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Exploring acidity-dependent PCET pathways in imino-bipyridyl cobalt complexes\*

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The electrochemical proton reactivity of transition metal complexes has received intensive attention in catalyst research. The proton-coupled electron transfer (PCET) process, influenced by the coordination geometry, determines the catalytic reaction mechanisms. Additionally, the  $pK_a$  value of a proton source, as an external factor, plays a crucial role in regulating the proton transfer step. Understanding the effects of variations in the  $pK_a$  values of Brønsted acids on the PCET process is therefore essential. This study compares the PCET pathways of two high-spin cobalt (Co) complexes with contrasting exchange coupling interactions under acidic conditions with high and low  $pK_a$  values. These findings reveal how proton reduction reactions in high-spin Co complexes are affected by the internal factor of the spin state, as well as an external factor related to the proton source. The corresponding reaction mechanisms are also proposed based on these observations.

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### Introduction

The development of catalysts employing homogeneous complexes for hydrogen gas production has garnered substantial research interest.<sup>1</sup> Advances in catalyst design have evolved from mimicking enzyme active sites to exploring transition metal complexes with diverse organic ligands.<sup>2–6</sup> Specifically, incorporating ligands with proton transfer functionalities can enhance catalytic reaction rates.<sup>3–12</sup> While some catalytic reactions occur exclusively at either the metal center or the ligand, the extensive study of redox-active ligands capable of modulating the redox potential of the central metal has provided new opportunities for catalyst optimization.<sup>13–15</sup> Additionally, chelating ligands such as pincer-type or macrocyclic compounds have been reported to effectively stabilize metal ions during electrochemical reactions.<sup>16–20</sup>

Since the choice of a proton-coupled electron transfer (PCET) pathway determines the overall catalytic efficiency,<sup>21-23</sup> it is essential to investigate individual steps and the effects of internal and external factors on pathway selection. The PCET process involves both proton transfer and electron transfer, which can occur either in a concerted mechanism (CPET) or through a stepwise mechanism involving separate proton and

### electron transfers, depending on internal or external factors. The intrinsic properties of coordination complexes, such as orbital overlap and spin interactions, are closely related to electron transfer processes, making them critical for PCET pathway analysis.<sup>24</sup> It is well established that the acidity of external proton sources influences the efficiency of proton reduction reactions;<sup>25</sup> however, the impact of acidity under opposing exchange-coupling conditions in complexes was not known. Considering the reaction between complexes and protons, the proton reactivity at the metal center should be assessed using hydricity values,<sup>26-28</sup> while the basicity of the ligand moieties is also important in determining proton transfer pathways. Additionally, the proton reaction site of a complex has to be identified by comparing the $pK_a$ value of the Brønsted acid used.<sup>29,30</sup> Changes in the nucleophilicity of the complex during electron transfer processes also make diverse proton transfer steps.

Previous studies have detailed the electrochemical reorganization and spin rearrangement in complexes [ImbpyCo  $(CH_3CN)_3](BF_4)_2$  (<sup>4</sup>[1]<sup>2+</sup>) (<sup>(2S+1)</sup>[X]<sup>Y</sup>; (2S + 1) = spin multiplicity, X = complex number, and Y = charge) and [ImbpyCoBpy  $(CH_3CN)](BF_4)_2$  (<sup>4</sup>[2]<sup>2+</sup>).<sup>31</sup> Both initially exhibit octahedral coordination, but upon electrochemical reduction, they reorganize into square planar and square pyramidal geometries, respectively, accompanied by the dissociation of labile  $CH_3CN$ ligands. These structural changes are coupled with spin-state rearrangements, resulting in ferromagnetic or antiferromagnetic interactions, depending on the differing contributions of orbitals in the highest singly occupied molecular orbital (SOMO). In <sup>5</sup>[1]<sup>+</sup>, the SOMO is primarily composed of ligand orbitals (96%, Imbpy p orbital 60%) with a minimal Co

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**Fig. 1** SOMO plots of (a)  ${}^{5}$ [1]<sup>+</sup> and (b)  ${}^{3}$ [2]<sup>+</sup>, leading to the ferromagnetic or antiferromagnetic spin coupling, respectively. B3LYP/Def2-SVP//Def2-TZVPPD solution phase calculations in CH<sub>3</sub>CN.

Scheme 1 Two Co complexes with opposite exchange coupling interactions.

contribution (4%, d orbital <1%), resulting in ferromagnetic spin interaction (Fig. 1a). Conversely, in  ${}^{3}[2]^{+}$ , the SOMO exhibits an increased Co d orbital contributions (16%) and significant overlap between the d orbital and Imbpy p orbitals (51%) leading to antiferromagnetic coupling (Fig. 1b). These opposing exchange coupling states are expected to influence the PCET pathway in proton reduction catalysis as the p $K_{a}$  value of proton sources varies.

In this study, the PCET pathways of high-spin Co complexes  ${}^{4}$ [1]<sup>2+</sup> and  ${}^{4}$ [2]<sup>2+</sup>, exhibiting opposing exchange coupling during electron transfer (Scheme 1), were investigated under conditions suppressing proton transfer steps.

### **Results and discussion**

#### **Electrochemical studies**

The proton reduction mechanism of high-spin Co complexes was previously elucidated in response to internal and external factors, by comparing the PCET pathways under conditions promoting proton transfer with strong acids.<sup>31</sup> Under the strongly acidic conditions of PhNH<sub>2</sub>·HBF<sub>4</sub> ( $pK_a = 10.6$  in CH<sub>3</sub>CN),<sup>32</sup> the complex <sup>4</sup>[1]<sup>2+</sup> followed an ET-CPET-PT pathway for proton reduction, whereas complex <sup>4</sup>[2]<sup>2+</sup> proceeded *via* an ET-PT-ET-PT pathway. Thus, to investigate the changes in the PCET pathway influenced by weaker acids, CVs

of complexes  ${}^{4}[1]^{2+}$  and  ${}^{4}[2]^{2+}$  were obtained under 2-picoline·HBF<sub>4</sub> ( $pK_a = 13.3$ ).<sup>33</sup> However, the proton reduction was observed through a mixed pathway rather than a single pathway (Fig. S1<sup>†</sup>). Subsequently, CVs obtained using 2,6lutidine HBF<sub>4</sub> ( $pK_a = 14.2$  in CH<sub>3</sub>CN),<sup>33</sup> an even weaker acid, revealed that proton reduction occurred through a single pathway: complex <sup>4</sup>[1]<sup>2+</sup> followed the ET-ET-CPET pathway, while complex  ${}^{4}[2]^{2+}$  proceeded *via* the ET-CPET pathway. Therefore, it is inferred that the  $pK_a$  range for the proton source at which the proton reduction mechanism changes is 13-14. However, chronoamperometry measurements under the 2,6-lutidine-HBF<sub>4</sub> conditions provided faradaic efficiency (FE) values of 74% for  ${}^{4}$ [1]<sup>2+</sup> and 39% for complex  ${}^{4}$ [2]<sup>2+</sup>. Due to the significantly low FE values, CV measurements were conducted using  $Et_3N \cdot HBF_4$  (p $K_a = 18.8$  in  $CH_3CN$ ) as the proton source. Et<sub>3</sub>N·HBF<sub>4</sub> ( $pK_a = 18.8$  in CH<sub>3</sub>CN)<sup>33</sup> was selected as a suitable proton source because it is in a range that enables Co-H formation without coordinating to the Co center (see Scheme S1 in the ESI<sup>†</sup>).<sup>26</sup> As the  $pK_a$  value of Et<sub>3</sub>N·HBF<sub>4</sub> exceeded that of the secondary amine-NH, the imino site of the complexes is not protonated. Comparative studies of the PCET pathways for the two Co complexes, based on the  $pK_a$ value of the proton donor, provide insights into the interplay between external factors controlling PT and internal factors governing ET, ultimately influencing PCET pathway selection.

Complexes  ${}^{4}$ [1]<sup>2+</sup> and  ${}^{4}$ [2]<sup>2+</sup> exhibited nearly identical first reduction potentials at -0.81 V and -0.85 V vs. Fc<sup>0/+</sup>, respectively (Fig. 2). Despite slight structural differences, the first reduction reactions of both complexes can be attributed to the Co(II/I) reduction reaction within a similar octahedral coordination environment. Interestingly, these reduction potentials are observed at significantly positive values compared to those of other known Co complexes.<sup>11,14,25</sup> This substantial potential shift is unlikely to be solely due to spin coupling and appears to result from electron transfer from Co d orbitals to the Imbpy  $\pi^*$  orbital, facilitated by electrochemical reorganization. However, during the cathodic scan, the second reduction current appeared at very different potentials at -1.65 V vs. Fc<sup>+/</sup>



**Fig. 2** CVs of (a)  ${}^{4}$ [**1**]<sup>2+</sup> and (b)  ${}^{4}$ [**2**]<sup>2+</sup> in the presence of Et<sub>3</sub>N·HBF<sub>4</sub>. Experimental conditions: 2 mM complex and 0–50 mM proton source in CH<sub>3</sub>CN.

<sup>0</sup> for  $[1]^{+/0}$  and  $-1.92 \text{ V} \nu s$ . Fc<sup>+/0</sup> for  $[2]^{+/0}$ , respectively. The  $[2]^{+/0}$ reduction required a more negative potential, likely due to the substantial influence of coulombic repulsion during the second electron transfer. In  ${}^{3}[2]^{+}$ , there is considerable overlap between the Co d and ligand p orbitals at the SOMO level, inducing antiferromagnetic coupling. This overlap causes the localized electron density between the Co center and the Imbpy ligand, leading to repulsive interactions with additional electrons. As a result, the second reduction occurs at the Bpy  $\pi^*$  orbital, where the electron density is less distributed. In contrast, the Co d orbitals in  ${}^{5}[1]^{+}$  exhibit minimal electron density, and the Co and Imbpy orbitals involve negligible overlap. Consequently, additional electrons are preferentially accommodated in the energetically lower Co d orbital, requiring less reduction energy. The cyclic voltammograms (CVs) of complexes  ${}^{4}[1]^{2+}$  and  ${}^{4}[2]^{2+}$  showed an increase in reductive current with an increase in the proton (Et<sub>3</sub>N·HBF<sub>4</sub>) concentration (Fig. 2), indicating catalytic activity for proton reduction. For  ${}^{4}[\mathbf{1}]^{2+}$ , the half-wave catalytic potential  $(E_{cat/2})$ was observed at -2.01 V vs. ferrocenium/ferrocene (Fc<sup>+/0</sup>), with the catalytic current beginning to rise at a potential 360 mV more negative than its second reduction potential. In contrast,

 ${}^{4}$ [2]<sup>2+</sup> exhibited a catalytic onset potential of -1.58 V vs. Fc<sup>+/0</sup>, which was 350 mV more positive than the [2]<sup>+/0</sup> potential. The onset potential was defined as the potential reaching 0.07 mA.

Chronoamperometry (CA) experiments were performed on both complexes (Fig. S2<sup>†</sup>), and the amount of hydrogen gas (H<sub>2</sub>) generated was quantified using gas chromatography (GC). For <sup>4</sup>[1]<sup>2+</sup>, CA conducted at -2.0 V vs. Fc<sup>+/0</sup> in the presence of 0.1 M Et<sub>3</sub>N·HBF<sub>4</sub> resulted in a faradaic efficiency (FE) of 99%. Similarly, CA for <sup>4</sup>[2]<sup>2+</sup> at -1.9 V vs. Fc<sup>+/0</sup> with 0.1 M Et<sub>3</sub>N·HBF<sub>4</sub> yielded an efficiency of 96% (Fig. S3<sup>†</sup>). Turnover frequency (TOF) values, determined using the Foot-of-the-Wave Analysis (FOWA) method, were calculated as 3140 s<sup>-1</sup> for <sup>4</sup>[1]<sup>2+</sup> and 4480 s<sup>-1</sup> for <sup>4</sup>[2]<sup>2+</sup> (Fig. S4,<sup>†</sup> Table 1). These TOF values were moderate and comparable to those of catalysts with pincertype ligands but lower than those of catalysts containing proton-relaying agents (Fig. S5, Table S1<sup>†</sup>).<sup>4,5,25,34</sup>

The CV profile of  ${}^{4}$ [1]<sup>2+</sup> obtained under weakly acidic conditions was markedly different from that obtained under strongly acidic conditions,<sup>31</sup> indicating that it follows an alternative PCET pathway (Scheme 2). The catalytic current was observed only after the second reduction potential, indicating that two ET steps precede the formation of catalytic species. Furthermore, a shoulder-shaped peak emerged just before the sharp increase in catalytic current, suggesting that a stepwise PT occurs, leading to the formation of a protonated species after the two ET steps, followed by an additional ET step to

Table 1 Catalytic parameters of <sup>4</sup>[1]<sup>2+</sup> and <sup>4</sup>[2]<sup>2+</sup>

Cat.	Proton source	Onset <sup>a</sup>	$E_{\rm cat/2}$	$\mathrm{FE}_{\mathrm{H}_2}$	TOF
${}^{4}[1]^{2+}$ ${}^{4}[2]^{2+}$ ${}^{4}[1]^{2+}$ ${}^{4}[2]^{2+}$ ${}^{4}[2]^{2+}$	${\operatorname{PhNH}}_2{\cdot}{\operatorname{HBF}}_4^b$ ${\operatorname{PhNH}}_2{\cdot}{\operatorname{HBF}}_4^b$ ${\operatorname{Et}}_3{\operatorname{N}}{\cdot}{\operatorname{HBF}}_4$ ${\operatorname{Et}}_3{\operatorname{N}}{\cdot}{\operatorname{HBF}}_4$	-1.39 V -1.32 V -1.71 V -1.58 V	-1.53 V -1.47 V -2.01 V -1.93 V	$88\%^{c}$ 100% <sup>c</sup> 99% <sup>d</sup> 96% <sup>d</sup>	$\begin{array}{c} 6540 \text{ s}^{-1} \\ 11200 \text{ s}^{-1} \\ 3140 \text{ s}^{-1} \\ 4480 \text{ s}^{-1} \end{array}$

<sup>*a*</sup> The catalytic onset potential was defined at -0.07 mA. <sup>*b*</sup> The results for PhNH<sub>2</sub>·HBF<sub>4</sub> were taken from ref. 31. <sup>*c*</sup> Chronopotentiometry was measured at an applied current of -0.4 mA. <sup>*d*</sup> Chronoamperometry was measured at an applied potential of  $E_{cat/2}$ .



Scheme 2 Proposed PCET pathways of  ${}^{4}[1]^{2+}$ , depending on the acidity of proton sources (solid arrows = weaker acid and dotted arrows = stronger acid).

generate Co(I)-H. Alternatively, under conditions where the PT step is more challenging, Co(I)-H may be generated through concerted proton–electron transfer (CPET) after the two sequential ET steps.

#### Mechanistic considerations via DFT calculations

The formation of  $Co(\pi)$ -H from  ${}^{4}[1]^{0}$  *via* a PT step, yielding  ${}^{4}[1-H]^{+}$ , is thermodynamically favorable with a Gibbs free energy change ( $\Delta G$ ) of -0.1 kcal mol<sup>-1</sup> through DFT calculations (Fig. 3). However, the activation energy for this transformation is relatively high at 30.0 kcal mol<sup>-1</sup> (Fig. S6†), rendering the step kinetically unfavorable. Under conditions of low applied potential, a CPET pathway from  ${}^{4}[1]^{0}$  to  ${}^{3}[1-H]^{0}$  will be accessible, with a  $\Delta G$  value of -83.6 kcal mol<sup>-1</sup>. However, under conditions of further negative potentials, an alternative reaction pathway is selected, leading to the formation of  $Co(\pi)$ -H in  ${}^{4}[1-H]^{+}$ . Subsequent further reduction forms  $Co(\pi)$ -H, facilitating proton reduction. These computational results align well with the experimentally observed CV curves, where two reduction peaks were observed at -1.9 V and -2.3 V at a proton concentration of 50 mM. Protonation at the imino-N site, which can

occur under strongly acidic conditions, is thermodynamically unfavorable, with a  $\Delta G$  value of 2.1 kcal mol<sup>-1</sup>. A stepwise ET– ET–PT–PT pathway from <sup>4</sup>[**1**-**H**]<sup>+</sup> to <sup>4</sup>[**1**]<sup>2+</sup> is endergonic ( $\Delta G$  = 2.4 kcal mol<sup>-1</sup>), indicating that additional ET is required. The most favorable pathway involves the formation of <sup>3</sup>[**1**-**H**]<sup>0</sup> from <sup>4</sup>[**1**]<sup>2+</sup> through an ET–ET–CPET pathway, followed by a proton



Scheme 3 Proposed PCET pathways of  ${}^{4}[2]^{2+}$ , depending on the acidity of proton sources (solid arrows = weaker acid and dotted arrows = stronger acid).



### **Reaction Coordinates**

Fig. 3 Energy diagram comparing different reaction pathways of <sup>4</sup>[1]<sup>2+</sup>. B3LYP/Def2-SVP//Def2-TZVPPD solution phase calculations in CH<sub>3</sub>CN.



Reaction Coordinates

Fig. 4 Energy diagram comparing different reaction pathways of  ${}^{4}$ [2]<sup>2+</sup>. B3LYP/Def2-SVP//Def2-TZVPPD solution phase calculations in CH<sub>3</sub>CN.

reaction to produce H<sub>2</sub> gas. The conversion of  ${}^{3}$ [**1**-H]<sup>0</sup> to  ${}^{5}$ [**1**]<sup>+</sup> is energetically favorable ( $\Delta G = -6.1$  kcal mol<sup>-1</sup>) with an activation energy ( $\Delta G^{\ddagger}$ ) of 12.9 kcal mol<sup>-1</sup> (Fig. S7<sup>†</sup>).

For complex  ${}^{4}[2]^{2+}$ , the CV recorded under mildly acidic conditions (using Et<sub>3</sub>N·HBF<sub>4</sub>) suggested a proton reduction mechanism involving an ET-CPET pathway, distinct from the stepwise ET-PT-ET process observed under strongly acidic conditions (Scheme 3). Protonation experiments using  ${}^{3}[2]^{+}$ and Et<sub>3</sub>N·DBF<sub>4</sub> showed no reactivity in <sup>2</sup>H NMR spectroscopy (Fig. S8<sup> $\dagger$ </sup>), indicating that, after the formation of <sup>3</sup>[2]<sup>+</sup>, a CPET step likely follows. The CV curve exhibited a sharp increase in current at a potential 350 mV more positive than the second reduction event. Electrochemical reorganization occurred during the first ET step and this reorganization leads to  ${}^{3}[2]^{+}$ , characterized by antiferromagnetic coupling between the highspin Co(II) d orbital and the Imbpy  $\pi^*$  orbital. This spin coupling prevents the second ET from occurring on the Co(II) d orbital, instead favoring an alternative  $\pi^*$  orbital. Under strongly acidic conditions, PT becomes more accessible; however, in weaker acidic environments, PT is challenging, requiring CPET for the formation of  $Co(\pi)$ -H.

The CPET step from  ${}^{3}[2]^{+}$  is favorable, with  $\Delta G = -70.2$  kcal mol<sup>-1</sup>, producing  ${}^{2}[2-H]^{+}$  (Fig. 4). An alternative pathway

involves protonation at the ligand imino-N site ( $\Delta G = -69.9 \text{ kcal mol}^{-1}$ ), but the subsequent PT to form Co(m)-H from <sup>2</sup>[**2-NH**]<sup>+</sup> requires a large energy input ( $\Delta G = 17.3 \text{ kcal mol}^{-1}$ ), necessitating an additional ET step. The more favorable pathway involves a PT step converting <sup>2</sup>[**2-H**]<sup>+</sup> to <sup>4</sup>[**2**]<sup>2+</sup> with H<sub>2</sub> gas release ( $\Delta G = -6.1 \text{ kcal mol}^{-1}$ ;  $\Delta G^{\ddagger} = 19.7 \text{ kcal mol}^{-1}$ ; Fig. S9†).

### Conclusion

As closing remarks, this study provides a comprehensive analysis of PCET pathways in high-spin Co complexes under varying acidic conditions, highlighting the influence of both internal and external factors on catalytic mechanisms. The spin state and exchange coupling interactions within the Co complexes significantly influence the PCET pathways. Complex  ${}^{5}[1]^{+}$  exhibits ferromagnetic coupling, leading to the ET–CPET pathway under weakly acidic conditions. In contrast, complex  ${}^{3}[2]^{+}$  shows antiferromagnetic coupling, favoring the CPET pathway under similar conditions. The  $p_{K_{a}}$  value of the proton source plays a pivotal role in determining the mechanism of proton reduction. As the acidity increases,  ${}^{5}[1]^{+}$  preferred the

CPET pathway, while  ${}^{3}[2]^{+}$  opted for the stepwise PT-ET pathway. By supporting the experimental results with computational data, the most plausible mechanism was proposed. This study demonstrates that, in addition to the finding that spin interactions within the complex dictate the electron transfer pathway, the  $pK_{a}$  value of the proton source serves as a critical determinant in selecting the overall PCET pathway, including the electron transfer steps.

### Experimental

### Materials and methods

All complexes were synthesized under a N<sub>2</sub> or Ar atmosphere using a glovebox and Schlenk techniques. Solvents were purified through a solvent purification system (Vigor) and stored over 4 Å molecular sieves until use. Tetrabutylammonium hexafluorophosphate (Acros,  $\geq$ 98%) was recrystallized from ethanol. Cobalt bromide (anhydrous, Sigma-Aldrich,  $\geq$ 99%), silver hexafluorophosphate (Alfa Aesar, 98%), 2,2'-bipyridine (Alfa Aesar, 98%), and sodium mercury amalgam (Acros, *ca.* 20% sodium) were used as received.

#### <sup>2</sup>H-NMR experimental details

Et<sub>3</sub>N·DBF<sub>4</sub> was obtained by reacting Et<sub>3</sub>N·HBF<sub>4</sub> with 5 ml of D<sub>2</sub>O at 60 °C for 4 hours. The solvent was removed under reduced pressure, and the residue dissolved in dichloromethane was dropped on *n*-hexane to precipitate as a powder. 1 equivalent of Na(Hg) (20 wt% Na) was added to a  ${}^{4}$ [2]<sup>2+</sup> complex solution with 2 ml of CH<sub>3</sub>CN for the reduction reaction. The reaction mixture was stirred at room temperature for 1 hour. The solution of  ${}^{3}$ [2]<sup>+</sup> in CH<sub>3</sub>CN was then cooled to -40 °C. A solution of Et<sub>3</sub>N·DBF<sub>4</sub> in CH<sub>3</sub>CN was added to the complex solution upon cooling to -40 °C while stirring in a glove box. A small amount of CD<sub>3</sub>CN was added for reference and <sup>2</sup>H NMR was taken while increasing the temperature from -40 °C to 25 °C. <sup>2</sup>H-NMR (61 MHz) spectra were recorded with a JEOL NMR spectrometer (JNM-ECS400) using a screw-cap NMR sample tube.

#### Electrochemistry

Electrochemical experiments were performed using an INTERFACE 1010 Е potentiostat/Galvanostat/ZRA. Electrochemical measurements were conducted in a 4-neck pear shaped cell equipped with a glassy carbon disk (3.0 mm diameter) working electrode, a platinum wire counter electrode, and a Ag/AgNO<sub>3</sub> (0.01 M)/CH<sub>3</sub>CN non-aqueous reference electrode (also containing 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub>), separated from the solution using a porous CoralPor tip. The working electrode was polished prior to each experiment with a 0.05 µm alumina polishing agent on a pad. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (<sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub>) in CH<sub>3</sub>CN freshly prepared with an anhydrous solvent and saturated with Ar or N<sub>2</sub>. At the conclusion of each experiment, the potentials were referenced against ferrocenium/ferrocene (Fc<sup>+/</sup> <sup>0</sup>) used as an external standard. Cyclic voltammetry experiments were performed while increasing the concentration of Et<sub>3</sub>N·HBF<sub>4</sub> in 10 mM increments, and the scan was conducted in the cathodic direction. The scan rates for all cyclic voltammograms were 100 mV  $s^{-1}$  unless otherwise noted. Chronoamperometry was performed with 10 mL of 2 mM catalyst solution in CH<sub>3</sub>CN with 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> and 0.1 M of Et<sub>3</sub>N·HBF<sub>4</sub> as a proton source in the working compartment. The electrolyte solution was constantly stirred during the chronoamperometry experiment with a stirring bar. At the conclusion of the experiment, 1 ml of headspace gas of the cell was sampled using a Hamilton 2.5 mL gas-tight syringe, and the sample was injected directly into GC equipment using TCD for H<sub>2</sub> detection. The faradaic efficiency of every product was calculated by dividing the measured amount of product by the charge passed during the chronopotentiometry measurement. The faradaic efficiency values of  ${}^{4}[1]^{2+}$  and  ${}^{4}[2]^{2+}$  were obtained from three repeated experiments each (Fig. S3<sup>†</sup>).

## Author contributions

J. L. and J. S. conceived the concept, designed all experiments and analyzed the results. J. L. performed all the experimental and computational studies. J. L. and D. J. synthesized complexes. J. L. and J. S. wrote the manuscript.

# Data availability

The data supporting this article have been included as part of the ESI.† Experimental methods, electrochemical details and DFT calculation details are provided.

# Conflicts of interest

There are no conflicts to declare.

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