with exponents of 0.45 and 1.35.) Single point energies including solvation were computed using the previous 3- $\zeta$  Los Alamos basis augmented with f-functions,<sup>39</sup> the 6-311G\*\*++ basis on organics,<sup>40</sup> and 6-311++G-3df on phosphorus.<sup>40a,41</sup> Solvent effects in acetonitrile were included using the PBF implicit solvation model<sup>42</sup> using a dielectric constant of 37.5 and probe radius of 2.19 Å. To determine accurate free energies for solvent molecules, the 1 atm ideal gas free energy of acetonitrile was computed using the appropriate statistical mechanics formulas, and the empirical free energy of vaporization (1.27 kcal/mol, derived from the vapor pressure)<sup>43</sup> was subtracted. The chemical potential of  $H^+$  (1 M) in  $CH_3CN$  was the ideal gas free energy ( $H - TS = ^5/2kT - (298 K)(26.04 \text{ e.u.})^{44} = -6.3$  kcal/mol) minus the free energy of hydration ( $\Delta G(1 \text{ atm} \rightarrow 1 \text{ M}) = 264.0$  kcal/mol)<sup>45</sup> plus the transfer free energy ( $\Delta G(1 \text{ M, aq} \rightarrow 1 \text{ M, } CH_3CN) = 5.7$  kcal/mol).<sup>46</sup> All calculations were completed with Jaguar.<sup>47</sup>

The formally "Co(0)" solvent complexes are best described as high spin, cationic Co(I) centers antiferromagnetically coupled to radical anionic pyridine ligands. The approximate projection scheme proposed by Yamaguchi<sup>48</sup> 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.  $S^2$  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(I) 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>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This material is 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

- (1) (a) Gray, H. B. *Nat. Chem.* **2009**, *1* (1), 7–7. (b) Harriman, A. *Philos. Trans. R. Soc., A* **2013**, *371* (1996), 1–16. (c) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103* (43), 15729–15735. (d) DuBois, D. L. *Inorg. Chem.* **2014**, *53* (8), 3935–3960. (e) Rakowski Dubois, M.; Dubois, D. L. *Acc. Chem. Res.* **2009**, *42* (12), 1974–1982. (f) Whipple, D. T.; Kenis, P. J. A. *J. Phys. Chem. Lett.* **2010**, *1* (24), 3451–3458. (g) Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. *Chem. Rev.* **2013**, *113* (8), 6621–



6658. (h) Qiao, J.; Liu, Y.; Hong, F.; Zhang, J. *Chem. Soc. Rev.* **2014**, *43* (2), 631–675. (i) Kondratenko, E. V.; Mul, G.; Baltrusaitis, J.; Larrazabal, G. O.; Perez-Ramirez, J. *Energy Environ. Sci.* **2013**, *6* (11), 3112–3135. (j) Inglis, J. L.; MacLean, B. J.; Pryce, M. T.; Vos, J. G. *Coord. Chem. Rev.* **2012**, *256* (21–22), 2571–2600. (k) Benson, E. E.; Kubiak, C. P.; Sathrum, A. J.; Smieja, J. M. *Chem. Soc. Rev.* **2009**, *38* (1), 89–99.
- (2) (a) Wang, M.; Chen, L.; Sun, L. *Energy Environ. Sci.* **2012**, *5* (5), 6763–6778. (b) Yang, J. Y.; Bullock, R. M.; DuBois, M. R.; DuBois, D. L. *MRS Bull.* **2011**, *36* (01), 39–47. (c) Thoi, V. S.; Sun, Y.; Long, J. R.; Chang, C. J. *Chem. Soc. Rev.* **2013**, *42* (6), 2388–2400. (d) McKone, J. R.; Marinescu, S. C.; Brunswig, B. S.; Winkler, J. R.; Gray, H. B. *Chem. Sci.* **2014**, *5* (3), 865–878.
- (3) (a) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81* (5), 447–474. (b) Khodakov, A. Y.; Chu, W.; Fongarland, P. *Chem. Rev.* **2007**, *107* (5), 1692–1744.
- (4) (a) Morris, A. J.; Meyer, G. J.; Fujita, E. *Acc. Chem. Rev.* **2009**, *42* (12), 1983–1994. (b) Kumar, B.; Llorente, M.; Froehlich, J.; Dang, T.; Sathrum, A.; Kubiak, C. P. *Annu. Rev. Phys. Chem.* **2012**, *63* (1), 541–569.
- (5) (a) Bligaard, T.; Nørskov, J. K.; Dahl, S.; Matthesen, J.; Christensen, C. H.; Sehested, J. *J. Catal.* **2004**, *224* (1), 206–217. (b) Ichikawa, S. *Chem. Eng. Sci.* **1990**, *45* (2), 529–535. (c) Parsons, R. Volcano Curves in Electrochemistry. In *Catalysis in Electrochemistry*; John Wiley & Sons, Inc.: New York, 2011; pp 1–15.
- (6) (a) Giannoccaro, P.; Vasapollo, G.; Nobile, C. F.; Sacco, A. *Inorg. Chim. Acta* **1982**, *61*, 69–75. (b) Khaskin, E.; Diskin-Posner, Y.; Weiner, L.; Leitius, G.; Milstein, D. *Chem. Commun.* **2013**, *49* (27), 2771–2773. (c) Dahloff, W. V.; Nelson, S. M. *J. Chem. Soc. A* **1971**, 2184–2190. (d) Semproni, S. P.; Milsmann, C.; Chirik, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 9211–9224.
- (7) Semproni, S. P.; Hojilla Atienza, C. C.; Chirik, P. J. *Chem. Sci.* **2014**, *5* (5), 1956–1960.
- (8) Obligation, J. V.; Semproni, S. P.; Chirik, P. J. *J. Am. Chem. Soc.* **2014**, *136* (11), 4133–4136.
- (9) (a) Müller, G.; Klinga, M.; Leskelä, M.; Rieger, B. Z. *Anorg. Allg. Chem.* **2002**, *628* (13), 2839–2846. (b) Chen, L.; Ai, P.; Gu, J.; Jie, S.; Li, B.-G. *J. Organomet. Chem.* **2012**, *716* (0), 55–61.
- (10) DuBois, D. L.; Miedaner, A.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1991**, *113* (23), 8753–8764.
- (11) (a) Simpson, T. C.; Durand, R. R., Jr. *Electrochim. Acta* **1988**, *33* (4), 581–583. (b) Arana, C.; Yan, S.; Keshavarz-K, M.; Potts, K. T.; Abruna, H. D. *Inorg. Chem.* **1992**, *31* (17), 3680–3682. (c) Chiericato, G., Jr.; Arana, C. R.; Casado, C.; Cuadrado, I.; Abruña, H. D. *Inorg. Chim. Acta* **2000**, *300–302*, 32–42. (d) Hossain, A. G. M. M.; Nagaoka, T.; Ogura, K. *Electrochim. Acta* **1997**, *42* (16), 2577–2585. (e) Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102* (24), 7361–7363. (f) Pearce, D. J.; Pletcher, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *197* (1–2), 317–330. (g) Isse, A. A.; Gennaro, A.; Vianello, E.; Floriani, C. *J. Mol. Catal.* **1991**, *70* (2), 197–208. (h) Grodkowski, J.; Neta, P.; Fujita, E.; Mahammed, A.; Simkhovich, L.; Gross, Z. *J. Phys. Chem. A* **2002**, *106* (18), 4772–4778. (i) Ogata, T.; Yanagida, S.; Brunswig, B. S.; Fujita, E. *J. Am. Chem. Soc.* **1995**, *117* (25), 6708–6716. (j) Tinnemans, A. H. A.; Koster, T. P. M.; Thewissen, D. H. M. W.; Mackor, A. *Recl. Trav. Chim. Pays-Bas* **1984**, *103* (10), 288–295. (k) Ogata, T.; Yamamoto, Y.; Wada, Y.; Murakoshi, K.; Kusaba, M.; Nakashima, N.; Ishida, A.; Takamuku, S.; Yanagida, S. *J. Phys. Chem.* **1995**, *99* (31), 11916–11922. (l) Lacy, D. C.; McCrory, C. C. L.; Peters, J. C. *Inorg. Chem.* **2014**, *53* (10), 4980–4988.
- (12) Scheuermann, M. L.; Semproni, S. P.; Pappas, I.; Chirik, P. J. *Inorg. Chem.* **2014**, *53* (18), 9463–9465.
- (13) (a) Laitar, D. S.; Müller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2005**, *127* (49), 17196–17197. (b) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. *J. Am. Chem. Soc.* **2010**, *132* (26), 8872–8873. (c) Eisenschmid, T. C.; Eisenberg, R. *Organometallics* **1989**, *8* (7), 1822–1824. (d) Thammavongsy, Z.; Seda, T.; Zakharov, L. N.; Kaminsky, W.; Gilbertson, J. D. *Inorg. Chem.* **2012**, *51* (17), 9168–9170.
- (14) Schneider, J.; Jia, H.; Muckerman, J. T.; Fujita, E. *Chem. Soc. Rev.* **2012**, *41* (6), 2036–2051.
- (15) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, No. 7, 1349–1356.
- (16) Kundu, S.; Brennessel, W. W.; Jones, W. D. *Inorg. Chem.* **2011**, *50* (19), 9443–9453.
- (17) Nelson, S. M.; D, W. V. *J. Chem. Soc. A* **1971**, No. 13, 2184–2190.
- (18) Khaskin, E.; Diskin-Posner, Y.; Weiner, L.; Leitius, G.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **2013**, *49* (27), 2771–2773.
- (19) Jitaru, M. *J. Univ. Chem. Technol. Metall.* **2007**, *42* (4), 333–344.
- (20) Zanello, P. *Inorganic Electrochemistry: Theory, Practice, and Applications*; The Royal Society of Chemistry: Cornwall, U.K., 2003.
- (21) (a) DuBois, D. L. Electrochemical Reactions of Carbon Dioxide. In *Encyclopedia of Electrochemistry, Vol 7A, Inorganic Chemistry*; Bard, A. J.; Stratmann, M.; Scholz, F.; Pickett, C. J., Eds.; Wiley-VCH: New York, 2006. (b) Schmidt, M. H.; Miskelly, G. M.; Lewis, N. S. *J. Am. Chem. Soc.* **1990**, *112* (9), 3420–3426.
- (22) (a) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109* (10), 2956–2962. (b) Chatt, J.; Kubota, M.; Leigh, G. J.; March, F. C.; Mason, R.; Yarrow, D. J. *J. Chem. Soc., Chem. Commun.* **1974**, No. 24, 1033–1034. (c) Karsch, H. H. *Chem. Ber.* **1977**, *110* (6), 2213–2221. (d) Evans, G. O.; Walter, W. F.; Mills, D. R.; Streit, C. A. *J. Organomet. Chem.* **1978**, *144* (2), C34–C38. (e) Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *102* (25), 7604–7606. (f) Carmona, E.; Gonzalez, F.; Poveda, M. L.; Marin, J. M.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105* (10), 3365–3366. (g) Alvarez, R.; Carmona, E.; Poveda, M. L.; Sanchez-Delgado, R. *J. Am. Chem. Soc.* **1984**, *106* (9), 2731–2732. (h) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1984**, *23* (18), 2731–2732. (i) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101* (7), 1767–1775. (j) Fujita, E.; Szalda, D. J.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110* (14), 4870–4871. (k) Hammouche, M.; Lexa, D.; Momenteau, M.; Saveant, J. M. *J. Am. Chem. Soc.* **1991**, *113* (22), 8455–8466. (l) Machan, C. W.; Chabolla, S. A.; Yin, J.; Gilson, M. K.; Tezcan, F. A.; Kubiak, C. P. *J. Am. Chem. Soc.* **2014**, *136* (41), 14598–14607.
- (23) Hansen, H. A.; Varley, J. B.; Peterson, A. A.; Nørskov, J. K. *J. Phys. Chem. Lett.* **2013**, *4* (3), 388–392.
- (24) Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70* (3), 1019–1028.
- (25) Rail, M. D.; Berben, L. A. *J. Am. Chem. Soc.* **2011**, *133* (46), 18577–18579.
- (26) (a) Mandal, S.; Shikano, S.; Yamada, Y.; Lee, Y.-M.; Nam, W.; Llobet, A.; Fukuzumi, S. *J. Am. Chem. Soc.* **2013**, *135* (41), 15294–15297. (b) Marinescu, S. C.; Winkler, J. R.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109* (38), 15127–15131. (c) Wiedner, E. S.; Roberts, J. A. S.; Dougherty, W. G.; Kassel, W. S.; DuBois, D. L.; Bullock, R. M. *Inorg. Chem.* **2013**, *52* (17), 9975–9988.
- (27) Izutsu, K. *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents*; Blackwell: Oxford, 1990; Vol. 35.
- (28) Kütt, A.; Rodima, T.; Saame, J.; Raamat, E.; Mäemets, V.; Kaljurand, I.; Koppel, I. A.; Garlyauskayte, R. Y.; Yagupolskii, Y. L.; Yagupolskii, L. M.; Bernhardt, E.; Willner, H.; Leito, I. *J. Org. Chem.* **2010**, *76* (2), 391–395.
- (29) Kütt, A.; Rodima, T.; Saame, J.; Raamat, E.; Mäemets, V.; Kaljurand, I.; Koppel, I. A.; Garlyauskayte, R. Y.; Yagupolskii, Y. L.; Yagupolskii, L. M.; Bernhardt, E.; Willner, H.; Leito, I. *J. Org. Chem.* **2011**, *76* (2), 391–395.
- (30) (a) Becica, J.; Jackson, A. B.; Dougherty, W. G.; Kassel, W. S.; West, N. M. *J. Chem. Soc., Dalton Trans.* **2014**, *43* (23), 8738–8748. (b) Jackson, A. B.; Schauer, C. K.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **2007**, *129* (35), 10628–10629. (c) Zecchin, S.; Zotti, G.; Pilloni, G. *Inorg. Chim. Acta* **1979**, *33*, L117–L118.
- (31) (a) Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *Chem. Commun.* **1975**, No. 15, 636–637. (b) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, No. 7, 708–711. (c) Herskovitz, T. *J. Am. Chem. Soc.* **1977**, *99* (7), 2391–2392.

(32) (a) Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc.* **1960**, 3705–3711. (b) Hathaway, B. J.; Holah, D. G.; Underhill, A. E. *J. Chem. Soc.* **1962**, 2444–2448. (c) Kawatsura, M.; Hartwig, J. F. *Organometallics* **2001**, *20* (10), 1960–1964. (d) Benito-Garagorri, D.; Becker, E.; Wiedermann, J.; Lackner, W.; Pollak, M.; Mereiter, K.; Kisala, J.; Kirchner, K. *Organometallics* **2006**, *25* (8), 1900–1913. (e) Bernskoetter, W. H.; Hanson, S. K.; Buzak, S. K.; Davis, Z.; White, P. S.; Swartz, R.; Goldberg, K. I.; Brookhart, M. *J. Am. Chem. Soc.* **2009**, *131* (24), 8603–8613.

(33) Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. *Pure Appl. Chem.* **2001**, *73* (11), 1795–1818.

(34) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005. (b) Schubert, E. M. *J. Chem. Educ.* **1992**, *69* (1), 62. (c) Grant, D. H. *J. Chem. Educ.* **1995**, *72* (1), 39. (d) Bain, G. A.; Berry, J. F. *J. Chem. Educ.* **2008**, *85* (4), 532.

(35) Zavarine, I. S.; Kubiak, C. P. *J. Electroanal. Chem.* **2001**, *495* (2), 106–109.

(36) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98* (7), 5648–5652. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37* (2), 785–789.

(37) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82* (1), 299–310.

(38) (a) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77* (7), 3654–3665. (b) Hehre, W. J.; Ditchfie, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56* (5), 2257–2261.

(39) Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114* (8), 3408–3420.

(40) (a) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. *J. Comput. Chem.* **1983**, *4* (3), 294–301. (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72* (1), 650–654.

(41) (a) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80* (7), 3265–3269. (b) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72* (10), 5639–5648.

(42) Tannor, D. J.; Marten, B.; Murphy, R.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M.; Goddard, W. A.; Honig, B. *J. Am. Chem. Soc.* **1994**, *116* (26), 11875–11882.

(43) (a) Putnam, W. E.; McEachern, D. M. J.; Kilpatrick, J. E. *J. Chem. Phys.* **1965**, *42*, 749–755. (b) Dojcansky, J.; Heinrich, J. *Chem. Zvesti* **1974**, *28* (2), 157–159.

(44) Chase, M. W. J. *NIST-JANAF Thermochemical Tables*, 4th ed.; NIST: Gaithersburg, MD, 1998.

(45) Tissandier, M. D.; Cowen, K. A.; Feng, W. Y.; Gundlach, E.; Cohen, M. H.; Earhart, A. D.; Coe, J. V.; Tuttle, T. R. *J. Phys. Chem. A* **1998**, *102* (40), 7787–7794.

(46) Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2007**, *111* (2), 408–422.

(47) Bochevarov, A. D.; Harder, E.; Hughes, T. F.; Greenwood, J. R.; Braden, D. A.; Philipp, D. M.; Rinaldo, D.; Halls, M. D.; Zhang, J.; Friesner, R. A. *Int. J. Quantum Chem.* **2013**, *113* (18), 2110–2142.

(48) Kitagawa, Y.; Saito, T.; Ito, M.; Shoji, M.; Koizumi, K.; Yamanaka, S.; Kawakami, T.; Okumura, M.; Yamaguchi, K. *Chem. Phys. Lett.* **2007**, *442* (4–6), 445–450.