Effect of Lewis Basic Amine Site on Proton Reduction Activity of NNN-Co Pincer Complex

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Electrochemical proton reduction is a promising energy storage method because H₂ molecule has a simple structure with a relatively low potential energy. Current interest in hydrogen catalysts has increased research efforts on synthetic analogs of hydrogenase active sites. In this study, we demonstrated the electrochemical H₂ evolution reactivity of $[NNN^{R}-Co(CH_3CN)_3]^{2+}$ (R = CH₂ (**1b**), NCH₃ (**2b**)) complexes and examined a proton-relay process in the H₂ evolution reaction (HER). Upon one-electron reduction, the Co(II) ion center in a high-spin state dissociated a CH₃CN ligand, while opening a reaction site. Cyclic voltammograms of the Co complexes indicated quasi-reversible Co(II/I) redox behaviors, and both complexes **1b** and **2b** showed catalytic H₂ evolution activity. Interestingly, **2b**, assisted by a proton-relaying NCH₃ group, exhibited more efficient catalytic activity than **1b**.

Keywords: [FeFe]-hydrogenase, Synthetic model, Cobalt pincer, Proton-relay agent, H₂ evolution reaction

Electrocatalytic and photocatalytic proton reduction are desirable methods for H_2 production.^{1,2} Although Pt is a benchmark catalyst for the H_2 evolution reaction (HER), researchers have utilized earth-abundant metals to achieve cost-effective catalysts.³ Nature uses [FeFe]-hydrogenase to promote H_2 evolution and splitting reactions,⁴ and many structural analogs have shown promising catalytic activities for HER.^{5,6,7}

Pincer ligands, such as an NNN-, PCP-, PNP-, PNN-types, have been shown to enable the versatile utilization of transition metal ions in catalytic reactions.⁸ The ability of these ligands to conserve central metal ions has expanded their applications in electrocatalytic HERs. Early work by Crabtree showed that Ni(II) coordinated by a redox-active NNN ligand promoted an HER at a 0.14 V overpotential with a TOF of $\sim 10^2 \text{ s}^{-1}$ in aqueous media (Figure 1).⁹ Later, other PCP-type complexes were reported for HERs with overpotentials in the range of 0.6-1 V.13 The side "arm" element of pincer ligands affects their catalytic efficiencies. Beweries and coworkers reported that the overpotential for $[P^{E1}C^{E1}P-NiCl)]$ with $E_1 = S$ was ~0.3 V lower than with $E_1 = O.^{10}$ Solvent-bound [PCP-Ni (CH_3CN) ⁺ intermediates were suggested to be the active species in the proton reaction. Yang and coworkers synthesized $[P^{E2}N^{E2}P$ -Co(CH₃CN)₂]²⁺ (E₂ = CH₂, NH, O) complexes and examined their electrochemical reactivities.¹¹ Fan and coworkers reported that air-stable [PNN-Ni(SC₆H₄CH₃)]⁺ promoted the reduction of trifluoroacetic acid at a 0.54 V overpotential with ~75% Faradaic efficiency (FE).12

In this study, we demonstrated that a pyridine-based NNNpincer ligand stabilized a Co ion during the electrochemical process and that a cofunctionalized amine pendant enhanced HER activity by relaying protons to the Co center.

The NNN-pincer-type ligand was synthesized by conjugating 2,6-bis(bromomethyl)pyridine and piperidine (or a piperazine derivative with -NCH₃). Metalation of the NNNpincer ligand with CoBr2 in dichloromethane afforded NNN^R-CoBr₂ (R = CH₂ (**1a**),¹⁴ NCH₃ (**2a**)¹⁴) complexes. Elimination of the bromide ligands by 2 equiv of $AgPF_6$ in acetonitrile (CH₃CN) solution provided the catalytically active species of $[NNN^{R}-Co(CH_{3}CN)_{3}](PF_{6})_{2}$ (R = CH₂ (1b), NCH₃ (2b)). Complexes 1a and 2a have been previously used for the hydrogenation of alkenes, but the electrocatalytic activity of the NNN-Co site coordinated by CH₃CN has not been reported. Diffusion of diethyl ether vapor into a saturated 1b solution in CH₃CN afforded reddish-brown crystals suitable for single crystal X-ray crystallography. Unfortunately, we could not obtain single crystals for 2b. 1b had an octahedral Co center coordinated by an NNN-donor and three CH₃CN ligands, as shown in Figure 2. The saturated ligand coordination of [NNN-Co(II) $(CH_3CN)_3$ ²⁺ around the Co center appeared to be different from the previous $[PNP-Co(II)(CH_3CN)_2]^{2+}$ case.¹¹ The Co center in **1b** twisted the N_1, N_2, N_3 ,-coordination plane, thereby to increase the asymmetry of the complex. The dihedral angle between the pyridine ring and the N1,N2,N3-plane was measured to be 12.74°. The Co-N_{pyridyl} distance was 2.051(5) Å, and the bond distance of Co-NCCH₃ (2.055 (6) Å) trans to Co-N_{pyridyl} was ~0.1 Å shorter than the two cis Co-NCCH₃ bonds (2.178(6) and 2.124(6) Å). The C-N



distance in the *trans* Co-NCCH₃ ligand was measured to be ~ 0.1 Å longer than that in the *cis* Co-NCCH₃.

The electronic properties of 1b and 2b were examined by comparing the stretching frequency of Co-NCCH₃. Complex 1b showed three v(CN) Infrared (IR) stretching frequencies at 2277, 2287, and 2313 cm⁻¹ with similar strengths (Supporting Information Figure S1), and 2b showed v(CN) frequencies at 2283 (stronger) and 2313 (weak) cm^{-1} (Supporting Information Figure S2). One electron-reduction shifted v(CN) values to lower frequencies: the reduction of 1b with ~1 equiv of Na/Hg in THF/CH₃CN (5:1) solution resulted in the appearance of two peaks at 2115 and 2202 cm^{-1} (Supporting Information Figure S1), whereas the corresponding reduction of 2b resulted in two peaks at 2134 and 2198 cm⁻¹ (Supporting Information Figure S2). The spin-only magnetic moments $(\mu_{\rm B})$ of the Co complexes were measured following the Evans method (295 K) (Supporting Information Figure S3).^{15,16} Complex **1b** had a solution $\mu_{\rm B}$ of 4.74, indicating a high-spin state of Co(II) with an S = 3/2 system of three unpaired electrons. Complex 2b had a similar $\mu_{\rm B}$ of 4.41. The spin state was dependent on the identity of a ligand. Unlike the cases of 1b and 2b, [PNP-Co(II) $(CH_3CN)_2$ ²⁺ has been reported to be a low-spin state $(\mu_{\rm B} = 2.0)$, but PNP-type Co complexes of high-spin states with $\mu_{\rm B} = 4.3-4.7$ values are also known.^{17,18}

The electrochemical behaviors of the Co complexes were examined by collecting cyclic voltammograms (CVs) in CH₃CN under an Ar atmosphere. The CV of **1b** revealed a quasi-reversible redox couple at a half-wave potential ($E_{1/2}$, determined as the average of the cathodic and anodic peak potentials) of -1.43 V vs. Fc^{0/+} assignable to Co(II/I) couple. The ratio of the cathodic-to-anodic peak current (i_{pc}/i_{pc})



Figure 2. ORTEP image of $[NNN^{CH2}$ -Co(CH₃CN)₃](PF₆)₂ (**1b**) with 50% probability ellipsoids. Counter ions (PF₆⁻) and hydrogen atoms are omitted for clarity. Selected bond distance (Å) and angles (°) are as follows: Co–N1 2.051(5), Co–N2 2.313(6), Co–N3 2.257(5), Co–N4 2.178(6), Co–N5 2.055(6), Co–N6 2.124(6), N1-Co-N5 177.7(2), N6-Co-N4 173.5(2), N3-Co-N2 153.60(19), N1-Co-N2 76.3(2), N1-Co-N3 77.3(2).

 i_{pa}) was 2.39 at a 25 mV/s scan rate and approached 1 upon increasing the scan rate (e.g., $i_{pc}/i_{pa} = 1.03$ at 1000 mV/s) (Figure 3). The NCH₃ group of **2b** induced a slightly positive shift in the Co(II/I) redox potential ($E_{1/2} = -1.34$ V vs. $Fc^{0/+}$) compared to **1b**. These potential values were consistent with those obtained by our density functional theory (DFT) calculation (calculated $E_{1/2} = -1.37$ V vs. Fc^{0/+} for 1b and -1.35 V vs. Fc^{0/+} for 2b) and similar to those of known Co-pyridyl complexes.¹⁹ The large i_{pc}/i_{pa} ratio at the low scan rate originated from structural distortion along with dissociation of the labile CH₃CN ligand. The initial complexes of 1b and 2b had three CH₃CN ligands, but electronreduction steps possibly dissociated one CH₃CN from the Co(I) center, as supported by two v(CN) frequencies. The DFT calculation results also suggested that dissociation of the CH₃CN ligand is favored after the reduction of Co(II) to Co(I). Ligand dissociation behavior of Co-CH₃CN by electron-reduction was observed for an analogous [PNP-Co $(CH_3CN)_2]^{2+}$ complex.¹¹

CVs of the Co complexes were obtained in the presence of proton sources. In the extended potential scan for **1b**, additional reduction peak appeared around -2.06 V vs. Fc^{0/+}, which is assignable as a Co(I/0) reduction.²⁰ The addition of 50 mM [HDBU]BF₄ (DBU = 1,8-diazabicyclo [5.4.0]undec-7-ene) as a proton source (pK_a = 24.3 in CH₃CN)²¹ to a solution of **1b** (5 mM in CH₃CN) resulted in an $E_{cat/2}$ at -2.28 V vs. Fc^{0/+} ($E_{cat/2}$ indicates a halfwave potential of the maximum catalytic current) (Supporting Information Figure S4). Complex **2b** exhibited an $E_{cat/2}$ at -2.31 V vs. Fc^{0/+} (Supporting Information Figure S5), showing similar catalytic activity as **1b**. However, under different reaction conditions in which acetic acid (pK_a = 22.3 in CH₃CN)²² was used as a proton source, the two complexes showed different catalytic activities. Under a low concentration of acetic acid (14 mM), **1b**



Figure 3. Cyclic voltammograms of $[NNN^{CH2}-Co(CH_3CN)_3]$ (PF₆)₂ (**1b**) (black line) and $[NNN^{NCH3}-Co(CH_3CN)_3](PF_6)_2$ (**2b**) (red line) in 0.1 M Bu₄NPF₆ at scan rates of (a) 25 mV/s and (b) 1000 mV/s.

and 2b (5 mM) showed comparable activities ($E_{cat/2}$ of $1\mathbf{b} = -2.19 \text{ V vs. Fc}^{0/+}$; $E_{\text{cat/2}}$ of $2\mathbf{b} = -2.05 \text{ V vs. Fc}^{0/+}$), whereas under a high concentration (98 mM) of acetic acid, 2b exhibited a higher catalytic efficiency than 1b (Figure 4, Supporting Information Figures S6 and S7). The TOF of 1b was calculated to be 37 s⁻¹, whereas TOF of **2b** was 69 s⁻¹ (see Supporting Information for the calculation details). Chronoamperometry for 2b was conducted at an applying potential of -1.98 V vs. Fc^{0/+}, which resulted in the FE of 39% (Supporting Information Figure S8). For complex 1b, the reduction current began to increase at -1.28 V vs. Fc^{0/+}, corresponding to an $E_{cat/2}$ at -1.77 V vs. Fc^{0/+}. For complex 2b, the reduction current increased at a more positive potential of -1.07 V vs. Fc^{0/+}, corresponding to an $E_{cat/2}$ at -1.55 V vs. Fc^{0/+}. The standard reduction potential of acetic acid in CH₃CN is -1.46 V vs. Fc^{0/+}.²³ As acetic acid is used as a proton source, the conjugate base (acetate) can bind to a Co ion during the catalytic cycle. A separate reaction of 2b with 1 equiv of [Bu₄N](CH₃COO) shifted the reductive potential negatively by ~0.3 V (Supporting Information Figure S9). The obtained J-V curve shapes of (2b + acetate)and (2b + acetic acid) appeared similar with a slight shift of potentials, which suggested probable coordination of acetate to the Co center. Nonetheless, the onset potential for the HER was shifted positively by ~0.5 V at higher concentrations, thus we assigned the active species to be $[NNN^{NCH3}-Co(CH_3CN)_2]^{2+}$. Acetic acid is known to cause homoconjugation in CH₃CN.²² The solution acidity may have been lowered while increasing the acetic acid concentration, which possibly caused the positive shift in the onset potential than that expected based on the original pK_a of acetic acid. For comparison, a CV of acetic acid (98 mM) in the absence of catalyst was added in Figure 4(b). We attempted to follow the effect of the pK_a of a proton source using a stronger acid, such as p-toluenesulfonic acid, but it was unsuccessful because the complexes were decomposed by the acid.

However, the trend of a positive shift in the onset potential by increasing the acid strength is commonly known for HER catalysts.^{24,25} The positive reduction potential of **2b** relative to **1b** suggested that the NCH₃ group of **2b** played a proton-relaying role that enhanced the catalytic activity.



Figure 4. Cyclic voltammograms of $[NNN^{CH2}-Co(CH_3CN)_3]$ (PF₆)₂ (**1b**), $[NNN^{NCH3}-Co(CH_3CN)_3](PF_6)_2$ (**2b**) in the absence and presence of (a) 50 mM of $[HDBU]BF_4$ and (b) 98 mM of acetic acid. CV of each proton source at the same concentration was added for comparison (gray line). Reaction conditions: 5 mM of complex in CH₃CN, Bu₄NPF₆ as electrolyte, 100 mV/s scan rate under N₂ atmosphere.



Figure 5. Proposed reaction mechanism for the electrochemical H_2 evolution by complex **2b**. The relative Gibbs free energy (ΔG , kcal/mol) and transition state energy (ΔG^{\ddagger} , kcal/mol) are given together. The ΔG was set to be zero after one-electron reduction.

We assumed a proton reduction pathway for **2b** based on the DFT calculation results. After one-electron reduction of Co(II/I), one CH₃CN ligand dissociates from the Co center, leaving two CH₃CN ligands. The open coordination site allows proton-relay between the NCH₃ pendant and Co center. DFT calculations provided the optimal electronic structures and free energy values for the reaction intermediates during the catalytic reaction (Figure 5).

Two pathways are possible depending on the proton transfer routes. One pathway involves direct proton-transfer to the Co center from a proton source in solution but is disfavored in the presence of a proton-relay agent because of a relatively higher energy barrier. The second pathway consists of **2b** first being one-electron reduced, after which the NCH₃ amine site is protonated. Upon protonation of the NCH₃ site, the proton remains ~4.745 Å away from the Co center. As the piperazine ring moiety changes to a twisted boat form, the proton at the NCH₃ site can be positioned to interact with the Co ion at a distance of 2.759 Å. Given that a proton is relayed from the NCH₃ site to the Co(I) center, the Gibbs free energy appears to increase by 23.97 kcal/mol for the formation of the Co^{III}-H intermediate. In the next electron-reduction step, the free energy of the Co^{II}-H intermediate was set to zero. The Co(II)-H bond length increases by ~0.1 Å compared to Co(III)-H. The additional protonation step at the NCH₃ site of Co^{II}-H species is energetically downhill ($\Delta G =$ -16.19 kcal/mol). As the NCH₃-bound H⁺ approaches Co^{II}-H closely (H⁺--HCo^{II} distance = 1.814 Å), the calculated TS ΔG^{\ddagger} is 9.54 kcal/mol. Ensuring a proton-relay agent in the catalyst appears to be critical for improving HER activity.

In summary, we have demonstrated the electrochemical proton reduction reactivity of $[NNN^{R}-Co(CH_3CN)_3]^{2+}$ complexes. A labile CH₃CN ligand was readily dissociated from the highspin Co(II) center by one-electron reduction, but the pincer-type NNN ligand successfully stabilized the high-spin Co ion during the electrochemical process. The opened coordination site enabled protons to access the Co site. The presence of an NCH₃ amine pendant promoted proton reduction by relaying protons to the Co center under acidic conditions. The catalytic efficiency was enhanced by the proton-relay agent. These results provide a novel example of the utilization of NNN pincer-type ligands for electrochemical HER and emphasize the essential role of a proton-relay agent in the secondary coordination sphere.

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Supporting Information. Additional supporting information may be found online in the Supporting Information section at the end of the article.

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