Studies of Cobalt-Mediated Electrocatalytic CO₂ Reduction Using a Redox-Active Ligand

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Supporting Information

ABSTRACT: The cobalt complex [CoII(N₄H)(Br)₂]⁺ (N₄H = 2,12-dimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]-heptadeca-1(7),2,11,13,15-pentaene) was used for electrocatalytic CO₂ 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 = 45% ± 6.4) near the CoII/III redox couple for [CoII(N₄H)(Br)₂]⁺ (E₁/₂ = −1.88 V FeCp₂/H⁺) with simultaneous H₂ evolution (f = 30% ± 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, CO₂ catalysis occurred near the formal CoI/0 redox couple, and attempts were made to isolate the triply reduced compound ([CoII(N₄H)₂]⁺). Instead, the doubly reduced ("CoV") compounds [CoIII(N₄H)]⁺ and [CoII(N₄H)(MeCN)]⁺ 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 H₂ evolution and CO₂ reduction electrocatalysis.

INTRODUCTION

Transition metal complexes supported by nitrogen-donor ligands constitute an important class of molecular electrocatalysts for CO₂ reduction.3 Whereas the earliest report featured phthalocyanine as a supporting ligand, a host of nitrogen-rich donor ligands have since been employed that include porphyrins,5 polypyridines,4 cyclam, and related unsaturated N₄-macrocycles.5 Convincing evidence has been provided in support of a hypothesis whereby reducing equivalents are stored on supporting polypyridine ligands during electrocatalytic CO₂ reduction.6 Redox noninnocence at the ligand may have a significant impact on both substrate and product selectivity.7 For example, bipyridyl-supported manganese and rhenium tricarbonyl catalysts reduce CO₂ rather than protons in the presence of water and/or weak acids.8 These findings encouraged our interest in exploring the importance of redox noninnocent ligand properties in electrocatalytic CO₂ reductions.

In the present study we continue the theme of elucidating a role for ligand redox noninnocence in the context of electrocatalytic CO₂ reduction by cobalt. We employ the ligand N₄H (N₄H = 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 pyridylidimine (PDI) moiety.9,10 Additionally, there is literature precedent for electrocatalytic CO₂ reduction with the PDI platform with cobalt.11 In particular, three prior studies employed the N₄H ligand for electrocatalytic CO₂ reduction and showed production of large amounts of H₂ relative to CO and low overall current efficiencies.5a,12 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 N₄-macrocyclic cobalt complexes,13 and there has been significant discussion about the activity of dissolved molecular complexes versus mercury adsorbed species in catalysis.14,15 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.16

The present combined synthetic/electrocatalytic study employs a glassy-carbon working electrode to investigate the cobalt-N₄H system for CO₂ reduction. The lead observation made pertains to preferential CO₂ reduction (to produce CO) relative to H₂ 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 CO₂ reduction electrocatalysis only if homogeneous...
Electrocatalytic CO2 Reduction with [CoIIIN4H(Br)2]+ in Wet MeCN. Cyclic voltammograms (CVs) of 0.3 mM solutions of [CoIIIN4H(Br)2]+ with nBu4NPF6 in MeCN were measured (Figure 1), and three reversible redox couples were observed at −0.40 V, −0.92 V, and −1.88 V (all potentials are referenced to the FeCp2+/0 couple). These redox events are assigned as the formal CoIIIN4H+, CoIIIBr+, and CoIII/V couples, respectively. When MeCN solutions of [CoIIIN4H(Br)2]+ were saturated with CO2, an increase in the magnitude of the reductive current appeared near the CoV/0 couple, suggesting the possibility of catalytic activity. Adding water increased the magnitude of the catalytic wave near the CoV/0 couple in the CV (Figure 1). A different current response was observed when no CO2 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 [CoIIIN4H(Br)2]+ were affected by CO2 and that H2O could enhance the catalytic wave.12a

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 concentrations 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 ± 4 M (measured by Karl Fischer) and likewise obtained low total current efficiencies for CO (fCO = 45% ± 6.4), with H2 production (fH2 = 30% ± 7.8) (Table 1).17 The solutions with 10 M H2O 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 [CoIIIN4H(Br)2]+ complex in MeCN (10 M H2O) w/o CO2. The FeCp2+/0 couple occurred at 0.13 V. See Experimental Section for conditions.15a The hydrogen detected was near the detection limit of the GC (0.035 ± 4 M) and accounts for the large error.

![Figure 1](image-url)
CPE experiments, 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 SiO₂ has a Co/Si ratio of ~0.1,⁹ and a monolayer coverage of electrodeposited Co oxide on Au has a Co/Au ratio of ~1.4.²⁰ 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 [Co⁹⁰NiH(Br)₂]⁺ were rinsed with fresh acetonitrile and water, and an additional 40 min electrolysis was run under identical conditions, except that the precatalyst [Co⁹⁰NiH(Br)₂]⁺ 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_CO = 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_CO = 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 CO₂ over H₂ is dramatically enhanced in the presence of [Co⁹⁰NiH(Br)₂]⁺. We also performed control CPE experiments with dissolved CoCl₂ which formed turbid solutions and produced H₂ in f_CO = 83% ± 4.0 and f_CO = 1% (6.9 ± 0.4 C). Note that it is known that CoCl₂ deposits cobalt material on glassy carbon.¹⁶c These observations provide evidence that any cobalt material deposited on the electrode is not responsible for the observed CO₂ reduction catalysis and that a molecular cobalt–N₄H complex is involved in the electrocatalytic process.

**Synthesis and Molecular Structure of [CoN₄].** Considering that electrocatalytic CO₂ reduction occurred at a potential very close to the Co⁰/⁰⁺ couple, we endeavored to isolate the reduced species and study its stoichiometric reactions with CO₂. This was accomplished by using [Co⁹⁰NiH(Br)₂]Br as a synthon.²¹ Reduction of [Co⁹⁰NiH(Br)₂]Br with 2 equiv KC₈ in THF afforded a dark-purple, benzene soluble product that analyzed as [CoN₄] (Scheme 1).²² The ¹H NMR spectrum of [CoN₄] in C₄D₄ 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 N₄H ligand (Figure S4 in the SI).²³ Further indication of the absence of an N–H bond comes from the lack of a ν(NH) in the FTIR-ATR spectrum of [CoN₄] (Figure S5 in the SI). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated benzene solution of [CoN₄].

The molecular structure of [CoN₄] revealed that the cobalt ion is four-coordinate and distorted square planar (Figure 2).

![Figure 2. X-ray crystal structure of [CoN₄] (left) and [CoN₄H(MeCN)]⁺ (right). Except for the NH group, hydrogen atoms are removed for clarity. Thermal ellipsoids displayed at 50% probability. The [BPh₄]⁻ counteranion in [CoN₄H(MeCN)][BPh₄] has been removed for clarity.](Image)

The amido nitrogen N₄ is planar (ΣC = 360.0°), 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 [Co⁹⁰NiH(MeCN)]²⁺ (vide infra; Table 2).

**Table 2. Comparison of metrical parameters from XRD data for [CoN₄], [CoN₄H(MeCN)]⁺, and [Co⁹⁰NiH(MeCN)]²⁺.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Distances (Å)</th>
<th>Bond Angles (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CoN₄]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co₁–N₁</td>
<td>1.800(2)</td>
<td></td>
</tr>
<tr>
<td>Co₁–N₂</td>
<td>1.888(2)</td>
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<tr>
<td>Co₁–N₃</td>
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<tr>
<td>Co₁–N₄</td>
<td>1.810(2)</td>
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</tr>
<tr>
<td>N₂–C₂</td>
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<td></td>
</tr>
<tr>
<td>N₃–C₃</td>
<td>1.330(2)</td>
<td></td>
</tr>
<tr>
<td>N₁–N₂</td>
<td>–</td>
<td>1.998(1)</td>
</tr>
<tr>
<td>C₁–C₂</td>
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<td>1.444(2)</td>
</tr>
<tr>
<td>C₃–C₄</td>
<td>1.436(2)</td>
<td>1.435(2)</td>
</tr>
</tbody>
</table>

Bond Distances (Å) | Co₁–N₁ | 1.807(1) | 1.848(1) |
| Co₁–N₂ | 1.920(1) | 1.971(1) |
| Co₁–N₃ | 1.921(1) | 1.966(1) |
| Co₁–N₄ | 2.023(1) | 2.105(1) |
| N₂–C₂  | 1.319(2) | 1.305(2) |
| N₃–C₃  | 1.325(2) | 1.294(2) |
| N₁–N₂  | 1.998(1) | 2.105(1) |
| C₁–C₂  | 1.444(2) | 1.476(3) |
| C₃–C₄  | 1.435(2) | 1.474(3) |

| Bond Angles (deg) | N₁–Co–N₄ | 155.48(2) | 172.67(4) |
| Co₁–N₂–N₃ | 160.92(2) | 162.10(3) |

Similarly short Co–Npy bond distances of 1.787(2) Å and 1.797(3) Å were observed for the related [PDI]CoCl complexes.²⁴,²⁵ For [CoN₄], the Co₁–N₁ contraction is accompanied by a shortening of the Co₁–N₄(amide) distance to 1.810(2) Å, down from 1.966(1) Å in [Co⁹⁰NiH(MeCN)]²⁺. Compared to other cobalt–amido bond distances, the Co₁–N₄ distance in [CoN₄] is unusually short. For comparison, Fryzik et al. has characterized several high-spin [CoPnP] complexes with Co–N₄(amide) bond distances ranging from 1.898(3) to 1.904(3) Å.²⁶ Cautlon and co-workers have reported a three coordinate S = 1 [CoPnP] complex which has a Co–N₄(amide) bond distance of 1.973(2) Å that shortens by ~0.03 Å when CO is bound.²⁷a Additionally, Mindiola and co-workers synthesized a different [CoPnP]₂(μ-N₄) complex with a Co–N₄(amide) distance of 1.928(2) Å.²⁷b Except for [CoPnP(CO)] and [CoPnP]₂(μ-N₄), the difference in spin state (paramagnetic [CoPnP] vs diamagnetic [CoN₄]) makes it difficult to meaningfully compare these bond distances to those in [CoN₄]. Finally, the imine C–N bond distances (1.330(2)

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**Scheme 1. Synthesis of [CoN₄], [CoN₄H(MeCN)]⁺, and [Co⁹⁰NiH(MeCN)]²⁺.**

\[\text{[CoN₄H(Br)]Br} \rightarrow \text{[CoN₄]} \rightarrow \text{[CoN₄H(MeCN)]⁺} \rightarrow \text{[Co⁹⁰NiH(MeCN)]²⁺} \]

**Conditions:** (a) 2KC₈, THF, RT; (b) NaB₈(MeCN)/H₂O (3:1), RT; (c) [H-DMF][OTf], MeCN, RT; (d) electrochemical reduction, \(E_{1/2} = -0.92\) V vs FeCp₂⁺/⁺.  

Å) in [CoN4] 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 [CoN4H(MeCN)]+.** We investigated the possibility of isolating the protonated form of [CoN4]. This was accomplished by dissolving purple [CoN4] in a 3:1 MeCN/H2O mixture, affording a dark-forest green solution (Scheme 1). The new species [CoN4H(MeCN)][BPh4] was isolated in 65% yield by precipitation with NaBPh4. The 1H NMR spectrum of [CoN4H(MeCN)+] contains sharp resonances in the diamagnetic region and includes a resonance at 2.43 ppm (1H, t, J=11.5 Hz) that integrates to one proton. This resonance is greatly diminished in the 1H NMR spectrum of the isotopomer [CoN4D(MeCN)+] (Figure S6 in the SI). The FTIR-ATR spectrum of [CoN4H(MeCN)+] contains an isotopically sensitive ν(NH) band at 3250 cm\(^{-1}\) that shifts to 2415 cm\(^{-1}\) when [CoN4D(MeCN)+] is used (ν(NH)/ν(ND) = 1.345; calcld = 1.370) (Figure S5 in the SI).

The X-ray crystal structure of the cation [CoN4H(MeCN)+] reveals a five-coordinate distorted square pyramidal (r=0.09) cobalt ion bound to N4H (Figure 2). In contrast to [CoN4], the amine nitrogen N4 is protonated and pyramidalized (Σ=338.8°). The Co1–N1 bond distance in [CoN4H(MeCN)+] is 1.807(1) Å, similar to that found in [CoN4]. However, in [CoN4H(MeCN)+] the Co1–N4 bond is elongated to 2.023(1) Å reflecting the protonation of the amidic ligand. An acetonitrile molecule occupies the fifth coordination site of the cobalt ion. As with [CoN4], the C2–N2 and C3–N3 imine bond lengths in [CoN4H(MeCN)+] are elongated to 1.319(2) Å and 1.325(2) Å, respectively, compared to those in [CoN4H(MeCN)+].

**Electrochemical Properties of [CoN4H(MeCN)+]** and [CoN4H(MeCN)+] and Electrocatalytic H2 Evolution. We also probed the electrochemical properties of [CoN4H(MeCN)+] and [CoN4H(MeCN)+]. The CV of [CoN4H(MeCN)+] (Figure 4) exhibits two reversible couples, consistent with the spectroscopic assignment of the product being a Co3+ ion bound to the neutral ligand N4H.

![Figure 3. X-ray crystal structure of [CoN4H(MeCN)+]. Except for the NH group, hydrogen atoms are removed for clarity. Thermal ellipsoids displayed at 50% probability. The [BPh4]− and [OTf]− counteranions in [CoN4H(MeCN)+][OTf][BPh4] have been removed for clarity.](Image 363x320 to 526x475)

![Figure 4. CV of 1 mM [CoN4H(MeCN)+] in MeCN before (black) and after (dashed blue) addition of 1 equiv [H-DMF][OTf]. Conditions: 0.1 M nBu4NPF6, reference electrode = silver wire (fe = internal FeCp2).](Image 379x635 to 510x749)
The CVs of [Co\textsuperscript{III}N\textsubscript{4}H\textsubscript{2}(Br)\textsubscript{2}]\textsuperscript{+} in the presence of CO\textsubscript{2} indicated that CO\textsubscript{2} reacts at the formal “Co\textsuperscript{II/0}” couple. On the basis of the reversibility of this couple and on the successful isolation of the [NiN\textsubscript{4}H] complex,\textsuperscript{10} we anticipated that treatment of cobalt–N\textsubscript{4}H complexes with the appropriate stoichiometric reductant would produce an analogous [CoN\textsubscript{4}H] complex. However, in all attempts the only tractable cobalt-containing product was [CoN\textsubscript{4}]. To summarize, treatment of either [Co\textsuperscript{II}N\textsubscript{4}H\textsubscript{2}(Br)\textsubscript{2}]\textsuperscript{+} or [Co\textsuperscript{II}N\textsubscript{4}H(MeCN)]\textsuperscript{2+} with 2 equiv KC\textsubscript{8} or NaHg only formed [CoN\textsubscript{4}]. The same occurred when 1 equiv KC\textsubscript{8} was reacted with [CoN\textsubscript{4}H(MeCN)]\textsuperscript{+}. The mechanism by which [CoN\textsubscript{4}] is formed is not known; however, a cobalt-hydrido species may result from isomerization of [CoN\textsubscript{4}H] and subsequently lose H\textsubscript{2} bimolecularly in the form of H\textsubscript{2} (Scheme 2).\textsuperscript{22} This contrasts the stability of [NiN\textsubscript{4}H], which does not appear to lose H\textsubscript{2} to form the corresponding [NiN\textsubscript{4}H] complex.

**Scheme 2. Plausible Outline for CO\textsubscript{2} Reduction Involving the Putative “[CoN\textsubscript{4}H]” Complex That Is Formed at the Formal Co\textsuperscript{II/0} Redox Couple; the “[CoN\textsubscript{4}H]” Complex Is Unstable to Loss of H\textsubscript{2} but Can Be Intercepted by CO\textsubscript{2}**

This loss of H\textsubscript{2} at the Co\textsuperscript{II/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 [CoN\textsubscript{4}] and [CoN\textsubscript{4}H(MeCN)]\textsuperscript{+}, 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 [PDI]CoX (X = halide, alkyl, H) complexes.\textsuperscript{8,10,24,25} From these studies, the sum of the results suggest that the electronic environments of [PDI]CoX species (formally Co\textsuperscript{II}) are usually best described as having an open-shell singlet configuration in which a low-spin Co\textsuperscript{II} ion is antiferromagnetically coupled to a ligand-based anion radical.\textsuperscript{24,25} The [NiN\textsubscript{4}H] complex, that Wieghardt and co-workers have characterized, formally contains a “Ni\textsuperscript{II}” ion but has elongated imine C–N bond lengths (1.353(7) Å and 1.351(8) Å).\textsuperscript{10} Along with DFT studies, the complex [NiN\textsubscript{4}H] was interpreted as containing a Ni\textsuperscript{II} ion bound to the dianionic ligand N\textsubscript{4}H\textsuperscript{2−}. The imine C–N bond lengths of [CoN\textsubscript{4}] and [CoN\textsubscript{4}H(MeCN)]\textsuperscript{+} are in between those of N\textsubscript{4}H\textsuperscript{2−} and N\textsubscript{4}H\textsubscript{2}, and close to those in the [PDI]CoX complexes, suggesting a description for [CoN\textsubscript{4}] having a Co\textsuperscript{II} ion bound to N\textsubscript{4} (and N\textsubscript{4}H\textsuperscript{2−} for [CoN\textsubscript{4}H(MeCN)]\textsuperscript{+}).

To supplement the crystallography, we also performed DFT calculations on [CoN\textsubscript{4}] and [CoN\textsubscript{4}H(MeCN)]\textsuperscript{+} 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 (N\textsubscript{4}H\textsuperscript{2−}) is antiferromagnetically coupled to a low-spin Co\textsuperscript{II} ion. For [CoN\textsubscript{4}] and [CoN\textsubscript{4}H(MeCN)]\textsuperscript{+}, 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 N\textsubscript{4}H may have implications on selectivity between H\textsubscript{2} evolution and CO\textsubscript{2} reduction electrocatalysis. This is important because the difficulty of decoupling CO\textsubscript{2} reduction from H\textsubscript{2} evolution remains an outstanding challenge in electrocatalysis. For example, some of the better H\textsubscript{2}-evolving molecular electrocatalysts are cobalt N\textsubscript{4}-macrocycles with imino-glyoximate ligands.\textsuperscript{34} However, to our knowledge there are no reports of successful electrocatalytic CO\textsubscript{2} reduction using cobalt complexes with these ligands.\textsuperscript{35} 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.\textsuperscript{36} Including this report, previous investigations from Peters,\textsuperscript{36} Deronzier\textsuperscript{30} and Lau\textsuperscript{37} have demonstrated that [Co\textsuperscript{II}N\textsubscript{4}H(X)\textsubscript{2}]\textsuperscript{+} (X = halogen) is a competent precatalyst for H\textsubscript{2} evolution. It was therefore surprising that [Co\textsuperscript{IV}N\textsubscript{4}H(MeCN)]\textsuperscript{+} is a competent precatalyst for CO\textsubscript{2} reduction under the appropriate conditions. The stability of the reduced N\textsubscript{4}H\textsuperscript{2−} ligand radical anion, and perhaps the ability to accommodate a second redox equivalent as demonstrated by [NiN\textsubscript{4}H], likely contributes to preferential CO\textsubscript{2} reduction in wet MeCN. Although the putative [CoN\textsubscript{4}H] complex is unstable to loss of H\textsubscript{2}, the electrogenerated [CoN\textsubscript{4}] intermediate is at least sufficiently stable under electrocatalytic conditions to be intercepted by CO\textsubscript{2} (Scheme 2). The mechanism by which CO and H\textsubscript{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 CO\textsubscript{2} reduction activity of a cobalt complex with a redox active pyridyldilimine moiety. In particular, we have shown that the formally “Co\textsuperscript{II}” complex [CoN\textsubscript{4}H(MeCN)]\textsuperscript{+} is a precatalyst for the reduction of CO\textsubscript{2} to CO in CO\textsubscript{2}-saturated solutions of MeCN with 10 M H\textsubscript{2}O (f\textsubscript{CO} = 45% ± 6.4), and does so preferentially to H\textsubscript{2} reduction even...
though the complex is known to be competent for electrocatalytic H₂-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 “Co⁰” complex [Co₄N₄(H(MeCN))]⁺ by protonation of the “Co⁰”-amido complex [Co₄N₄], 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 Co⁰ ions antiferromagnetically coupled to a ligand-radical-anion (N₄H⁺ and N₄⁻), a result consistent with the [PDI]CoX literature.⁹ The stability of the N₄H⁺ ligand radical anion and ability to accommodate a second redox equivalent may contribute to the preferential reduction of CO₂ over H₂ 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.³¹H and ¹³C chemical shifts are reported in ppm relative to residual solvent as internal nonaqueous reference electrode (also contained 0.1 M Bu₄NClO₄ in MeCN with 0.3 mM catalyst, and the second chamber held the auxiliary electrode in 19 mL of 0.1 M nBu₄NClO₄ in MeCN with 20 mM FeCp₂. 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/AgNO₃ (1 mM)/MeCN nonaqueous reference electrode separated from the solution by a Vycor frit (Bioanalytical Systems, Inc.) and externally referenced to an Ag/AgNO₃ reference electrode under vigorous stirring (the stir plate was set to 900 rpm). The amount of CO and H₂ 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 H₂ produced by the amount of CO and H₂ 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 [Co⁶⁺N₄H(Br)₂]⁺ and CO₂ 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 (h = 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 × 10⁻⁹ Torr is maintained in the analytical chamber, which rises to 5 × 10⁻⁸ 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⁻-flow 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.** [Co⁵⁺N₄H(Br)₂]Br and [Co⁶⁺N₄H(Br)₂]Br were synthesized on a Schlenk line according to literature methods.³⁸ Repurification and syntheses were conducted in a Vacuum Atmospheres, Co. drybox under a nitrogen atmosphere. Solvents were dried using a JC-Meyer solvent system and otherwise degassed with N₂ before use. KC₈ and [H-DMF][OTf] were synthesized according to literature procedures.³⁸,³⁹

**Preparation of [Co₄N₄H(Br)₂]Br.** Following a slightly modified procedure from Busch,³⁸ 2,6-diacyclopentidine (1.00 g, 6.13 mmol) and CoBr₂ (1.35 g, 6.17 mmol) were dissolved in 20 mL of degassed EtOH and treated with 0.5 mL of H₂O. 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 mL), and the resulting dark-purple heterogeneous mixture was stirred for 12 h at 50 °C and afterward cooled to room temperature. The purple solid was collected on a glass fritted funnel and washed with EtO and dried over P2O5 for 24 h (2.5 g, 84%). FTIR-ATR: (solid powder, cm⁻¹) 3193, 3056, 2930, 2862, 1585, 1567. The elemental analysis match literature but are reported here for convenience: Anal. Calcd (found) for [CoIII(Br)₂]Br·0.5H₂O (C₁₅H₂₂Br₂CoN₄O₄·0.5H₂O): %C 32.34 (32.07); %H 6.43 (6.49); %N 11.74 (11.35).

Preparation of [CoIII(Br)₂]Br. The salt [CoIII(Br)₂]Br was prepared according to literature procedures.18 Aerobic solution was treated with KC₈ (28 mg, 0.2 mmol) in two aliquots with stirring, and was brought into an oxygen-free "wet" box. A small amount of water was added (∼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%). 1H NMR (CDCl₃, 400 MHz): δ 6.85 (3H, m, Ar-H), δ 8.63 (1H, t, J = 11.5 Hz, H₂), δ 4.20 (2H, d, J = 16.4 Hz, CH₂), δ 3.65 (2H, d, J = 13.5 Hz, CH₂) (2H, q, J = 11.5, CH₂), δ 3.12 (2H, d, J = 12.4, CH₂), δ 2.92 (6H, s, CH₃), δ 2.28 (4H, m, CH₂). Anal. Calcd (found) for [CoIII(Br)₂]Br·0.5H₂O: %C 32.34, (32.07); %H 3.98, (4.04); %N 10.06, (9.78).

Preparation of [CoIII(N)₃]. Solid [CoIII(N)₃]Br·2Br (294 mg, 0.616 mmol) and KClO₃ (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 KC₈ 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 in a sealed flask, and THF solvent was added via syringe. By GC analysis, the amount of H₂ produced corresponded to a 20% yield based on [CoIII(N)₃]Br product. 1H NMR (CDCl₃, 300 MHz): δ 8.15 (1H, t, J = 7.5 Hz, Ar-H), δ 7.62 (2H, d, J = 7.5 Hz, Ar-H), δ 4.28 (4H, br s, CH₂), δ 3.55 (4H, br s, CH₂), δ 2.25 (4H, br s, CH₂), δ 0.99 (6H, s, CH₃), δ 164.8 (q, J = 3.2 Hz, Ph), δ 148.2 (ortho-C₆H₅) δ 136.7 (q, J = 1.34 Hz, B₃H₅) δ 126.6 (q, J = 2.65 Hz, B₃H₅) δ 124.6 (meta-C₆H₅) δ 116.4 (para-C₆H₅). UV–vis: λmax (MeCN, nm (ε, M⁻¹ cm⁻¹)) 331 (6900), 430 (4750), 687 (1300), 845 (sh). FTIR-ATR (cm⁻¹) 3251, 3047, 2979, 2935, 2920, 2873, 2840, 1579, 1475, 1426, 1386, 1306, 1257, 1142, 1060. Anal. Calcd (found) for [CoIII(N)₃(MeCN)][B₃H₅]Br·C₄H₃BCO₃N₅: %C 72.68 (72.67); %H 6.69 (6.63); %N 10.34 (10.26).

Yield of H₂ from Treatment of [CoIII(N)₃(MeCN)][B₃H₅]Br with [H-DMF][OTf]. Solid [CoIII(N)₃(MeCN)][B₃H₅]Br (20 mg, 0.030 mmol) was dissolved in 5 mL of MeCN in a 250 mL round-bottom flask and sealed. A stock solution of [H-DMF][OTf] in MeCN was added causing a 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 (±4%)).

Preparation of [CoIII(N)₃(MeCN)][OTf][B₃H₅]. Solid [CoIII(N)₃(MeCN)][B₃H₅] (74.1 mg, 0.109 mmol) was dissolved in 5 mL of MeCN in a 20 mL vial. [H-DMF][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 over Et₂O affording red crystals (78.8 mg, 87%). μeff = 1.60 μB (MeCN-d₃, 20 °C). UV–vis: λmax (MeCN, nm (ε, M⁻¹ cm⁻¹)) 358 (990), 445 (1220), 450 (1210). FTIR-ATR (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 [CoIII(N)₃(MeCN)][OTf][B₃H₅]: %C 72.68 (72.67); %H 6.69 (6.63); %N 10.34 (10.26).

Preparation of [CoIII(N)₃(MeCN)][B₃H₅]₂. Under a flow of N₂, solid Co(BF₄)₂·6H₂O (1.04 g, 3.1 mmol) and diacetyl-
(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 CoIIi precatalyst to the CoI 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 μLD2O and spiked with a DMF internal standard (the concentration of DMF was near the expected formate electrolysis), and the solution was probed with 1H 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 dL MeCN−d3 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 1H 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 μLD2O and a 13C NMR spectrum was collected; no resonances consistent with oxalate, carbonate, or formate were detected.


(23) An NH resonance appears at 6.43 ppm (1H, t, JHH = 11.5 Hz) for [CoIIi(NH3)(H)(Br)]4+ in methanol-d4.


(29) The same amount of H2 was obtained when excess acid was used. When 1/2 equiv acid was used, the yield of H2 was reduced to 20% based on [CoIIi(H(MeCN))4].


(31) See Figure S10 of the SI for CV of isolated [CoIIii(NH3)(H(MeCN))]4+.


