

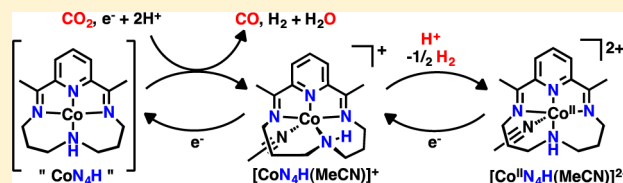
Studies of Cobalt-Mediated Electrocatalytic CO<sub>2</sub> Reduction Using a Redox-Active Ligand

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## Supporting Information

**ABSTRACT:** The cobalt complex [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup> (N<sub>4</sub>H = 2,12-dimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]-heptadeca-1(7),2,11,13,15-pentaene) was used for electrocatalytic CO<sub>2</sub> reduction in wet MeCN with a glassy carbon working electrode. When water was employed as the proton source (10 M in MeCN), CO was produced ( $f_{\text{CO}} = 45\% \pm 6.4$ ) near the Co<sup>I/0</sup> redox couple for [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup> ( $E_{1/2} = -1.88$  V FeCp<sub>2</sub><sup>+0</sup>) with simultaneous H<sub>2</sub> evolution ( $f_{\text{H}_2} = 30\% \pm 7.8$ ). Moreover, we successfully demonstrated that the catalytically active species is homogeneous through the use of control experiments and XPS studies of the working glassy-carbon electrodes. As determined by cyclic voltammetry, CO<sub>2</sub> catalysis occurred near the formal Co<sup>I/0</sup> redox couple, and attempts were made to isolate the triply reduced compound (“[Co<sup>0</sup>N<sub>4</sub>H]”). Instead, the doubly reduced (“Co<sup>I</sup>”) compounds [CoN<sub>4</sub>] and [CoN<sub>4</sub>H(MeCN)]<sup>+</sup> were isolated and characterized by X-ray crystallography. Their molecular structures prompted DFT studies to illuminate details regarding their electronic structure. The results indicate that reducing equivalents are stored on the ligand, implicating redox noninnocence in the ligands for H<sub>2</sub> evolution and CO<sub>2</sub> reduction electrocatalysis.



## INTRODUCTION

Transition metal complexes supported by nitrogen-donor ligands constitute an important class of molecular electrocatalysts for CO<sub>2</sub> reduction.<sup>1</sup> Whereas the earliest report featured phthalocyanine as a supporting ligand, a host of nitrogen-rich donor ligands have since been employed that include porphyrins,<sup>3</sup> polypyridines,<sup>4</sup> cyclam, and related unsaturated N<sub>4</sub>-macrocycles.<sup>5</sup> Convincing evidence has been provided in support of a hypothesis whereby reducing equivalents are stored on supporting polypyridine ligands during electrocatalytic CO<sub>2</sub> reduction.<sup>6</sup> Redox noninnocence at the ligand may have a significant impact on both substrate and product selectivity.<sup>7</sup> For example, bipyridyl-supported manganese and rhenium tricarbonyl catalysts reduce CO<sub>2</sub> rather than protons in the presence of water and/or weak acids.<sup>8</sup> These findings encouraged our interest in exploring the importance of redox noninnocent ligand properties in electrocatalytic CO<sub>2</sub> reductions.

In the present study we continue the theme of elucidating a role for ligand redox noninnocence in the context of electrocatalytic CO<sub>2</sub> reduction by cobalt. We employ the ligand N<sub>4</sub>H (N<sub>4</sub>H = 2,12-dimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]-heptadeca-1(7),2,11,13,15-pentaene), chosen because it contains a potentially redox-active pyridyldiimine (PDI) moiety.<sup>9,10</sup> Additionally, there is literature precedent for electrocatalytic CO<sub>2</sub> reduction with the PDI platform with cobalt.<sup>11</sup> In particular, three prior studies employed the N<sub>4</sub>H ligand for electrocatalytic CO<sub>2</sub> reduction and showed production of large amounts of H<sub>2</sub> relative to CO and low overall current efficiencies.<sup>5a,12</sup> The latter observation is

consistent with appreciable current being consumed to reductively degrade the molecular precursor. The catalytic role of resulting heterogeneous material must therefore be considered but was difficult to assess owing to the choice of mercury as the working electrode. Mercury electrodes are known to strongly adsorb N<sub>4</sub>-macrocyclic cobalt complexes,<sup>13</sup> and there has been significant discussion about the activity of dissolved molecular complexes versus mercury adsorbed species in catalysis.<sup>14,15</sup> Reports that some nominally discrete homogeneous molecular cobalt-based electrocatalysts form catalytically active heterogeneous deposits, even on glassy carbon electrode surfaces, encourage added caution to be taken when defining likely contributors to observed overall electrocatalysis.<sup>16</sup>

The present combined synthetic/electrocatalytic study employs a glassy-carbon working electrode to investigate the cobalt-N<sub>4</sub>H system for CO<sub>2</sub> reduction. The lead observation made pertains to preferential CO<sub>2</sub> reduction (to produce CO) relative to H<sub>2</sub> evolution when wet organic solvent is used. To begin to develop a better understanding of this system, synthetic studies are described wherein reduced and protonated cobalt species that we presume are relevant to overall electrocatalysis are characterized. The structural data obtained for these species are correlated to DFT calculations and suggest that redox noninnocent ligand behavior is likely operative. Of course, the molecular studies described are directly relevant to the overall CO<sub>2</sub> reduction electrocatalysis only if homogeneous

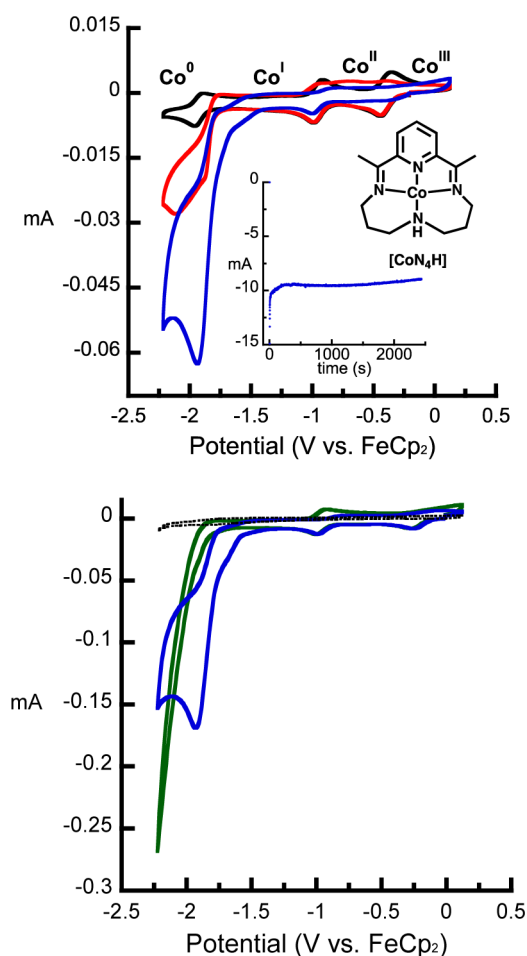
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catalysis is operative. Several control experiments support a dominant role for homogeneous species in the observed CO<sub>2</sub> electrocatalysis, despite the fact that some heterogeneous cobalt material forms on the electrode surface during electrocatalysis.

## RESULTS

**Electrocatalytic CO<sub>2</sub> Reduction with [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup> in Wet MeCN.** Cyclic voltammograms (CVs) of 0.3 mM solutions of [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup> with *n*Bu<sub>4</sub>NPF<sub>6</sub> in MeCN were measured (Figure 1), and three reversible redox couples were



**Figure 1.** (Top) Cyclic voltammograms of 0.3 mM [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup> in MeCN (black), addition of CO<sub>2</sub> (red), and addition of water to make a 10 M solution in MeCN (blue). Inset shows a plot of current vs time for a 40-min controlled potential electrolysis experiment (potential held at  $-2.13$  vs FeCp<sub>2</sub><sup>+0</sup>). (Bottom) CV of 0.7 mM [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup> in MeCN with 10 M H<sub>2</sub>O with CO<sub>2</sub> (blue) and without CO<sub>2</sub> (green); the dashed black line is the background current in MeCN with 10 M H<sub>2</sub>O and CO<sub>2</sub> with no added cobalt complex. Conditions: scan rate = 0.100 V/s; supporting electrolyte is 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>; working electrode = glassy carbon; reference electrode = isolated Ag/AgNO<sub>3</sub> (1 mM) with 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>; counter electrode = glassy carbon.

observed at  $-0.40$  V,  $-0.92$  V, and  $-1.88$  V (all potentials are referenced to the FeCp<sub>2</sub><sup>+0</sup> couple). These redox events are assigned as the formal Co<sup>III/II</sup>, Co<sup>II/I</sup>, and Co<sup>I/0</sup> couples, respectively. When MeCN solutions of [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup> were saturated with CO<sub>2</sub>, an increase in the magnitude of the reductive current appeared near the Co<sup>I/0</sup> couple, suggesting the possibility of catalytic activity. Adding water increased the

magnitude of the catalytic wave near the Co<sup>I/0</sup> couple in the CV (Figure 1). A different current response was observed when no CO<sub>2</sub> was present (Figure 1, bottom). These findings are generally consistent with an early study by Tinnemans et al. in 1984, where it was first demonstrated that CVs of [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup> were affected by CO<sub>2</sub> and that H<sub>2</sub>O could enhance the catalytic wave.<sup>12a</sup>

Tinnemans et al. and Che et al. performed controlled potential electrolysis (CPE) experiments under various conditions, and CO was produced in 20–30% Faradaic efficiency at  $-1.8$  V in MeCN with water concentrates as high as 3 M (Table S2 in the Supporting Information [SI]). We obtained similar results and observed turbid solutions after an extended 40 min CPE in MeCN with water concentrations as low as  $0.035 \pm 4$  M (measured by Karl Fischer) and likewise obtained low total current efficiencies for CO ( $f_{\text{CO}} = 24\%$ ) and little to no H<sub>2</sub> ( $f_{\text{H}_2} = <1\%$ ). However, increasing the water concentration to 10 M gave substantially higher Faradaic efficiencies for CO ( $f_{\text{CO}} = 45\% \pm 6.4$ ), with H<sub>2</sub> production ( $f_{\text{H}_2} = 30\% \pm 7.8$ ) (Table 1).<sup>17</sup> The solutions with 10 M H<sub>2</sub>O

**Table 1.** Results of Controlled Potential Electrolysis (CPE) Experiments Held at  $-2.0$  V vs a Ag/AgNO<sub>3</sub> Reference Electrode<sup>a</sup> for 40 Min

comments	q/ C	f <sub>CO</sub> / %	f <sub>H<sub>2</sub></sub> / %
[CoN <sub>4</sub> H(Br) <sub>2</sub> ] <sup>+</sup> in MeCN (10 M H <sub>2</sub> O) w/ CO <sub>2</sub>	22 ± 3.2	45 ± 6.4	30 ± 7.8
[CoN <sub>4</sub> H(Br) <sub>2</sub> ] <sup>+</sup> in MeCN (10 M H <sub>2</sub> O) w/o CO <sub>2</sub>	40 ± 4.5	0	63 ± 3.5
CoCl <sub>2</sub> in MeCN (10 M H <sub>2</sub> O) w/ CO <sub>2</sub>	6.9 ± 0.4	<1%	83 ± 4.0
background in MeCN (10 M H <sub>2</sub> O) w/CO <sub>2</sub> w/bare electrode	2.1 ± 1.3	<1%	61 ± 13*
background in MeCN (10 M H <sub>2</sub> O) w/ CO <sub>2</sub> w/ used electrode	2.9 ± 1.3	<1%	66 ± 17*

<sup>a</sup>The reference electrode was externally referenced to a solution containing ferrocene in MeCN with 0.1 M *n*Bu<sub>4</sub>NClO<sub>4</sub>. The FeCp<sub>2</sub><sup>0/+</sup> couple occurred at 0.13 V. See Experimental Section for conditions. <sup>\*</sup>The hydrogen detected was near the detection limit of the GC (~1000 ppm) and accounts for the large error.

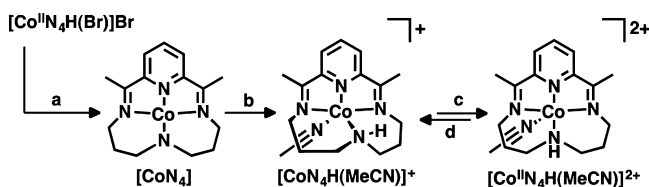
did not become turbid, and a UV–vis spectrum of the working solution after a CPE displayed features that were similar to those observed for [Co<sup>II</sup>N<sub>4</sub>H(Br)]<sup>+</sup> and [Co<sup>II</sup>N<sub>4</sub>H(MeCN)]<sup>2+</sup> (*vide infra*) (Figure S1 in the SI); though quantification was not possible because the exact speciation could not be established, the spectrum indicates that a [Co<sup>II</sup>N<sub>4</sub>H]<sup>2+</sup> complex is the majority species present. Over the course of these 40-min CPE experiments 22 ± 3.2 C were passed, and a plot of current vs time was relatively constant (Figure 1, inset). These data correspond to a TON<sub>CO</sub> of 4.1 ± 0.9 and TON<sub>H<sub>2</sub></sub> of 2.8 ± 1.0. In contrast to the original report,<sup>12a</sup> no formate or oxalate was detected under any set of conditions. Substitution of CO<sub>2</sub> with NaHCO<sub>3</sub> (30 mM, saturated) in bulk electrolysis experiments did not yield any reduced CO<sub>2</sub> products.

It has been previously reported that, in the case of hydrogen evolution by a *tris*(glyoximate) cobalt clathro chelate precatalyst complex, the catalytic species is a cobaltous material electro-deposited onto the electrode surface at negative potentials rather than the molecular complex.<sup>16a</sup> To test whether the catalytic species in the present study might be an electro-deposited film, the electrode surface was probed with XPS, and several informative control experiments were conducted. After a

CPE experiment, the electrode was removed and washed with fresh acetonitrile and water, and the surface was then probed by XPS. A very low coverage of <0.3 atom % cobalt was found on the surface (Figure S2 and S3, Table S3 in the SI), corresponding to a Co/C ratio of <0.004. For comparison, a monolayer coverage of e-beam deposited Co on SiO<sub>2</sub> has a Co/Si ratio of ~0.1,<sup>19</sup> and a monolayer coverage of electro-deposited Co oxide on Au has a Co/Au ratio of ~1.4.<sup>20</sup> This suggests that there is significantly less than a monolayer coverage of Co deposited onto the glassy carbon electrodes post-CPE, although rigorous quantification of Co coverage would require additional experiments beyond the scope and intent of this manuscript. To test whether the deposited material was catalytically active, electrodes that were used for CPE experiments with [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup> were rinsed with fresh acetonitrile and water, and an additional 40 min electrolysis was run under identical conditions, except that the precatalyst [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup> was not added to the solution. For these background experiments with the “used electrodes”, 2.9 ± 1.3 C of charge were passed with *f*<sub>CO</sub> = <1%. The results are similar to those obtained from the background CPE experiments in which a clean unused electrode was used with no dissolved precatalyst (2.1 ± 1.3 C, *f*<sub>CO</sub> = <1%). For these control experiments, the amount of charge passed is appreciably less than those containing dissolved precatalyst complex (22 ± 3.2 C), and more importantly, selectivity for CO<sub>2</sub> over H<sup>+</sup> is dramatically enhanced in the presence of [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup>. We also performed control CPE experiments with dissolved CoCl<sub>2</sub> which formed turbid solutions and produced H<sub>2</sub> in *f*<sub>H<sub>2</sub></sub> = 83% ± 4.0 and *f*<sub>CO</sub> = <1% (6.9 ± 0.4 C). Note that it is known that CoCl<sub>2</sub> deposits cobalt material on glassy carbon.<sup>16c</sup> These observations provide evidence that any cobalt material deposited on the electrode is not responsible for the observed CO<sub>2</sub> reduction catalysis and that a molecular cobalt–N<sub>4</sub>H complex is involved in the electrocatalytic process.

**Synthesis and Molecular Structure of [CoN<sub>4</sub>].** Considering that electrocatalytic CO<sub>2</sub> reduction occurred at a potential very close to the Co<sup>I/0</sup> couple, we endeavored to isolate the reduced species and study its stoichiometric reactions with CO<sub>2</sub>. This was accomplished by using [Co<sup>II</sup>N<sub>4</sub>H(Br)]Br as a synthon.<sup>21</sup> Reduction of [Co<sup>II</sup>N<sub>4</sub>H(Br)]Br with 2 equiv KC<sub>8</sub> in THF afforded a dark-purple, benzene soluble product that analyzed as [CoN<sub>4</sub>] (Scheme 1).<sup>22</sup> The <sup>1</sup>H NMR spectrum of [CoN<sub>4</sub>] in C<sub>6</sub>D<sub>6</sub> is that of a diamagnetic species and contains four aliphatic and two aromatic C–H resonances but is missing the resonance expected for the NH group of the N<sub>4</sub>H ligand (Figure S4 in the SI).<sup>23</sup> Further indication of the absence of an N–H bond comes from the lack of a ν(NH) in the FTIR-ATR spectrum of [CoN<sub>4</sub>] (Figure S5 in the SI). Crystals suitable for

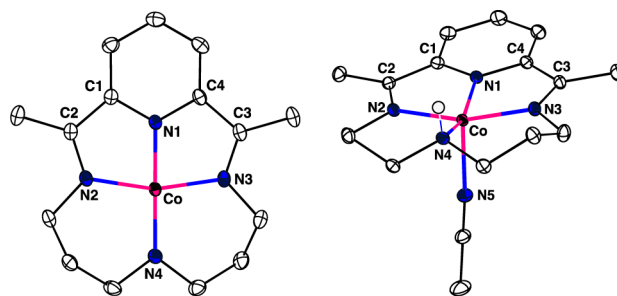
**Scheme 1. Synthesis of [CoN<sub>4</sub>], [CoN<sub>4</sub>H(MeCN)]<sup>+</sup>, and [Co<sup>II</sup>N<sub>4</sub>H(MeCN)]<sup>2+</sup>**



<sup>a</sup>Conditions: (a) 2KC<sub>8</sub>, THF, RT; (b) NaBPh<sub>4</sub>, MeCN/H<sub>2</sub>O (3:1), RT; (c) [H-DMF][OTf], MeCN, RT; (d) electrochemical reduction, *E*<sub>1/2</sub> = –0.92 V vs FeCp<sub>2</sub><sup>+0</sup>.

X-ray diffraction were obtained by slow diffusion of pentane into a concentrated benzene solution of [CoN<sub>4</sub>].

The molecular structure of [CoN<sub>4</sub>] revealed that the cobalt ion is four-coordinate and distorted square planar (Figure 2).



**Figure 2.** X-ray crystal structure of [CoN<sub>4</sub>] (left) and [CoN<sub>4</sub>H(MeCN)]<sup>+</sup> (right). Except for the NH group, hydrogen atoms are removed for clarity. Thermal ellipsoids displayed at 50% probability. The [BPh<sub>4</sub>]<sup>–</sup> counteranion in [CoN<sub>4</sub>H(MeCN)][BPh<sub>4</sub>]<sup>+</sup> has been removed for clarity.

The amido nitrogen N4 is planar ( $\Sigma\angle = 360.0^\circ$ ), and no hydrogen was found in the difference map. The cobalt–pyridine Co1–N1 bond distance is 1.800(2) Å, a contraction compared to 1.848(1) Å in [Co<sup>II</sup>N<sub>4</sub>H(MeCN)]<sup>2+</sup> (*vide infra*; Table 2).

**Table 2. Comparison of metrical parameters from XRD data for [CoN<sub>4</sub>], [CoN<sub>4</sub>H(MeCN)]<sup>+</sup>, and [Co<sup>II</sup>N<sub>4</sub>H(MeCN)]<sup>2+</sup>**

	[CoN <sub>4</sub> ]	[CoN <sub>4</sub> H(MeCN)] <sup>+</sup>	[Co <sup>II</sup> N <sub>4</sub> H(MeCN)] <sup>2+</sup>
Bond Distances (Å)			
Co1–N1	1.800(2)	1.807(1)	1.848(1)
Co1–N2	1.881(2)	1.920(1)	1.957(1)
Co1–N3	1.888(2)	1.921(1)	1.971(1)
Co1–N4	1.810(2)	2.023(1)	1.966(1)
N2–C2	1.330(2)	1.319(2)	1.303(2)
N3–C3	1.330(2)	1.325(2)	1.294(2)
Co1–N5	–	1.998(1)	2.105(1)
C1–C2	1.442(2)	1.444(2)	1.476(3)
C3–C4	1.436(2)	1.435(2)	1.474(3)
Bond Angles (deg)			
N1–Co–N4	178.81(5)	155.48(2)	172.671(4)
N2–Co–N3	162.91(5)	160.92(2)	162.101(3)

Similarly short Co–N<sub>py</sub> bond distances of 1.787(2) Å and 1.797(3) Å were observed for the related [PDI]CoCl complexes.<sup>24,25</sup> For [CoN<sub>4</sub>], the Co1–N1 contraction is accompanied by a shortening of the Co1–N<sub>4</sub>(amido) distance to 1.810(2) Å, down from 1.966(1) Å in [Co<sup>II</sup>N<sub>4</sub>H(MeCN)]<sup>2+</sup>. Compared to other cobalt–amido bond distances, the Co1–N4 distance in [CoN<sub>4</sub>] is unusually short. For comparison, Fryzuk et al. has characterized several high-spin [Co<sup>I</sup>PNP] complexes with Co–N<sub>amido</sub> bond distances ranging from 1.898(3) to 1.904(3) Å.<sup>26</sup> Caulton and co-workers have reported a three coordinate *S* = 1 [Co<sup>I</sup>PNP] complex which has a Co–N<sub>amido</sub> bond distance of 1.973(2) Å that shortens by ~0.03 Å when CO is bound.<sup>27a</sup> Additionally, Mindiola and co-workers synthesized a different [Co<sup>I</sup>PNP]<sub>2</sub>(μ-N<sub>2</sub>) complex with a Co–N<sub>amido</sub> distance of 1.928(2) Å.<sup>27b</sup> Except for [Co<sup>I</sup>PNP(CO)] and [Co<sup>I</sup>PNP]<sub>2</sub>(μ-N<sub>2</sub>), the difference in spin state (paramagnetic [Co<sup>I</sup>PNP] vs diamagnetic [CoN<sub>4</sub>]) makes it difficult to meaningfully compare these bond distances to those in [CoN<sub>4</sub>]. Finally, the imine C–N bond distances (1.330(2)

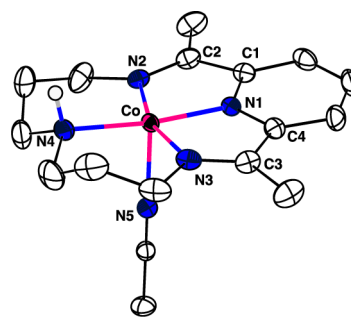
Å) in  $[\text{CoN}_4]$  are longer than expected for a redox-innocent PDI moiety, which complicates the oxidation state assignment of the cobalt ion and is discussed further below.

**Synthesis and Molecular Structure of  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$ .** We investigated the possibility of isolating the protonated form of  $[\text{CoN}_4]$ . This was accomplished by dissolving purple  $[\text{CoN}_4]$  in a 3:1 MeCN/ $\text{H}_2\text{O}$  mixture, affording a dark-forest green solution (Scheme 1). The new species  $[\text{CoN}_4\text{H}(\text{MeCN})][\text{BPh}_4]$  was isolated in 65% yield by precipitation with  $\text{NaBPh}_4$ . The  $^1\text{H}$  NMR spectrum of  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  contains sharp resonances in the diamagnetic region and includes a resonance at 2.43 ppm (1H, t,  $J_{\text{N-H}} = 11.5$  Hz) that integrates to one proton. This resonance is greatly diminished in the  $^1\text{H}$  NMR spectrum of the isotopomer  $[\text{CoN}_4\text{D}(\text{MeCN})]^+$  (Figure S6 in the SI). The FTIR-ATR spectrum of  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  contains an isotopically sensitive  $\nu(\text{NH})$  band at  $3250\text{ cm}^{-1}$  that shifts to  $2415\text{ cm}^{-1}$  when  $[\text{CoN}_4\text{D}(\text{MeCN})]^+$  is used ( $\nu(\text{NH})/\nu(\text{ND}) = 1.345$ ; calcd = 1.370) (Figure S5 in the SI).

The X-ray crystal structure of the cation  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  reveals a five-coordinate distorted square pyramidal ( $\tau = 0.09$ ) cobalt ion bound to  $\text{N}_4\text{H}$  (Figure 2). In contrast to  $[\text{CoN}_4]$ , the amine nitrogen N4 is protonated and pyramidalized ( $\Sigma\angle = 338.8^\circ$ ). The Co1–N1 bond distance in  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  is 1.807(1) Å, similar to that found in  $[\text{CoN}_4]$ . However, in  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  the Co1–N4 bond is elongated to 2.023(1) Å reflecting the protonation of the amido ligand. An acetonitrile molecule occupies the fifth coordination site of the cobalt ion. As with  $[\text{CoN}_4]$ , the C2–N2 and C3–N3 imine bond lengths in  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  are elongated to 1.319(2) Å and 1.325(2) Å, respectively, compared to those in  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})]^{2+}$ .

**Synthesis and Molecular Structure of  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})]^{2+}$ .** We explored the stoichiometric reactivity of  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  with acid. Treating  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  with one equivalent of  $[\text{H-DMF}][\text{OTf}]$  ( $\text{p}K_a = 6.1$ )<sup>28</sup> in MeCN resulted in an immediate color change from dark-forest green to orange-red. The headspace of the reaction analyzed by GC confirmed production of 1/2 equiv  $\text{H}_2$  ( $47\% \pm 4$ ). A similar experiment was performed in a sealed J-young tube with  $[\text{H-DMF}][\text{OTf}]$  and  $[\text{CoN}_4\text{D}(\text{MeCN})]^+$ , and it was found that the  $^1\text{H}$  NMR spectrum contained an  $\text{H}_2$  resonance but showed no evidence of coupling from incorporation of deuterium. *This result suggests that the proton on the  $\text{N}_4\text{H}$  ligand is not incorporated into the  $\text{H}_2$  product.*

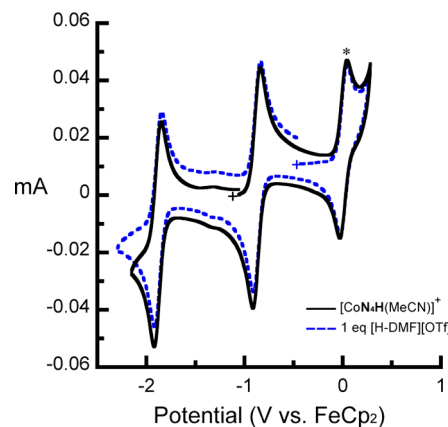
The orange-red solution resulting from treatment of  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  with  $[\text{H-DMF}][\text{OTf}]$  contained a paramagnetic  $S = 1/2$  cobalt complex ( $\mu_{\text{eff}} = 1.6\ \mu_{\text{B}}$ , RT in  $\text{CD}_3\text{CN}$ ). This conclusion is supported by the 77 K EPR spectrum (Figure S7 in the SI) of a frozen solution of the purified material, which was isolated in 87% yield and analyzed as  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})][\text{OTf}][\text{BPh}_4]$ . The UV–vis and EPR spectra of the product are nearly identical to those very recently reported by Deronzier and co-workers (Figure S8 in the SI) in the context of photochemical  $\text{H}_2$  production.<sup>30</sup> The molecular structure of  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})]^{2+}$  was determined by X-ray diffraction and revealed a five-coordinate ( $\tau = 0.18$ ) cobalt complex with two outer sphere anions (Figure 3). The amine on  $\text{N}_4\text{H}$  is H-bonded to the triflate anion as indicated from the  $\text{N4}\cdots\text{O1}$  distance of 2.844(2) Å. Compared to  $[\text{CoN}_4]$  and  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$ , the complex  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})]^{2+}$  has noticeably shorter imine C–N bond lengths (1.303(2) Å and 1.294(3) Å) (Table 2). These shorter bond lengths are



**Figure 3.** X-ray crystal structure of  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})]^{2+}$ . Except for the NH group, hydrogen atoms are removed for clarity. Thermal ellipsoids displayed at 50% probability. The  $[\text{BPh}_4]^-$  and  $[\text{OTf}]^-$  counteranions in  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})][\text{OTf}][\text{BPh}_4]$  have been removed for clarity.

consistent with the spectroscopic assignment of the product being a  $\text{Co}^{\text{II}}$  ion bound to the neutral ligand  $\text{N}_4\text{H}$ .

**Electrochemical Properties of  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  and  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})]^{2+}$  and Electrocatalytic  $\text{H}_2$  Evolution.** We also probed the electrochemical properties of  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  and  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})]^{2+}$ . The CV of  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  (Figure 4) exhibits two reversible couples,



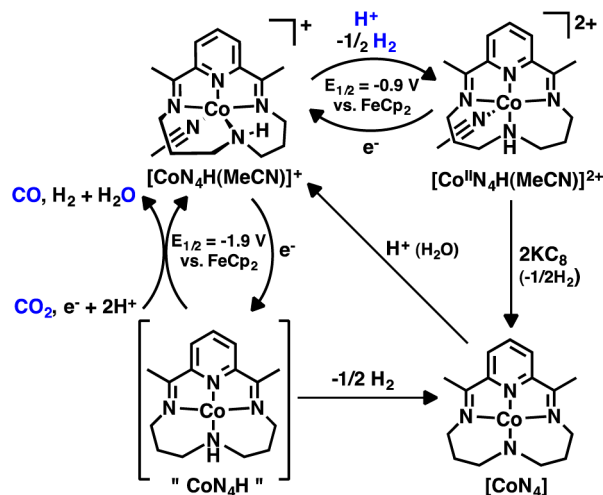
**Figure 4.** CV of 1 mM  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  in MeCN before (black) and after (dashed blue) addition of 1 equiv  $[\text{H-DMF}][\text{OTf}]$ . Conditions: 0.1 M  $n\text{Bu}_4\text{NPF}_6$ ; reference electrode = silver wire (\* = internal  $\text{FeCp}_2$ ).

one oxidation at  $-0.88\text{ V}$  vs  $\text{FeCp}_2^{+/0}$  (formally the  $\text{Co}^{\text{I/II}}$  couple) and one reduction at  $-1.88\text{ V}$  vs  $\text{FeCp}_2^{+/0}$  (formally the  $\text{Co}^{1/0}$  couple).<sup>31</sup> Addition of 1 equiv  $[\text{H-DMF}][\text{OTf}]$  caused the solution to turn orange red, but there was no change in the CV except that the resting state potential shifted positive of the redox couple at  $-0.88\text{ V}$ , indicative of an oxidation state change. Notably, addition of excess  $[\text{H-DMF}][\text{OTf}]$  or toxic acid ( $\text{TsOH}\cdot\text{H}_2\text{O}$ ) resulted in the formation of a catalytic wave near the  $\text{Co}^{\text{II/I}}$  couple consistent with electrocatalytic  $\text{H}_2$  evolution (Figure S9 in the SI). CPE experiments were conducted at two potentials for  $\text{TsOH}\cdot\text{H}_2\text{O}$  ( $\text{p}K_a = 8$ )<sup>32</sup> and 2,6-dichloroanilinium tetrafluoroborate ( $[\text{2,6-DCA}][\text{BF}_4]$ ,  $\text{p}K_a = 5.1$ ),<sup>33</sup> the results of which are presented in Table S4 in the SI. These experiments confirm  $\text{H}_2$  as the major product with  $>85\%$  Faradaic efficiency.

## DISCUSSION

The CVs of  $[\text{Co}^{\text{III}}\text{N}_4\text{H}(\text{Br})_2]^+$  in the presence of  $\text{CO}_2$  indicated that  $\text{CO}_2$  reacts at the formal “ $\text{Co}^{\text{I}/0}$ ” couple. On the basis of the reversibility of this couple and on the successful isolation of the  $[\text{NiN}_4\text{H}]$  complex,<sup>10</sup> we anticipated that treatment of cobalt– $\text{N}_4\text{H}$  complexes with the appropriate stoichiometric reductant would produce an analogous  $[\text{CoN}_4\text{H}]$  complex. However, in all attempts the only tractable cobalt-containing product was  $[\text{CoN}_4]$ . To summarize, treatment of either  $[\text{Co}^{\text{III}}\text{N}_4\text{H}(\text{Br})]^+$  or  $[\text{Co}^{\text{III}}\text{N}_4\text{H}(\text{MeCN})]^{2+}$  with 2 equiv  $\text{KC}_8$  or  $\text{NaHg}$  only formed  $[\text{CoN}_4]$ . The same occurred when 1 equiv  $\text{KC}_8$  was reacted with  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$ . The mechanism by which  $[\text{CoN}_4]$  is formed is not known; however, a cobalt-hydrido species may result from isomerization of  $[\text{CoN}_4\text{H}]$  and subsequently lose  $\text{H}\bullet$  bimolecularly in the form of  $\text{H}_2$  (Scheme 2).<sup>22</sup> This contrasts the stability of  $[\text{NiN}_4\text{H}]$ , which does not appear to lose  $\text{H}_2$  to form the corresponding  $[\text{NiN}_4]$  complex.

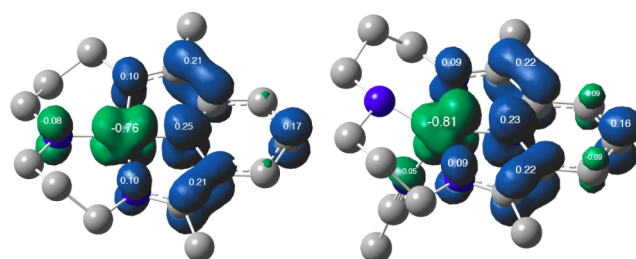
**Scheme 2. Plausible Outline for  $\text{CO}_2$  Reduction Involving the Putative “ $[\text{CoN}_4\text{H}]$ ” Complex That Is Formed at the Formal  $\text{Co}^{\text{I}/0}$  Redox Couple; the “ $[\text{CoN}_4\text{H}]$ ” Complex Is Unstable to Loss of  $\text{H}_2$  but Can Be Intercepted by  $\text{CO}_2$**



This loss of  $\text{H}_2$  at the  $\text{Co}^{\text{I}/0}$  redox event may be a consequence of ligand noninnocence and its interaction with the cobalt ion. To probe this possibility, we explored the electronic structures of the reduced complexes we prepared. On the basis of the charge of  $[\text{CoN}_4]$  and  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$ , the cobalt ions are in the +1 oxidation state. However, the imine C–N bond distances suggest a more complicated description of the electronic structures. Several research groups have investigated  $[\text{PDI}]\text{CoX}$  ( $X = \text{halide, alkyl, H}$ ) complexes.<sup>9,10,24,25</sup> From these studies, the sum of the results suggest that the electronic environments of  $[\text{PDI}]\text{CoX}$  species (formally  $\text{Co}^{\text{I}}$ ) are usually best described as having an open-shell singlet configuration in which a low-spin  $\text{Co}^{\text{II}}$  ion is antiferromagnetically coupled to a ligand-based anion radical.<sup>24,25</sup> The  $[\text{NiN}_4\text{H}]$  complex, that Wieghardt and co-workers have characterized, formally contains a “ $\text{Ni}^0$ ” ion but has elongated imine C–N bond lengths (1.353(7) Å and 1.351(8) Å).<sup>10</sup> Along with DFT studies, the complex  $[\text{NiN}_4\text{H}]$  was interpreted as containing a  $\text{Ni}^{\text{II}}$  ion bound to the dianionic ligand  $\text{N}_4\text{H}^{2-}$ . The imine C–N bond lengths of  $[\text{CoN}_4]$  and  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  are in between those of  $\text{N}_4\text{H}^{2-}$  and  $\text{N}_4\text{H}$ , and close to those in the  $[\text{PDI}]\text{CoX}$  complexes, suggesting a

description for  $[\text{CoN}_4]$  having a  $\text{Co}^{\text{II}}$  ion bound to  $\text{N}_4^{\bullet-}$  (and  $\text{N}_4\text{H}^{\bullet-}$  for  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$ ).

To supplement the crystallography, we also performed DFT calculations on  $[\text{CoN}_4]$  and  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  and found that in both cases the open-shell singlet configuration was 4.4 and 4.6 kcal/mol, respectively, lower in enthalpy than the closed-shell configuration. A surface plot of the atomic spin density (Figure 5) supports the hypothesis that an anion radical ( $\text{N}_4^{\bullet-}$ ,



**Figure 5.** Mulliken atomic spin-density surface of  $[\text{CoN}_4]$  (left) and  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  (right) (isovalue = 0.003). Hydrogen atoms removed for clarity.

$\text{N}_4\text{H}^{\bullet-}$ ) is antiferromagnetically coupled to a low-spin  $\text{Co}^{\text{II}}$  ion. For  $[\text{CoN}_4]$  and  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$ , the atomic spin-density on the cobalt ion is 0.75 and 0.81, respectively, with the remaining spin density distributed throughout the ligand.

The redox noninnocence of  $\text{N}_4\text{H}$  may have implications on selectivity between  $\text{H}_2$  evolution and  $\text{CO}_2$  reduction electrocatalysis. This is important because the difficulty of decoupling  $\text{CO}_2$  reduction from  $\text{H}_2$  evolution remains an outstanding challenge in electrocatalysis. For example, some of the better  $\text{H}_2$ -evolving molecular electrocatalysts are cobalt  $\text{N}_4$ -macrocycles with imino-glyoximate ligands.<sup>34</sup> However, to our knowledge there are no reports of successful electrocatalytic  $\text{CO}_2$  reduction using cobalt complexes with these ligands.<sup>35</sup> Recent investigations into the electronic structure of reduced cobalt and nickel complexes with imino-glyoximate ligands have suggested redox noninnocence, albeit with deleterious side reactions resulting in ligand modification.<sup>36</sup> Including this report, previous investigations from Peters,<sup>34</sup> Deronzier<sup>30</sup> and Lau<sup>37</sup> have demonstrated that  $[\text{Co}^{\text{III}}\text{N}_4\text{H}(\text{X})_2]^+$  ( $X = \text{halogen}$ ) is a competent precatalyst for  $\text{H}_2$  evolution. It was therefore surprising that  $[\text{Co}^{\text{III}}\text{N}_4\text{H}(\text{Br})_2]^+$  is a competent precatalyst for  $\text{CO}_2$  reduction under the appropriate conditions. The stability of the reduced  $\text{N}_4\text{H}^{\bullet-}$  ligand radical anion, and perhaps the ability to accommodate a second redox equivalent as demonstrated by  $[\text{NiN}_4\text{H}]$ , likely contributes to preferential  $\text{CO}_2$  reduction in wet MeCN. Although the putative  $[\text{CoN}_4\text{H}]$  complex is unstable to loss of  $\text{H}_2$ , the electrogenerated  $[\text{CoN}_4\text{H}]$  intermediate is at least sufficiently stable under electrocatalytic conditions to be intercepted by  $\text{CO}_2$  (Scheme 2). The mechanism by which  $\text{CO}$  and  $\text{H}_2$  are formed, either by two competing or one synchronous path, is still undetermined and currently under investigation.

## CONCLUSIONS

In this report, we have explored the  $\text{CO}_2$  reduction activity of a cobalt complex with a redox active pyridyldiimine moiety. In particular, we have shown that the formally “ $\text{Co}^{\text{I}}$ ” complex  $[\text{CoN}_4\text{H}(\text{MeCN})]^+$  is a precatalyst for the reduction of  $\text{CO}_2$  to  $\text{CO}$  in  $\text{CO}_2$ -saturated solutions of MeCN with 10 M  $\text{H}_2\text{O}$  ( $f_{\text{CO}} = 45\% \pm 6.4$ ), and does so preferentially to  $\text{H}^+$  reduction even

though the complex is known to be competent for electrocatalytic H<sub>2</sub>-evolution. XPS measurements of glassy carbon electrodes post-CPE and other control experiments support the assertion that the dissolved molecular complex, rather than an electrodeposited film, is responsible for the observed electrocatalysis. In addition, we have isolated the formally “Co<sup>Ib</sup>” complex [CoN<sub>4</sub>H(MeCN)]<sup>+</sup> by protonation of the “Co<sup>Ia</sup>”-amido complex [CoN<sub>4</sub>], both of which were characterized by X-ray crystallography. Along with the molecular structures, broken symmetry DFT calculations suggest they are nominally described as low-spin Co<sup>II</sup> ions antiferromagnetically coupled to a ligand radical-anion (N<sub>4</sub>H<sup>•-</sup> and N<sub>4</sub><sup>•-</sup>), a result consistent with the [PDI]CoX literature.<sup>9</sup> The stability of the N<sub>4</sub>H<sup>•-</sup> ligand radical anion and ability to accommodate a second redox equivalent may contribute to the preferential reduction of CO<sub>2</sub> over H<sup>+</sup> in the presence of large concentrations of water.

## EXPERIMENTAL SECTION

**General and Physical Methods.** All reagents were purchased from commercial sources and used as received unless otherwise noted. Solvents were sparged with nitrogen and dried over columns containing molecular sieves or alumina. The deuterated solvents were degassed and dried over activated 3 Å sieves prior to use. NMR spectra were recorded on Varian 300, 400, and 500 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in ppm relative to residual solvent as internal standards and are singlets unless otherwise stated. Identification of <sup>13</sup>C shifts were made on the basis of standard 2D methods (HSQC and HMBC). Elemental analyses were performed on a Perkin Elmer 2400 CHNS analyzer. Electronic absorbance spectra were recorded with a Cary 50 spectrometer. Fourier transform infrared ATR spectra were collected on a Thermo Scientific Nicolet iS5 spectrometer with diamond ATR crystal (utilized iD5 ATR insert). GC measurements were collected using an Agilent Technologies 7890A GC system with front and back TCD channels. X-band EPR spectra were recorded on a Bruker EMX spectrometer. Electrochemical experiments were conducted using a Biologic VSP-300 five-channel potentiostat using the EC Lab Express version 5.53 software package.

**Electrochemical Methods. Cyclic Voltammetry.** Unless otherwise stated, the working electrode was a 0.071 cm<sup>2</sup> diameter glassy carbon disk electrode (CH instruments), and the counter electrode was carbon rod (99.999% Strem). The reference electrode was a Ag/AgNO<sub>3</sub> (1.0 mM)/MeCN nonaqueous reference electrode (also contained 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>) separated from the solution by a Vycor frit (Bioanalytical Systems, Inc.) and externally referenced to ferrocene. Alternately, the reference electrode was a silver wire with an internal ferrocene standard (internally referenced CVs contain an asterisk indicating the FeCp<sub>2</sub><sup>+0</sup> couple).

**Controlled-Potential Electrolysis.** Controlled-potential electrolysis experiments were conducted at ambient pressure in a sealed two-chamber cell where the first chamber held the working and reference electrodes in 40 mL of 0.1 M *n*Bu<sub>4</sub>NClO<sub>4</sub> in MeCN with 0.3 mM catalyst, and the second chamber held the auxiliary electrode in 19 mL of 0.1 M *n*Bu<sub>4</sub>NClO<sub>4</sub> in MeCN with 20 mM FeCp<sub>2</sub>. The two chambers were separated by a fine porosity glass frit. A 6 cm × 1 cm × 0.3 cm glassy carbon plate (Tokai Carbon U.S.A.) was used as the working electrode, about a quarter of which was submerged in the solution. The auxiliary electrode was a nichrome wire (EISCO scientific). The reference electrode was a Ag/AgNO<sub>3</sub> (1 mM)/MeCN nonaqueous reference electrode separated

from the solution by a Vycor frit (Bioanalytical Systems, Inc.) and contained 0.1 M *n*Bu<sub>4</sub>NClO<sub>4</sub>. The cell was prepared with degassed solvent on a Schlenk line with N<sub>2</sub> or CO<sub>2</sub> for 30 min and then sealed before the beginning of each controlled-potential electrolysis experiment. Each controlled-potential electrolysis experiment was conducted for 40 min at the specified potential (−2.0 V vs the Ag/AgNO<sub>3</sub> reference electrode) under vigorous stirring (the stir plate was set to 900 rpm). The amount of CO and H<sub>2</sub> evolved was quantified from an analysis of the headspace with an Agilent 7890A gas chromatograph using a thermal conductivity detector. Faradaic efficiencies were determined by dividing the measured CO and H<sub>2</sub> produced by the amount of CO and H<sub>2</sub> expected on the basis of the charge passed during the controlled-potential electrolysis measurement.

**X-ray Photoelectron Spectroscopy.** The surface composition of the carbon electrode surface after a 40-min bulk electrolysis in the presence of [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup> and CO<sub>2</sub> was determined via XPS on a Kratos Axis Nova spectrometer with DLD (Kratos Analytical; Manchester, UK). The excitation source for all analysis was monochromatic Al Kα<sub>1,2</sub> (*hν* = 1486.6 eV) operating at 30 mA and 15 kV. The X-ray source was directed 45° with respect to the sample normal. A base pressure of 1 × 10<sup>−9</sup> Torr is maintained in the analytical chamber, which rises to 5 × 10<sup>−9</sup> Torr during spectral acquisition. All spectra were acquired using the hybrid lens magnification mode and slot aperture, resulting in an analyzed area of 700 μm × 400 μm. Survey scans were collected using 160 eV pass energy, while narrow region scans used 20 eV; charge compensation via the attached e<sup>−</sup>-flood source was not necessary in this study. The following sequence of scans was performed: Survey (−5–1200 eV), Na 1s (1068–1076 eV), O 1s (528–538 eV), Ag 3d (364–378 eV), C 1s (280–292 eV), Si 2s (146–161 eV) and Co 3p (52–70 eV).

Subsequent peak fitting and composition analysis was performed using CasaXPS version 2.3.16 (Casa Software Ltd.; Teignmouth, UK). Energy scale correction for the survey and narrow energy regions was accomplished by setting the large component in the C 1s spectrum, corresponding to a C 1s C(=C) transition, to 284.8 eV. All components were fitted using a Gaussian 30% Lorentzian convolution function. For quantification, Shirley baselines were employed where there was a noticeable change in CPS before and after the peak in the survey spectrum; otherwise, linear was chosen. Atomic percentages were calculated using the CasaXPS packages for regions and/or components and are reported herein. Calculations were performed using region or component areas normalized to relative sensitivity factors specific to the instrument conditions with deconvolution from the spectrometer transmission function.

**Synthetic Methods.** [Co<sup>I</sup>N<sub>4</sub>H(Br)]Br and [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]Br were synthesized on a Schlenk line according to literature methods.<sup>21</sup> Remaining manipulations and syntheses were conducted in a Vacuum Atmospheres, Co. drybox under a nitrogen atmosphere. Solvents were dried using a J.C.-Meyer solvent system and otherwise degassed with N<sub>2</sub> before use. KC<sub>8</sub> and [H-DMF][OTf] were synthesized according to literature procedures.<sup>38,39</sup>

**Preparation of [Co<sup>II</sup>N<sub>4</sub>H(Br)]Br.** Following a slightly modified procedure from Busch,<sup>21</sup> 2,6-diacetylpyridine (1.00 g, 6.13 mmol) and CoBr<sub>2</sub> (1.35 g, 6.17 mmol) were dissolved in 20 mL of degassed EtOH and treated with 0.5 mL of H<sub>2</sub>O. Dropwise addition of 3,3'-diaminodipropylamine to the blue-

green solution caused the solution to become dark-red and opaque. After complete addition of 3,3'-diaminodipropylamine, the solution was treated with glacial acetic acid (1  $\mu\text{L}$ ), and the resulting dark-purple heterogeneous mixture was stirred for 12 h at 50  $^{\circ}\text{C}$  and afterward cooled to room temperature. The purple solid was collected on a glass fritted funnel and washed with  $\text{Et}_2\text{O}$  and dried over  $\text{P}_2\text{O}_5$  for 24 h (2.5 g, 84%). FTIR-ATR: (solid powder,  $\text{cm}^{-1}$ ) 3193, 3056, 2930, 2862, 1585, 1567. The elemental analysis match literature but are reported here for convenience: Anal. Calcd (found) for  $[\text{Co}^{\text{III}}\text{N}_4\text{H}(\text{Br})]\text{Br}\cdot 0.5\text{H}_2\text{O}$  ( $\text{C}_{15}\text{H}_{23}\text{Br}_2\text{CoN}_4\text{O}_{0.5}$ ): %C 37.06, (37.22); %H 4.77, (4.48); %N 11.53, (11.39). Post drying with  $\text{P}_2\text{O}_5$ . Anal. Calcd (found) for  $[\text{Co}^{\text{III}}\text{N}_4\text{H}(\text{Br})]\text{Br}$  ( $\text{C}_{15}\text{H}_{22}\text{Br}_2\text{CoN}_4$ ): %C 37.76, (37.28); %H 4.75, (4.93); %N 11.74, (11.35).

**Preparation of  $[\text{Co}^{\text{III}}\text{N}_4\text{H}(\text{Br})_2]\text{Br}$ .** The salt  $[\text{Co}^{\text{III}}\text{N}_4\text{H}(\text{Br})_2]\text{Br}$  was prepared according to literature procedures.<sup>18</sup> Aerobic oxidation of in situ prepared  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{Br})_2]$  in the presence of 1 equiv  $\text{HBr}_{(\text{aq})}$  overnight afforded a green solution. Recrystallization was accomplished by diffusion of  $\text{Et}_2\text{O}$  into MeOH solutions of  $[\text{Co}^{\text{III}}\text{N}_4\text{H}(\text{Br})_2]\text{Br}$ . The solid was dried under reduced pressure with  $\text{P}_2\text{O}_5$ .  $^1\text{H}$  NMR ( $\text{MeOD}-d_3$ , 400 MHz):  $\delta$  8.57 (3H, m, Ar-H),  $\delta$  6.43 (1H, t,  $J = 11.5$ , NH),  $\delta$  4.20 (2H, d,  $J = 16.4$ , CH),  $\delta$  3.65 (2H, t,  $J = 13.5$ , CH),  $\delta$  3.48 (2H, q,  $J = 11.5$ , CH),  $\delta$  3.12 (2H, d,  $J = 12.4$ , CH),  $\delta$  2.92 (6H, s,  $\text{CH}_3$ ),  $\delta$  2.28 (4H, m,  $\text{CH}_2$ ). Anal. Calcd (found) for  $[\text{Co}^{\text{III}}\text{N}_4\text{H}(\text{Br})_2]\text{Br}$  ( $\text{C}_{15}\text{H}_{22}\text{Br}_3\text{CoN}_4$ ): %C 32.34, (32.07); %H 3.98, (4.04); %N 10.06, (9.78).

**Preparation of  $[\text{CoN}_4]$ .** Solid  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{Br})]\text{Br}$  (294 mg, 0.616 mmol) and  $\text{KC}_8$  (178 mg, 1.32 mmol) were placed in a 20 mL scintillation vial with a stir bar (the stir bar had been previously stirred over  $\text{KC}_8$  in THF). THF (10 mL) was added at room temperature, and the vigorously stirring solution immediately became inky-purple and warm. Small amounts of bubbles were observed. After 30 min, the solution was filtered through Celite, and the filtrate was dried *in vacuo*. The solid was washed with 10 mL of toluene and passed through a medium porosity glass fritted funnel to remove insoluble material. The toluene was removed *in vacuo* to yield an analytically pure dark-purple solid (161 mg, 83%). X-ray quality crystals were grown by pentane vapor diffusion into a saturated benzene solution. The material could be further purified by saturating a solution in toluene and adding pentane and storing the solution at  $-35$   $^{\circ}\text{C}$  for several days and washing the crystals with cold pentane on a glass fritted funnel (10% yield). To determine gaseous products, the reaction was conducted in a sealed flask, and THF solvent was added via syringe. By GC analysis, the amount of  $\text{H}_2$  produced corresponded to a 20% yield based on  $[\text{CoN}_4]$  product.  $^1\text{H}$  NMR ( $\text{C}_6\text{H}_6$ , 300 MHz):  $\delta$  8.15 (1H, t,  $J = 7.5$  Hz, Ar-H),  $\delta$  7.62 (2H, d,  $J = 7.5$  Hz, Ar-H),  $\delta$  4.28 (4H, br s,  $\text{CH}_2$ ),  $\delta$  3.55 (4H, br s,  $\text{CH}_2$ ),  $\delta$  2.25 (4H, br s,  $\text{CH}_2$ ),  $\delta$  0.99 (6H, s,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{H}_6$ , 100 MHz)  $\delta$  117.3 (meta- $\text{C}_{\text{py}}$ ),  $\delta$  114.2 (para- $\text{C}_{\text{py}}$ ),  $\delta$  57.7 ( $\text{CH}_2$ ),  $\delta$  53.4 ( $\text{CH}_2$ ),  $\delta$  34.3 ( $\text{CH}_2$ ),  $\delta$  17.0 ( $\text{C}_{\text{Me}}$ ). FTIR-ATR: ( $\text{cm}^{-1}$ ) 3105, 3070, 2905, 2808, 2745, 2663, 1571, 1530, 1510, 1485, 1446, 1380, 1355, 1337, 1317, 1260, 1194, 1177, 1152, 1136, 1125, 1013. UV-vis:  $\lambda_{\text{max}}$  (THF, nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ )) 375 (8300), 452 (shoulder, 2100), 544 (8300), 650 (1400), 773 (1750). Anal. Calcd (found) for  $[\text{CoN}_4]$  ( $\text{C}_{15}\text{H}_{21}\text{CoN}_4$ ): %C 56.96 (56.69); %H 6.69 (6.79); %N 17.71 (17.51). Alternatively, solid  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})_2][\text{BPh}_4]_2$  (100 mg, 0.1 mmol) was suspended in 5 mL of THF and stirred with a stir bar that had been previously stirred over  $\text{KC}_8$ . The solution was treated with  $\text{KC}_8$  (28 mg, 0.2 mmol) in two roughly equal portions causing the reaction to become dark

inky-purple. After stirring for 5 min, 2 mL of pentane was added and allowed to stir for an additional 1 min after which the solution was passed through a filter pipet containing glass-fiber filter paper and a Celite pad, removing white/gray solid ( $\text{KBPh}_4$  and C). The resulting homogeneous inky-purple filtrate was reduced to dryness *in vacuo*, and the resulting solid was treated with 5 mL benzene followed by 1 mL of pentane and again filtered through a filter pipet with glass wool. The resulting filtrate was reduced to dryness *in vacuo* (this process was repeated at least one more time). The resulting product was identical to  $[\text{CoN}_4]$  and analytically pure.

**Preparation of  $[\text{CoN}_4\text{H}(\text{MeCN})][\text{BPh}_4]$ .** Solid  $[\text{CoN}_4]$  (107 mg, 0.339 mmol) was dissolved in MeCN (15 mL) with  $\text{NaBPh}_4$  (118 mg, 0.345 mmol), and degassed  $\text{H}_2\text{O}$  (2 mL) was added causing a color change from dark purple to dark green and was brought into an oxygen-free "wet" box. A small amount of water was added ( $\sim 0.5$ –5 mL) until crystallization was induced, and the resulting mixture was allowed to rest at room temperature for several days. The dark-green crystals were isolated on a glass fritted filter funnel and dried under reduced pressure for at least 12 h (149 mg, 65%).  $^1\text{H}$  NMR ( $\text{MeCN}-d_3$ , 400 MHz):  $\delta$  8.48 (1H, t,  $J = 7.7$  Hz, Ar-H),  $\delta$  7.71 (2H, d,  $J = 7.7$  Hz, Ar-H),  $\delta$  7.27 (8H, br s, Ar-H),  $\delta$  6.99 (8H, t,  $J = 7.3$  Hz, Ar-H),  $\delta$  6.84 (4H, t,  $J = 7.1$  Hz, Ar-H),  $\delta$  4.47 (2H, d,  $J = 14.2$  Hz, CH),  $\delta$  3.29 (2H, t,  $J = 13.4$  Hz, CH),  $\delta$  2.86 (2H, t,  $J = 11.3$  Hz, CH),  $\delta$  2.75 (2H, q,  $J = 11.5$  Hz, CH),  $\delta$  2.42 (1H, t,  $J = 11.5$ , NH),  $\delta$  2.22 (2H, d,  $J = 14.9$ , CH),  $\delta$  1.96 (s, coordinated MeCN),  $\delta$  1.82 (2H, q,  $J = 12.9$ , CH),  $\delta$  1.63 (6H, s,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{H}_6$ , 100 MHz)  $\delta$  164.8 (q,  $J = 49.5$ ,  $\text{BPh}_4$ ),  $\delta$  148.2 (ortho- $\text{C}_{\text{py}}$ ),  $\delta$  136.7 (q,  $J = 1.34$ ,  $\text{BPh}_4$ ),  $\delta$  126.6 (q,  $J = 2.65$ ,  $\text{BPh}_4$ ),  $\delta$  124.6 (meta- $\text{C}_{\text{py}}$ ),  $\delta$  122.7 ( $\text{BPh}_4$ ),  $\delta$  116.6 (para- $\text{C}_{\text{py}}$ ),  $\delta$  54.2 ( $\text{CH}_2$ ),  $\delta$  52.5 ( $\text{CH}_2$ ),  $\delta$  29.6 ( $\text{CH}_2$ ),  $\delta$  16.6 ( $\text{C}_{\text{Me}}$ ). UV-vis:  $\lambda_{\text{max}}$  (MeCN, nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ )) 331 (6900), 430 (4750), 687 (1300), 845 (sh). FTIR-ATR: ( $\text{cm}^{-1}$ ) 3251, 3047, 2979, 2935, 2920, 2873, 2840, 1579, 1475, 1426, 1386, 1306, 1257, 1142, 1060. Anal. Calcd (found) for  $[\text{CoN}_4\text{H}(\text{MeCN})][\text{BPh}_4]$ ,  $\text{C}_{41}\text{H}_{45}\text{BCoN}_5$ : %C 72.68 (72.67); %H 6.69 (6.63); %N 10.34 (10.26).

**Yield of  $\text{H}_2$  from Treatment of  $[\text{CoN}_4\text{H}(\text{MeCN})][\text{BPh}_4]$  with  $[\text{H-DMF}][\text{OTf}]$ .** Solid  $[\text{CoN}_4\text{H}(\text{MeCN})][\text{BPh}_4]$  (20.0 mg, 0.030 mmol) was dissolved in 5 mL of MeCN in a 250 mL round-bottom flask and sealed. A stock solution of  $[\text{H-DMF}][\text{OTf}]$  in MeCN was added (1.0 mL, 30 mM), causing the immediate color change from dark green to orange-red. After 10 min, the headspace was sampled with a gas-tight syringe and injected into a GC. The yield was based on a calibrated method experiment (47% yield ( $\pm 4\%$ )).

**Preparation of  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})][\text{OTf}][\text{BPh}_4]$ .** Solid  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})][\text{BPh}_4]$  (74.1 mg, 0.109 mmol) was dissolved in 5 mL of MeCN in a 20 mL vial.  $[\text{H-DMF}][\text{OTf}]$  (25.0 mg, 0.112 mmol) in 1 mL MeCN was added causing the immediate color change from dark green to orange-red. After 0.5 h the solution was layered under  $\text{Et}_2\text{O}$  affording red crystals (78.8 mg, 87%).  $\mu_{\text{eff}} = 1.60 \mu_{\text{B}}$  ( $\text{MeCN}-d_3$ , 20  $^{\circ}\text{C}$ ). UV-vis:  $\lambda_{\text{max}}$  (MeCN, nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ )) 358 (990), 445 (1220), 450 (1210). FTIR-ATR: ( $\text{cm}^{-1}$ ) 3235, 3082, 3048, 3026, 2995, 2982, 2940, 2924, 2886, 2873, 1582, 1478, 1464, 1426, 1366, 1326, 1286, 1251, 1237, 1220, 1170, 1157, 1144, 1093, 1077, 1064, 1051, 1024. Anal. Calcd (found) for  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})][\text{OTf}][\text{BPh}_4]$ ,  $\text{C}_{42}\text{H}_{45}\text{BCoF}_3\text{N}_5\text{O}_3\text{S}$ : %C 61.02 (60.79); %H 5.49 (5.66) %N 8.47 (8.47).

**Preparation of  $[\text{Co}^{\text{II}}\text{N}_4\text{H}(\text{MeCN})_2][\text{BPh}_4]_2$ .** Under a flow of  $\text{N}_2$ , solid  $\text{Co}(\text{BF}_4)_2\cdot 6\text{H}_2\text{O}$  (1.04 g, 3.1 mmol) and diacetyl-

pyridine (0.50 g, 3.1 mmol) were dissolved in 30 mL of degassed MeCN in a 500 mL Schlenk round-bottom flask. The pale-orange solution was treated dropwise with 3,3'-diaminodipropylamine (0.41 g, 3.1 mmol) in 5 mL of water (degassed) via addition funnel, and the solution turned slightly darker orange. The addition funnel was replaced under a stream of N<sub>2</sub> with a reflux condenser and heated to boiling upon which it turned from pale orange to very dark purple-red. The solution was refluxed overnight and afterward cooled to room temperature. The reflux condenser was replaced under a stream of N<sub>2</sub> with a new addition funnel and was treated dropwise with NaBPh<sub>4</sub> (2.00 g, 5.8 mmol) in 20 mL MeCN/H<sub>2</sub>O (1:3) solution. The reaction mixture was exposed to vacuum and brought into a glovebox (wet-box) and treated with 40 mL of water, causing the precipitation of purple-red crystals which were isolated on a frit and washed one time with water and dried until a free-flowing powder. The solid was used to prepare a saturated MeCN solution (160 mL) of the compound and was recrystallized by slow diffusion of Et<sub>2</sub>O, which yielded the pure compound as dark purple-black needles. The crystals were isolated on a glass fritted funnel and dried to constant weight at room temperature and analyzed as [Co<sup>II</sup>N<sub>4</sub>H(MeCN)<sub>2</sub>]-[BPh<sub>4</sub>]<sub>2</sub> (yield 2.47 g = 78%). Anal. Calcd (found) for [Co<sup>II</sup>N<sub>4</sub>H(MeCN)<sub>2</sub>][BPh<sub>4</sub>]<sub>2</sub>, C<sub>67</sub>H<sub>68</sub>B<sub>2</sub>CoN<sub>6</sub>: %C 77.54 (77.05); %H 6.60 (6.55) %N 8.10 (8.06). When one equivalent (rather than excess) of NaBPh<sub>4</sub> was used in the synthesis, the product was obtained in 33% crystalline yield. Anal. Calcd (found) for [Co<sup>II</sup>N<sub>4</sub>H(MeCN)<sub>2</sub>][BPh<sub>4</sub>]<sub>2</sub>, C<sub>67</sub>H<sub>68</sub>B<sub>2</sub>CoN<sub>6</sub>: %C 77.54 (77.40); %H 6.60 (6.47) %N 8.10 (8.17). Spectroscopic measurements matched those obtained for [Co<sup>II</sup>N<sub>4</sub>H(MeCN)]<sup>+</sup>[OTf]<sup>-</sup>[BPh<sub>4</sub>].

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Additional experimental details, UV-vis and FTIR and NMR spectra, computational details, and X-ray crystallographic information. 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.

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(17) The remaining unaccounted charge could be ascribed to catalyst decomposition or nonproductive side reactions associated with the reduced cobalt complex. If one includes the two electrons needed to reduce the Co<sup>III</sup> precatalyst to the Co<sup>I</sup> state, then an overall Faradaic efficiency of 83% ± 9 is obtained.

(18) After a bulk electrolysis an aliquot of the solution was removed, and KOH was added to basify the solution. A 200 μL aliquot was diluted with 200 μL MeCN-*d*<sub>3</sub> and spiked with a DMF internal standard (the concentration of DMF was near the expected formate concentration based on current efficiency and charge passed during electrolysis), and the solution was probed with <sup>1</sup>H NMR spectroscopy. No formate resonance was detected. Alternatively, a 10 mL aliquot was removed after bulk electrolysis, and the solvent was removed *in vacuo*. The remaining solids were taken into 400 μL D<sub>2</sub>O and a <sup>13</sup>C NMR spectrum was collected; no resonances consistent with oxalate, carbonate, or formate were detected.

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(22) GC analysis of the headspace confirmed H<sub>2</sub> as an additional product (<20% yield based on [CoN<sub>4</sub>] product). Reactions with 3 or more equiv of reductant gave intractable products.

(23) An NH resonance appears at 6.43 ppm (1H, t, *J*<sub>N-H</sub> = 11.5 Hz) for [Co<sup>III</sup>N<sub>4</sub>H(Br)<sub>2</sub>]<sup>+</sup> in methanol-*d*<sub>3</sub>.

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