Push or Pull? Proton Responsive Ligand Effects in Rhenium Tricarbonyl CO₂ Reduction Catalysts

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Supporting Information Placeholder

ABSTRACT: Proton responsive ligands offer control of catalytic reactions through modulation of pH-dependent properties, second coordination sphere stabilization of transition states, or by providing a local proton source for multi-proton, multi-electron reactions. Two *fac*-[Re(α -diimine)(CO)₃Cl] complexes with α -diimine = 4,4'- (or 6,6'-) dihydroxy-2,2'-bipyridine (4DHBP and 6DHBP) have been prepared and analyzed as electrocatalysts for reduction of carbon dioxide. Consecutive electrochemical reduction of these complexes yields species identical to those obtained by chemical deprotonation. An energetically feasible mechanism for reductive deprotonation is proposed in which the bpy anion is protonated followed by loss of H₂ and 2H⁺. Cyclic voltammetry reveals a two-electron, three-wave system owing to competing EEC and ECE pathways. The chemical step of the ECE pathway might be attributed to the reductive deprotonation, but cannot be distinguished from chloride dissociation. The rate obtained by digital simulation is approximately 8 s⁻¹. Under CO₂, these competing reactions generate a two-slope catalytic waveform with onset potential of -1.65 V vs Ag/AgCl. Reduction of CO₂ to CO by the [Re(4DHBP-2H⁺)(CO)₃]⁻ suggests the interaction of CO₂ with the deprotonated species or a third reduction followed by catalysis. Conversely, the reduced form of [Re(6DHBP)(CO)₃Cl] converts CO₂ to CO with a single turnover.

1. INTRODUCTION

Advances in the chemistry of carbon dioxide are needed to enable efficient, cost-effective methods for recycling the end-product of combustion into liquid fuels and C1 chemicals.¹⁻⁶ Direct electrochemical reduction of CO₂ is unfavorable with E^0 (CO₂/CO₂•⁻) = -1.90 V vs. NHE in water at pH 7, but the energy requirement for CO₂ reduction is substantially lower for proton-assisted, multi-electron processes. For example, the standard potential for the 8-proton, 8-electron reduction of CO₂ to methane and H₂O is only -0.24 V vs. NHE at pH 7; however, the difficulty of orchestrating numerous electron- and proton-transfer steps becomes a kinetic limitation. Transition metal catalysts are well-suited to mediate the electron transfers and bond formations necessary for CO₂ activation and reduction and provide selectivity for a single product in many cases.

The *fac*-[Re(α -diimine)(CO)₃X]ⁿ⁺ (X = halide; n = 0 or X = neutral ligand, n = 1) family of complexes selectively catalyzes the reduction of CO₂ to CO.⁷⁻¹⁹ Electrocatalysis is effective in solution and using surface-bound catalysts while photochemical systems have been identified with or without separate sensitizers. Mechanistic studies have revealed one-electron or two-electron pathways for catalysis. The photocatalytic one-electron chemistry relies on the α -diimine ligand functioning as an electron reservoir while imparting radical character to the Re center, thus providing properties different from the typical 17e⁻ metal complexes such as Re[•](CO)₅.²⁰ As an illustration of 1e⁻ chemistry, [Re(dmb)(CO)₃Cl]⁻ (dmb = 4,4'-dimethyl-2,2'-bipyridine) undergoes dissociative substitution of Cl⁻ by solvent to produce the ligand radical, [Re(dmb•)(CO)₃(S)] (S = solvent).^{11,21} Reaction of two metal radicals with CO₂ is slow ($k \sim 0.003$ s⁻¹) due to equilibrium in favor of the six-coordinate ligand radical over the five-coordinate Re-centered radical. The product is a μ_2 -

η^2 -CO₂ bridged species which reacts with CO₂ as an oxide acceptor to produce CO and CO₃²⁻. The two-electron pathway is expected to dominate electrochemically and involves η^1 coordination of CO₂ to the five-coordinate anion [Re(α -diimine)(CO)₃]⁻.²² Recent experimental results supported by DFT calculations have revealed the reaction of ¹³CO₂ with [Re(dmb)(CO)₃(COOH)] to produce CO and the bicarbonate product [Re(dmb)(CO)₃(O¹³CO₂H)].²³ In practical consideration, CO is an ideal target since it readily separates from the reaction mixture and can be used in the synthesis of liquid alkanes by the Fisher-Tropsch process.

Recent research efforts in our group and others have focused on catalytic hydrogenation of CO₂ to formic acid or the reverse dehydrogenation of formic acid using transition metal complexes of hydroxy-bipyridine type ligands.²⁴⁻³⁰ Hydrogenation of CO₂ using Rh, Ir, and Ru complexes of 4,4'-dihydroxy-2,2'-bipyridine (4DHBP) is enhanced in basic media due to the acid/base equilibrium of the ligand and the strong electron donating property in the oxyanion form (Figure 1). Ligands with the OH group adjacent to the metal center experience the electronic effects of deprotonation and also exploit the oxyanion as a pendant base adjacent to the catalytic site. Reversible hydrogen storage has been demonstrated by [{Cp*Ir(Cl)}₂(thbpm)]²⁺ (Cp* = pentamethylcyclopentadiene, thbpm = 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine) which catalyzes CO₂ hydrogenation at high pH as the oxyanion and formic acid dehydrogenation at low pH as the pyridinol form.²⁶ The proximal base lowers the activation energy for heterolytic cleavage of H₂ to form the metal hydride which then undergoes insertion of CO₂.³⁰

Figure 1. 4,4'-dihydroxy-2,2'-bipyridine acid-base equilibrium and Hammett values.

To the best of our knowledge, the 4DHBP or 6DHBP ligands have not been studied for CO₂ reduction using rhenium tricarbonyl catalysts. The highly active electrocatalyst, [Re(^tBu₂bpy)(CO)₃Cl] (^tBu₂bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) has been identified for CO₂ reduction, but the origin of improved catalysis remains ambiguous.³¹ One suggested explanation is greater nucleophilicity of the Re center in reduced species due to electron-donating ^tBu groups although the activity comes at the expense of a greater overpotential. Based on precedent for CO₂ hydrogenation, we hypothesized that the influence of electron donation could be pushed to the extreme using 4DHBP and 6DHBP. Furthermore, there is increasing interest in designing electrocatalysts for CO₂ reduction with pendant acids since typical mechanisms proceed through [M-COOH]⁺ intermediates generated by protonation of [M-CO₂]⁻ species.^{32,22}

This paper reports the preparation, physical properties, and application in CO₂ reduction electrocatalysis of [Re(4DHBP)(CO)₃Cl] and [Re(6DHBP)(CO)₃Cl]. Unexpectedly, we have discovered reductive electrolytic deprotonation of the ligands proven by full and partial chemical deprotonation in combination with spectroelectrochemical IR (SEC-IR) experiments. To the best of our knowledge this is the first example for Re(CO)₃ complexes of this process happening twice and also on the same ligand that accepts the electron. This phenomenon nullifies the “push” of the electron-donating substituents which instead exert a “pull” since the reduction occurs primarily at ligand sites. Despite this “pull”, [Re(4DHBP)(CO)₃Cl] is still a viable CO₂ reduction electrocatalyst which likely requires a third electron to initiate catalysis. The [Re(6DHBP)(CO)₃Cl] reacts stoichiometrically with CO₂.

2. EXPERIMENTAL DETAILS

2.1. General. The ligands 4,4'-dihydroxy-2,2'-bipyridine, 6,6'-dihydroxy-2,2'-bipyridine^{33,79} and known complexes [Re(^tBu₂bpy)(CO)₃Cl] and [Re(OMe₂bpy)(CO)₃Cl]³¹ were prepared according to literature procedures. Re(CO)₅Cl was purchased from Aldrich. Anhydrous DMF, CD₃CN, and CH₃CN were stored over activated molecular sieves under Ar. Electrospray mass spectra (ESI-MS) were measured using a Thermo Finnigan mass spectrometer. NMR spectra were recorded on a 400 MHz Bruker Avance spectrometer at room temperature. Chemical shifts in ppm are referenced to the solvent peaks. NMR spectra of deprotonated complexes (i.e., with the oxyanion ligand) were measured by first dissolving the complex in CD₃CN in a J-Young tube then adding 2 eq. Bu₄NOH as a 1 M solution in MeOH. Solutions were stable for at least 3 hours. If the mixtures were taken to dryness and re-dissolved in CD₃CN, several minor species were present. Thus, data in Table 1 are chemical shifts prior to evaporation of the MeOH and H₂O generated by deprotonation. NMR spectra of reduced complexes were obtained by electrolyzing [Re(4DHBP)(CO)₃Cl] or [Re(6DHBP)(CO)₃Cl] in CD₃CN with 0.1 M Bu₄NPF₆ under Ar. After consumption of two equivalents of charge, an aliquot was rapidly transferred to a

J-Young tube with positive argon flow. The solution was immediately frozen in liquid nitrogen then degassed by three freeze-pump-thaw cycles under high vacuum to remove any air contamination. Electronic absorption spectra were measured using an Agilent 8453 diode array spectrophotometer. Aqueous pH titrations were carried out in Britton-Robinson buffer and 1% CH₃CN co-solvent. Starting at pH ~1.5, the pH was adjusted with concentrated NaOH. pK_a values were determined from the sigmoidal least-squares fit of ϵ vs. pH. Cyclic voltammograms (CVs) were recording using a three-electrode configuration with a glassy carbon working electrode and Pt counter electrode. The reference electrode was Ag/AgCl (3 M KCl) separated from the working solution by two Vycor frits and the supporting electrolyte was 0.1 M Bu₄NPF₆. The reference was calibrated internally using ferrocene. Spectroelectrochemical UV-vis experiments were performed in a standard H-cell using a Pt mesh working electrode. Simulated voltammograms were generated using Digisim[®]³⁴. Preparative-scale electrolysis experiments were performed in a three compartment cell with fine porosity glass frits separating each compartment. The working electrode was a 5 cm² mercury pool connected through a Pt wire sealed in glass. The uncompensated cell resistance was approximately 30 Ω . Gaseous products were analyzed by GC on an Agilent 6890N GC with HP-MOLSIV (30 m $\times$ 0.32 mm $\times$ 1.5 μ m) and GS-CARBON-PLOT (15 m $\times$ 0.32 mm $\times$ 1.5 μ m) columns. CO was quantified via a methanizer by a calibrated FID detector. Spectroelectrochemical IR (SEC-IR) experiments were performed using an OTTLE cell from Specac equipped with a gold mini-grid working electrode, Rh counter electrode, an Ag wire pseudo-reference electrode and CaF₂ windows. Solutions were approximately 1 mM Re complex and 100 mM Bu₄NPF₆. Solutions were purged with Ar prior to introduction into the cell via syringe. Background scans were collected using pure solvent without electrolyte. Data were collected as an average of 2-4 scans with 2 cm⁻¹ resolution using a MCT detector. Details of X-ray crystallography and DFT calculations are provided as Supporting Information.

2.2. Synthesis of [Re(4DHBP)(CO)₃Cl]. 4DHBP (52.0 mg, 0.284 mmol) in MeOH (1 mL) and toluene (8 mL) was heated until the ligand dissolved and Re(CO)₅Cl (100. mg, 0.284 mmol) was added in a single portion. The mixture was heated at reflux for 1h then allowed to stand at room temperature for 5 days after which a crop of yellow microcrystals was collected by filtration, washed with diethyl ether, and dried under vacuum to provide 95 mg (70% yield). X-ray quality crystals were grown by evaporation of a mixture of DMSO and acetone. ν_{CO} (DMF): 2015, 1907, 1885. ¹H NMR (CD₃CN, RT): δ 9.03 (s, -OH), 8.66 (d, J = 8.7), 7.69 (d, J = 2.5), 7.03 (dd, J = 7.0, 2.5). ESI-MS(+): m/z calcd for [M - HCl + CH₃OH + Na⁺]⁺ 516.0, found 516.7; [M - CO + Na⁺]⁺ 491.0, found 490.7. Anal. calc'd: C, 31.62; H, 1.63; N, 5.67. found: C 31.33; H, 1.64; N, 5.55. UV-vis, CH₃CN, λ_{max} (ϵ / M⁻¹cm⁻¹): 193 (64,200), 223 (41,100), 254 (22,200), 348 (3700); [Re(4DHBP-2H⁺)(CO)₃]⁻: 193 (114,200), 255 (56,700), 342 (11,600).

2.3. Synthesis of [Re(6DHBP)(CO)₃Cl]. The procedure for [Re(4DHBP)(CO)₃Cl] was followed using 6DHBP (104 mg, 0.568 mmol) and Re(CO)₅Cl (200 mg, 0.568 mmol). After cooling to room temperature, the product was isolated by precipitation with diethyl ether, collected by vacuum filtration, and dried under vacuum to provide 273 mg (71% yield). ν_{CO} (DMF): 2016, 1911, 1878. ¹H NMR (CD₃CN, RT): δ 9.74 (s, -OH), 7.93 (t, J = 7.9), 7.84 (d, J = 8.1), 7.09 (d, J = 8.1). ESI-MS(+): m/z calcd for [M - HCl + CH₃OH + Na⁺]⁺ 516.0, found 516.7; [M - CO + Na⁺]⁺ 491.0, found 490.7. Anal. calc'd: C, 31.62; H, 1.63; N, 5.67. found: C 31.61; H, 1.56; N, 5.70. UV-vis,

CH₃CN, λ_{max} (ϵ / M⁻¹cm⁻¹): 193 (155,100), 332 (27,000) 345 (32,400), 254 (22,200), 400 (11,800); [Re(6DHBP-2H⁺)(CO)₃]⁺: 193 (350,300), 395 (36,400), 416 (28,600).

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. The complexes [Re(4DHBP)(CO)₃Cl] and [Re(6DHBP)(CO)₃Cl] were obtained as analytically pure solids from the reaction of the ligands with Re(CO)₅Cl. The X-ray structure of [Re(4DHBP)(CO)₃Cl] (see Figure S1 and Tables S1–S3) confirmed bidentate α -diimine coordination and the neutral pyridinol nature of the ligand. Bond distances and angles in the Re coordination sphere are nearly identical to the structure of [Re(bpy)(CO)₃Cl].¹² The 2.0(2)° dihedral angle between rings of 4DHBP is identical to [Re(bpy)(CO)₃Cl]. Strong hydrogen bonding between the hydroxyl groups of 4DHBP and the oxygen atom of a co-crystallized DMSO molecule was observed. (Table S3–S4).

NMR data (Table 1 and Figure S2) show three ¹H resonances for the bipyridine ligands in agreement with a facial arrangement of CO ligands. The –OH resonances of [Re(6DHBP)(CO)₃Cl] and [Re(4DHBP)(CO)₃Cl] appear at 9.76 and 9.02 ppm, respectively, in dry CD₃CN but broaden in the presence of small quantities of H₂O. Although many possible coordination modes are possible for the 2-hydroxypyridine ligand,³⁵ the appearance of the –OH resonance and bipyridine symmetry confirms bidentate α -diimine coordination. Upon deprotonation, the ¹H resonances shift upfield, consistent with the electron-rich nature of the ligand expected from a change in σ_p .³⁶ ¹H NMR were also measured after electrochemical reduction in which case resonances are also shifted upfield by *ca.* 0.7 to 1 ppm from the parent complexes. The nature of these species will be discussed below.

Table 1. NMR data for [Re(4DHBP)(CO)₃Cl] and [Re(6DHBP)(CO)₃Cl].^a

Compound	isolated	chemically deprotonated ^b	2e ⁻ reduced ^c
[Re(4DHBP)(CO) ₃ Cl] ^d	9.02 ^e		
	8.66 (d)	7.97 (d)	7.99 (d)
	7.69 (d)	6.78 (d)	6.89 (d)
	7.03 (dd)	6.14 (dd)	6.16 (dd)
[Re(6DHBP)(CO) ₃ Cl] ^f	9.76 ^e		
	7.93 (t)	7.14 (t)	7.25 (dd)
	7.84 (d)	6.64 (d)	6.74 (d)
	7.09 (d)	6.13 (d)	6.25 (d)

^a ppm in CD₃CN. ^b Prepared *in-situ* using 2eq. Bu₄NOH. ^c Prepared by electrochemical reduction in CD₃CN. ^d Low field to high field: H2, H5, and H3. ^e Observed only in strictly anhydrous CD₃CN. ^f Low field to high field: H4, H5, and H3. d = doublet, t = triplet, dd = doublet of doublets.

Three CO stretching bands in the solution IR spectra confirm the facial orientation of the CO ligands (Table 2).³⁷ The $\nu(\text{CO})$ for [Re(4DHBP)(CO)₃Cl] and [Re(6DHBP)(CO)₃Cl] are among the lowest energies reported for [Re(α -diimine)(CO)₃Cl] complexes due to increased Re($d\pi$)→CO backbonding.^{37,38} IR spectra were recorded with incremental addition of Bu₄NOH and two stoichiometric deprotonation reactions were observed with each resulting in small red shifts of $\nu(\text{CO})$ (Figures 4, 5, S11, S12 and Table 2). The three CO stretches for facial coordination were preserved, and no further changes in the spectra were observed with addition of excess base.

3.2. Electronic Absorption Spectra. Typical absorption spectra of *fac*-[Re(α -diimine)(CO)₃Cl] complexes exhibit broad,

high energy MLCT bands with low oscillator strength. These properties are attributed to strong $d\pi \rightarrow \pi^*(\text{CO})$ back bonding and a large energy separation between the Re($d\pi$) and bpy(π^*) orbitals which are weakly coupled.³⁸ The spectrum of [Re(4DHBP)(CO)₃Cl] in CH₃CN features the expected MLCT band at 355 nm which is blue-shifted relative to [Re(bpy)(CO)₃Cl] (384 nm) in accord with the electron-donating substituents having stronger influence on the ligand π^* orbitals than on Re($d\pi$) orbitals.³⁸ Titration with Bu₄NOH (Figure 2A) revealed two unique but similar pK_as for ligand –OH groups. There is a single isosbestic point at 228 nm for < 0.6 eq. OH⁻ as the local λ_{max} shifted from 223 to 230 nm. From 0.6 to 2 eq. base, the UV maximum shifted to 254 nm while the low energy band increased in intensity and blue shifts from λ_{max} = 355 to 340 nm.

The absorption spectrum of [Re(6DHBP)(CO)₃Cl] (Figure 2B) exhibits a structured transition with λ_{max} = 338 nm (ϵ = 1.7×10^4 M⁻¹ cm⁻¹) which is atypical of this family of compounds. According to time-dependent DFT calculations, this transition is intraligand ($\pi \rightarrow \pi^*$) mixed with ($n_{(\text{OH})} \rightarrow \pi^*$) (Table S5 and Figure S3) Weak, low energy MLCT or (M+Cl)LCT charge transfer transitions are calculated at 380, 355, and 337 nm. Titration in CH₃CN using Et₃N as the base revealed two pK_as for ligand –OH groups. For < 1 eq. Et₃N, isosbestic points appeared at 242, 268, 286, and 356 nm while the 338 nm band decreased and the absorption from 375 to 450 nm increased. The red shifted absorption in the pyridinol form is consistent with a higher energy HOMO. Above 1 eq. base, the intense band at *ca.* 400 nm continued to increase while the low energy tail decreased in absorbance. The titrations in CH₃CN reveal two acid-base reactions despite the molecular symmetry. Similarly, two pK_as were reported for [Rh(6DHBP)(CO)₂]⁺.³⁹

Emission of protonated and deprotonated species were examined briefly under the premise that flash-quench studies could be used to study reduced species. Both [Re(4DHBP)(CO)₃Cl] and [Re(6DHBP)(CO)₃Cl] exhibit the MLCT emission found in this family of complexes; however, reductive quenching was ineffective owing to the short lived excited states (<10 ns) and deprotonation of the complexes by most reductive quenchers.

Acid-base behavior in water was investigated for comparison to pK_a values of related complexes (Figures S4). In H₂O/1% CH₃CN, the sigmoidal inflection point at 260 nm of an ϵ vs. pH plot provides pK_a = 5.6 for [Re(4DHBP)(CO)₃Cl] The pK_a of [Re(6DHBP)(CO)₃Cl] is 4.5 as calculated from the sigmoidal fit of ϵ at 378 nm vs. pH. A single spectroscopic transition for each compound indicates close or identical pK_a values in H₂O. By definition,⁴⁰ the pK_a for a two-proton acid-base equilibrium with equal pK_a is twice the pH at the inflection point; therefore, the measured pH values of the inflection point imply pK_a of 11.2 and 9; however, owing to the non-intuitive nature of such pK_a values, the average pK_a is often reported at the inflection point. Our values are in the expected range of 4.4 to 7.3 reported for related Co(III), Ir(III), and Ru(II) with 4- or 6DHBP ligands.^{41,27,28,42,43}

3.3. UV-vis Spectroelectrochemistry. Figure 2C and 2D present changes in absorption spectra upon electrochemical reduction. During reduction of [Re(4DHBP)(CO)₃Cl] (Figure 2C) with V = -1.2 V vs. Ag/AgCl spectra exhibited a decrease in the 233 nm band and increases at 245 and 370 nm with several isosbestic points (black traces). Without changing the applied potential, isosbestic points at 209, 229, and 388 were lost (red traces) then isobestic points appeared at 214, 241, and 365 nm (blue traces). It was not possible to isolate 1e⁻ reduced compounds even at potentials anodic of the first reduction by CV suggesting these species are unstable to disproportionation, or the first two

reduction potentials are very similar. The experiment was repeated for $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ (Figure 2D). Again, the final $2e^-$ reduced species was formed at the onset of $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ reduction at -1.2 V; however the spectrum of the $1e^-$ reduced species can be isolated (red trace) as indicated by two sets of clear isosbestic points.

Figure 2. *A and B:* Acid/base titrations in CH_3CN of $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ (A) using Bu_4NOH with the black, red, and blue spectra corresponding to 0, 0.6, and 2 eq. OH^- and $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ (B) using Et_3N as the base. The black, red, and blue spectra correspond to 0, 1.5, and 10 eq. Et_3N . *C and D:* Spectroelectrochemical reduction of $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ (C) and $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ (D) at -1.2 V vs. Ag/AgCl . In C, black spectra indicate mixtures of $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ and singly reduced species, blue spectra are due to mixtures of singly- and doubly-reduced species while red spectra are obtained with all three forms present. In D, The black, red, and blue spectra are $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ singly-reduced and doubly-reduced species, respectively.

Careful comparison of Figures 2A/C and 2B/D shows chemical deprotonation and electrochemical reduction produce complexes with strikingly similar electronic absorption spectra in agreement with NMR and IR data mentioned previously. In the following sections, cyclic voltammetry (CV) and spectroelectrochemical IR are used to further characterize these species. The CV behavior is unique among $[\text{Re}(\alpha\text{-diimine})(\text{CO})_3\text{Cl}]$ complexes, and IR experiments show that electrochemical reduction leads to reductive deprotonation of the ligand thus producing the same species obtained by chemical deprotonation. While counterintuitive, there is precedent for this phenomenon in $[\text{Re}(\text{bpy})(\text{CO})_3(\text{imidazole})]$ in which the imidazole N-H bond is cleaved after $1e^-$ reduction of the bpy.⁴⁴

3.4. Cyclic Voltammetry of $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ under Argon. For reference, the CVs of $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ are shown in Figure 3 (trace a) and S6 as an example of the known electrochemistry for $[\text{Re}(\alpha\text{-diimine})(\text{CO})_3\text{Cl}]$ complexes. The CV is typical of an EEC mechanism (eq. i-iv) with chloride dissociation as the chemical step. Agreement between $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ and data published for $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ in DMF including re-oxidation and subsequent reduction of newly formed species was found.⁴⁵ In

Figure 3a, the redox couple I/B is $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3(\text{DMF})]^{+/0}$, the II/A couple is $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]^{0/-}$, and peak III is reduction of $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3(\text{Cl})]^-$ which is followed by ligand dissociation (eq iii and iv).

The reductive CV of $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ (Figures 3 and S7) exhibits a three wave pattern ($E_p^c = -1.56$, -1.76 , and -2.03 V) with each wave irreversible except for peak R1 above 0.75 V s^{-1} . Peak I is diffusion controlled with $D = 2.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ from a plot of i_p^c vs $v^{1/2}$ according to the Randles-Sevcik equation,⁴⁶ and is reasonable in comparison to $2.65 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ reported for iron *meso*-tetraphenylporphyrin in DMF.⁴⁷ The ratio of current at peaks R2 and R3 depends on scan rate indicating competing reactions on the CV timescale (Figure S7). Bulk electrolysis cathodic of R3 consumed $2e^-$ per molecule indicating peaks R2 and R3 comprise a one-electron, two-wave system.

Figure 3. Multi-scan reductive cyclic voltammograms for 2.0 mM solutions of $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ (trace a) and $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ (trace b-d) and in DMF with $v = 0.1$ V s^{-1} . In trace c, the complex was reduced exhaustively by $2e^-$. The CV in trace d was recorded in the presence of 2 eq. Bu_4NOH .

The re-oxidation peak O1 at $E_p^a = 0$ V is not the anodic counterpart of R1. Its appearance requires reduction beyond R2 (SI). The potential of O1 is similar to the Re-Re dimer oxidation in acetonitrile⁴⁵; however, no dimer was observed during SEC-IR experiments in this work (see below). Multi-scan reductive CVs inclusive of O1 show the system is chemically reversible but electrochemically irreversible (SI). No peaks of solvent complexes were observed. The potential of O2 at $+1$ V is similar to the $2\text{Cl}^-/\text{Cl}_2$ couple and is suggestive of Cl^- dissociation after reduction and slow re-association at the O1 wave. Oxidation O3 at

1.38V is a characteristic of $[\text{Re}^{\text{I}}(\alpha\text{-diimine})(\text{CO})_3\text{Cl}]$ complexes;⁴⁵ however, in this case O3 comprises $2e^-$ /molecule as determined by comparison of its current to $[\text{Re}^{\text{I}}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$.

A reductive CV after bulk electrolysis and consumption of $2e^-$ /molecule (Figure 3c) shows the absence of reductive waves, the presence of a new peak O4 at 0.87 V, and larger current for O2. In trace **d**, the CV was recorded in the presence of 2eq. Bu_4NOH to deprotonate the ligand. The features are identical to trace **c** suggesting the same species are formed upon chemical deprotonation or electrochemical reduction.

The unusual reductive electrochemistry of $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ relative to $[\text{Re}^{\text{I}}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ is clear by examination of Figures 3 and S6-S7. The increased electron donating ability of the 4,4'-OH groups relative to ^tBu shifts the first reduction cathodically. The quasi-reversible nature of R1 and the scan-rate dependence on R2 and R3 currents suggest a process in which two products of R1 are reduced separately. The minimal mechanism to account for this behavior is competing EEC and ECE processes as shown in Scheme 1; however, as will be discussed subsequently, electrochemical reduction triggers reductive deprotonation of $1e^-$ or $2e^-$ reduced species. Furthermore, Cl^- dissociation can occur from any reduced or deprotonated species. At minimum, we approximate the rate of consumption for species B as $k_1 = 8 \text{ s}^{-1}$ by digital simulation of R1 according to an EC mechanism (Figures S8).

The CV of $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ (Figure S9) exhibits features similar to $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ and the results are discussed in the SI.

Scheme 1. Minimal mechanism for $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ reduction.

3.5. Spectroelectrochemical IR The sensitivity of $\nu(\text{CO})$ to oxidation state and coordination environment provides a handle for investigation by SEC-IR.^{9,48,10} The $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ was studied in DMF and in CH_3CN since the sampling window is wider in the latter solvent. The results are the same in both solvents. The first reduction (Figure 4a) leads to a decrease in the CO stretches at 2019, 1911, and 1893 and the weak band at 1627 cm^{-1} and growth of a new species with $\nu(\text{CO})$ 2012, 1900, and 1881 cm^{-1} (blue spectrum). This species disappears during the second reduction and the final species exhibits $\nu(\text{CO})$ 2002, 1886, and 1865, an intense absorption at 1605 and a weak band at 1532 cm^{-1} (red trace). The spectral changes were reversed upon re-oxidation (4b).

Chemical deprotonation with two equivalents Bu_4NOH yielded a species for which the IR spectrum is identical to the doubly reduced species (Figure 4c, red). Spectral changes during oxidation of this species mirrored those observed in set b with the exception of a new CO stretch at 2033 cm^{-1} and a poorly resolved shoulder at 1931 cm^{-1} . The high energy stretch is consistent with solvent coordination as in $[\text{Re}(\text{4DHBP})(\text{CO})_3(\text{CH}_3\text{CN})]^+$ according to literature for related complexes.¹⁰

Figure 4. Solution IR of $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ in CH_3CN during electrochemical reduction (a) and re-oxidation (b), upon oxidation (c) and reduction (d) of the chemically deprotonated species.

The SEC-IR experiments were repeated on $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$. In CH_3CN , the IR spectrum shows CO stretches at 2022, 1915, and 1887 cm^{-1} (Figure S11). The species formed after single reduction or deprotonation with 1eq. base is insoluble in CH_3CN ; however, the doubly reduced species is soluble with IR absorptions at 1994, 1879, 1843 (CO stretches), 1614, and 1512 cm^{-1} . Re-oxidation of the electrochemically generated species is reversible but also produces new $\nu(\text{CO})$ 2032 and 1934 cm^{-1} attributed to $[\text{Re}(\text{6DHBP})(\text{CO})_3(\text{CH}_3\text{CN})]$. The spectrum of the chemically deprotonated complex is identical to the doubly reduced species and its oxidation also yields $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{6DHBP})(\text{CO})_3(\text{CH}_3\text{CN})]$.

All species associated with $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ are soluble in DMF and electrochemical reduction is shown in Figure 5a. CO stretches of $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ at 2016, 1910, and 1879 cm^{-1} disappear during the first reduction as peaks at 2002, 1893, and 1858 cm^{-1} appear (blue spectrum). Further reduction produces a species with $\nu(\text{CO})$ 1990, 1877, and 1840 cm^{-1} (red spectrum). As in CH_3CN , the process is reversed by applying an oxidizing potential. The experiment was repeated in THF, DMSO, and pyridine and identical CO stretches were obtained proving that the $1e^-$ and $2e^-$ reduced species do not coordinate solvent. In Figure 5b, $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ was partially deprotonated with 1eq Bu_4NOH (bold, black spectrum). This sample was then reduced (red spectrum) and subsequently re-oxidized (blue to thin black spectra). Spectra throughout this sequence were identical to those obtained during electrolysis in the absence of base.

Figure 5. Solution IR of $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ in DMF during electrochemical reduction (a) and a partial deprotonation, reduction, re-oxidation sequence (b). In (b), the initial singly deprotonated species (bold black spectrum) was electrochemically reduced (red spectrum) then re-oxidized to the thin black spectrum.

SEC-IR data for $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ in CH_3CN provides benchmarks for typical behavior during reduction (Table 2).¹⁰ One-electron reduction yields $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]^-$ with a bipyridine-localized radical. Exchange of Cl^- for solvent produced $[\text{Re}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]$ as indicated by a blue shift in $\nu(\text{CO})$. Further reduction produced the five-coordinate anion $[\text{Re}(\text{bpy})(\text{CO})_3]^-$ with $\nu(\text{CO}) = 1947$ and 1843 cm^{-1} . We preformed SEC-IR measurements on $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ in DMF for direct comparison to the new DHBP complexes (Figure S12 and Table 2). The 1e^- reduced $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]^-$ dissociates Cl^- but does not bind solvent as indicated by a red-shift in $\nu(\text{CO})$. Data for $[\text{Re}(\text{OMe}_2\text{bpy})(\text{CO})_3\text{Cl}]$ are identical to $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$.

Table 2. Select $\nu(\text{CO})$ data for $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$, $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$, and related complexes.

Complex ^a	$\nu(\text{CO}) / \text{cm}^{-1}$	solvent
$[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$	2019, 1911, 1893	CH_3CN
$[\text{Re}(\text{4DHBP}-\text{H}^+)(\text{CO})_3\text{Cl}]^-$ ^b	2012, 1900, 1881	CH_3CN
$[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3]^-$ ^c	2002, 1886, 1865	CH_3CN
$[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ ^b	2016, 1910, 1879	DMF
$[\text{Re}(\text{6DHBP}-\text{H}^+)(\text{CO})_3\text{Cl}]^-$ ^b	2002, 1893, 1858	DMF
$[\text{Re}(\text{6DHBP}-2\text{H}^+)(\text{CO})_3]^-$ ^c	1990, 1877, 1840	DMF
$[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ ^d	2020, 1914, 1897	CH_3CN
$[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]^-$ ^d	1998, 1885, 1867	CH_3CN
$[\text{Re}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]$ ^d	2011, 1895	CH_3CN
$[\text{Re}(\text{bpy})(\text{CO})_3]^-$ ^d	1947, 1843	CH_3CN
$[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$	2018, 1913, 1890	DMF
$[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]^-$	1992, 1878, 1860	DMF
$[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3]$	1988, 1865	DMF
$[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3]^-$	1934, 1832	DMF

^a This work unless otherwise noted. ^b Mono-deprotonated complexes with presumed Cl^- ligand. ^c Doubly-deprotonated complexes. ^d Reference 10.

Comparison of SEC-IR data to the spectra of chemically deprotonated species shows that identical substances are produced in each process. The high energy CO stretches of doubly reduced

species are clearly different from the expected five-coordinate anion exemplified by $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3]^-$. The electrochemical deprotonation can be related to $[\text{Re}(\text{bpy})(\text{Im-H})(\text{CO})_3]^+$ ($\text{Im-H} = \text{imidazole}$) in which an initial 1e^- reduction at $-1.64 \text{ V vs. Fc}^{+/0}$ to $[\text{Re}(\text{bpy}^*)(\text{Im-H})(\text{CO})_3]$ is followed by electron transfer and cleavage of the imidazole NH bond yielding $[\text{Re}(\text{bpy})(\text{Im}^-)(\text{CO})_3]$. The first reduction is reversible by CV indicating a slow electron transfer/NH bond cleavage step. This species is then reduced again at bpy at potentials 190 mV more negative than the first reduction.⁴⁴ In the case of DHBP complexes, the first reduction is quasi-reversible at elevated scan rates and two candidates for the chemical step are OH bond cleavage and Cl^- dissociation. The ΔE of $\sim 200 \text{ mV}$ between the first and second reduction waves (R1 and R2) is analogous to the observed redox potentials in $[\text{Re}(\text{bpy})(\text{Im-H})(\text{CO})_3]^+$ and $[\text{Re}(\text{bpy})(\text{Im}^-)(\text{CO})_3]$.

3.6. Calculated IR Spectra. IR and CV experiments demonstrate reductive deprotonation of DHBP complexes and CV data show loss Cl^- ; however, the point at which Cl^- is lost (after single or double deprotonation) is unclear. IR spectra are unchanged in a variety of solvents negating solvent coordination to deprotonated species. DFT calculations were performed to investigate the coordination environment of Re and the nature of IR bands near 1530 and 1605 cm^{-1} .

Calculated IR spectra for species derived from mono- and double deprotonation reactions are shown in Figures S13 and S14. The $\nu(\text{CO})$ agree well with experimental data. Experimental CO stretching frequencies are shifted to lower energy upon mono-deprotonation to $[\text{Re}(\text{4DHBP}-\text{H}^+)(\text{CO})_3\text{Cl}]^-$, while calculated values for the solvent complex $[\text{Re}(\text{4DHBP}-\text{H}^+)(\text{CO})_3(\text{DMF})]$ are unchanged from $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ and stretching frequencies of the five-coordinate $[\text{Re}(\text{4DHBP}-\text{H}^+)(\text{CO})_3]$ are shifted to higher energy. Energetically, loss of Cl^- from the singly deprotonated species is uphill by $2.7 \text{ kcal mol}^{-1}$. The calculated CO stretches for doubly deprotonated $[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3]^-$ are slightly blue shifted; however this species is the best candidate given CV and SEC-IR data.

Features from 1500 to 1630 cm^{-1} are well-reproduced by the calculations. For $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$, three bipyridine stretches contribute to the peaks at 1620 , 1614 , and 1568 cm^{-1} . In the singly deprotonated species, one ring stretching mode shifts to 1594 cm^{-1} . In the doubly deprotonated species, the asymmetric and symmetric ring stretches are found at 1602 and 1590 cm^{-1} corresponding to the strong absorption at 1609 cm^{-1} in Figure 4. The broad absorption of the doubly deprotonated species near 1535 cm^{-1} in Figure 4 appears at 1507 in the calculated spectrum and is attributed to two stretching modes of almost pure C=O character. Similarly for $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$, ring stretches are calculated at 1603 , 1590 , and 1508 cm^{-1} . Upon deprotonation, these modes decrease in intensity and strong CO stretching modes appear at 1510 and 1490 cm^{-1} . Experimentally, the absorption at 1512 cm^{-1} (Figure S11) is assigned as the C=O stretching mode.

3.6. Possible Mechanism of Reductive Deprotonation.

Calculations were carried out for the two-electron reduction of $[\text{Re}(\text{4DHBP})(\text{CO})_3(\text{DMF})]^+$ assuming that the solvent molecule is dissociated in the process. As shown in Table S6, the standard free energy of the resulting $[\text{Re}(\text{4DHBP})(\text{CO})_3]^-$ species was predicted to be 2.34 eV vs. NHE above the starting complex. Protonation of the C atoms at the 5- and 5'-positions of the ligand anion (4DHBP^{2-}), resulting in its partial dearomatization to form the $[\text{Re}(\text{4DHBP}+2\text{H}^+)(\text{CO})_3]^+$ intermediate, was predicted to be exoergic (-0.97 eV). This intermediate was further predicted to be capable of eliminating two protons and an H_2 molecule in an

exoergic reaction (-0.69 eV) to form $[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3]^-$, the doubly deprotonated product of the starting species. The free-energy profile for this pathway is shown in Figure S15.

Similar calculations were carried out for the one-electron reduction of $[\text{Re}(\text{4DHBP})(\text{CO})_3(\text{DMF})]^+$ assuming that the solvent molecule remains coordinated to the metal center throughout the pathway. The reduced $[\text{Re}(\text{4DHBP})(\text{CO})_3(\text{DMF})]$ was predicted to lie 1.39 eV vs. NHE above the starting species (Table S7). Protonation of either C atom at the 5- or 5'-position resulted in the partially dearomatized $[\text{Re}(\text{4DHBP}+\text{H}^+)(\text{CO})_3(\text{DMF})]^+$ intermediate in an exoergic reaction (-0.51 eV). Because the production of H_2 requires two electrons, and this is only a singly reduced species, a possible route to the singly deprotonated product of the starting complex is the disproportionation of this reduced and protonated intermediate,

The elimination of $\frac{1}{2}\text{H}_2$ and H^+ from one molecule of $[\text{Re}(\text{4DHBP}+\text{H}^+)(\text{CO})_3(\text{DMF})]^+$ (i.e., half the disproportionation reaction) to form $[\text{Re}(\text{4DHBP}-\text{H}^+)(\text{CO})_3(\text{DMF})]^0$ was also predicted to be exoergic (-0.12 eV), and the free-energy profile of this pathway is shown in Figure S10. These results indicate that the two- and one-electron reduction of $[\text{Re}(\text{4DHBP})(\text{CO})_3(\text{DMF})]^+$ leading to the formation of its doubly and singly deprotonated species, respectively, is energetically feasible, and provide a plausible explanation for the experimental results presented above.

To verify the production of H_2 , bulk electrolysis experiments were carried out in a sealed vessel. After two-electron reduction of $[\text{Re}(\text{4DHBP})(\text{CO})_3(\text{Cl})]$ or $[\text{Re}(\text{6DHBP})(\text{CO})_3(\text{Cl})]$, approximately 0.1 eq. H_2 was detected in the headspace. While not quantitative, zero H_2 was detected when the experiment was repeated in the absence of Re complex.

3.7. Cyclic Voltammetry of $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ under CO_2 Atmosphere. In CO_2 saturated DMF, $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ exhibits a catalytic current coincident with peak II at -1.65 V and an increase in slope at -1.85 V (Figure 6). Current increases to a maximum at -2.4 V. The current enhancement, i_c/i_p , where i_c and i_p are the peak current in the presence of CO_2 and the current at -1.85 V in the absence of CO_2 , is 12.3 . Under identical conditions, i_c/i_p for $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ is 4.7 at -2.05 V. With 5% water added, catalytic current is attenuated in contrast to the effects of water on catalysis using $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ and of weak acids on related complexes.^{8,49,50} In the presence of 2 eq. OH^- and CO_2 , the catalytic waveform is similar but shifted positive by *ca.* 0.05 V. It is noteworthy to recall the absence of reductive waves for the deprotonated complex and the formation of $[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3]^-$ during electrolysis. The appearance of a catalytic current under CO_2 indicates further reduction of the Re center in $[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3]^-$ or interaction of $[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3]^-$ with CO_2 followed by reduction. It is not possible to distinguish between pathways in the absence of an observable third reduction wave. DFT calculations did not yield a stationary state for the $[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3(\text{CO}_2)]^-$, but a stable structure for $[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3(\text{CO}_2)]^{2-}$ was reached. Ishitani and coworkers have demonstrated CO_2 capture in the form of an organic carbonate in the Re(I) oxidation state.⁵¹ In the current work, we did not examine an exhaustive set of possibilities. Assessment of the data in relation to the CO_2 chemistry of reduced quinones that capture CO_2 but are not catalytic clarifies reactivity at the Re center as opposed to deprotonated ligands.⁵²⁻⁵⁴

The appearance of two slopes in the catalytic CO_2 reduction wave using $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ is explained by the two pathways for formation of $[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3(\text{CO}_2)]^-$ on the CV timescale (Scheme 1, species E).

Figure 6. Cyclic voltammograms of 2.0 mM $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ (A) and $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ (B) in DMF under Ar and CO_2 in the absence (blue) or presence of 2 eq. Bu_4NOH (red) or with 5% H_2O (black dashes). $v = 0.1$ V s^{-1} .

The current response in the presence of CO_2 does not permit straightforward calculation of catalytic rate constants. A simplified EC_{cat} mechanism⁵⁵ does not apply owing to the shallow slope of the catalytic wave and absence of a plateau current. A plot of limiting current vs. $[\text{CO}_2]^{1/2}$ is linear confirming first-order dependence on $[\text{CO}_2]$, but the slope of the catalytic wave also decreases dramatically at lower $[\text{CO}_2]$. A foot-of-the-wave analysis⁴⁷ is not appropriate owing to the bimodal catalytic wave and shallow slope which deviates from ideal behavior. Furthermore, E^0 for the catalytic couple which is reduction of $[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3]^-$ or its CO_2 adduct was not observable. Although rates cannot be compared directly, the current density by CV is nearly identical for $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ meaning the overpotential for catalysis is not greatly increased for the $-\text{OH}$ substituted complex.

In CO_2 saturated DMF, the CV of $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ exhibits increased current with onset at -1.6 V and a plateau at -2.1 V (Figure 8B blue trace). The current enhancement at -2 V is 2.7 . In the presence of 5% water, the current was unchanged but the overpotential decreased by 0.13 V. A chemically deprotonated sample showed a similar current under CO_2 ; however, this wave is largely independent of $[\text{CO}_2]$ (Figure S16) and thus is not catalytic in nature.

3.8. Bulk Electrolysis of $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ under CO_2 . The CVs of $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ (catalytic) and $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ (non-catalytic) suggest reduction of CO_2 . Bulk electrolysis experiments were carried out for 1 h with an applied potential of -2 V vs. Ag/AgCl for product analysis. Select electrolysis data are summarized in Table 3. In dry DMF, the $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ perform poorly compared to $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$. The high activity of $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ in dry DMF is curious since protons are necessary for catalysis by the proposed mechanisms.²² An alternative mechanism, in which CO_2 serves as an oxide acceptor could be involved under anhydrous conditions.^{21,23} The $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ consumed 4.1 C in 1 h and produced *ca.* 450 μL of CO with $95 \pm 2\%$ Faradaic efficiency (FE). A control experiment produced *ca.* 6 μL of CO. Adding base had little effect on catalysis. A control experiment produced *ca.* 6 μL of CO. Electrolysis in the presence of 5% water by volume was investigated. A control experiment

produced 300 μL CO and 135 μL H_2 . $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ produced CO quantitatively with nearly identical initial rates with the latter showing slightly better stability. The mechanistic effect of water on catalysis using $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ remains speculative. While protonation of bound CO_2^- is possible, the acid-base properties of the ligand cannot be ignored. Since electrochemical reduction generates the ligand-deprotonated species, re-protonation by water could favor reduction of the Re instead of reductive deprotonation.

Table 3. Summary of bulk electrolysis experiments with an applied potential of -2 V .^a

Compound	Condition	q/C	Faradaic Efficiency / %
$[\text{Re}(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$	dry DMF	16.2	quantitative
	5% $\text{H}_2\text{O}/\text{DMF}$	20.1	quantitative
$[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$	dry DMF	4.1	95 ± 2
	5% $\text{H}_2\text{O}/\text{DMF}$	15.5	110 ± 9^b
	dry DMF + base	4.1	86

^a Solutions were electrolyzed for 1 h. All experiments were vigorously stirred. ^b about 15% of the CO is produced by direct reduction at the electrode.

In dry DMF, $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ consumed a comparable charge to $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$; however, only 19 μL of CO was produced. Because of the low catalytic current for CO_2 reduction by $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ the FE is estimated as 6%. No formate was detected by ion chromatography. In DMF / 5% water, the $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ catalyst performed poorly, producing barely any gaseous product over the control experiment although at least 5 C of charge were consumed in addition to the 2e^- needed to reduce the catalyst. The product conversion was improved to 70% FE at -1.7 V (304 μL compared to 8 μL in a control experiment), but the turnover number was still < 1 . The absence of catalysis supports the $[\text{CO}_2^-]$ -independent current by CV while the production of < 1 eq. CO suggests slow product release and decomposition of intermediates at highly negative potentials. While our original hypotheses stated that the local proton source might facilitate protonation of a CO_2^- ligand or accelerate catalysis through secondary coordination sphere interactions, ligand based reactivity can also impede catalysis. This was discussed by Tanaka and co-workers for *cis* and *trans* isomers of $[\text{Ru}(\text{tpy})(\text{bpyO})(\text{CO})]^+$ (tpy = 2,2':6',2''-terpyridine, bpyO = 2,2'-bipyridin-6-onato) in which reduction of the *trans* isomer triggered CO release while the reduced *cis* isomer underwent attack of the pyridinato oxygen on the CO ligand.²⁵

4. CONCLUSIONS

Two *fac*- $[\text{Re}(\alpha\text{-diimine})(\text{CO})_3\text{Cl}]$ complexes have been designed with proton responsive ligands, 4DHBP or 6DHBP, to pursue the hypotheses that electron donating 4,4'-OH groups would generate a strongly nucleophilic "Re(-1)" center and 6,6'-OH groups could further facilitate catalysis by providing a proximal proton source or lowering transition state energies of rate-determining steps. We have discovered atypical properties for these complexes including stepwise electrochemical reductive electrochemical cleavage of the OH bond yielding the equivalent chemically deprotonated species. A mechanism for this net loss of two H atoms is proposed in which bipyridine doubly-reduced anions are protonated and de-aromatized. Net loss of H_2 and two H^+ yields the deprotonated products.

While the chemical steps associated with the first two reductions occur on the ligand, the $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ is still a competent electrocatalysts for reduction of CO_2 to CO indicating the binding of CO_2 to $[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3]^+$ (Re(I) formal oxidation state) followed by an electron transfer step or reduction of this species (Re(0) formal oxidation state) with subsequent CO_2 binding and catalysis. Experimentally, these two pathways could not be distinguished. The $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ is not an electrocatalysts despite homologous properties to $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ and the observation of enhanced current under CO_2 by CV. Approximately one turnover of CO could be obtained under optimized conditions in preparatory scale experiments suggesting the intermediate formed after CO release is unstable.

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SUPPORTING INFORMATION

X-ray structures, NMR spectra, experimental and calculated IR data, electronic transitions and orbitals from TD-DFT data, experimental and simulated cyclic voltammograms, and Cartesian coordinates of calculated structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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TOC Figure

Push or Pull? Proton Responsive Ligand Effects in Rhenium Tricarbonyl CO₂ Reduction Catalysts

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2.2. X-ray Crystallography. A crystal of $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}] \cdot 2(\text{CH}_3)_2\text{SO}$ was mounted on the end of a glass fiber. Data were collected with a Bruker Kappa Apex II diffractometer. Data collected at 173 K indicated triclinic symmetry and space group $P-1$ was used for the solution and refinement of the structure. The intensity data were corrected for absorption using the multi-scan method (SADABS).^{1,2} The structure was solved by Patterson heavy atom methods.³ Non-hydrogen atoms were refined with anisotropic displacement parameters except for the carbon atoms in the disordered DMSO molecule with an occupancy factor of 0.23. Most hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic thermal parameters. The hydrogen atoms on O14 and O24 of the 4DHBP ligand were located on a difference Fourier map and included in fixed positions. A disordered model was used for one DMSO molecule and the occupancy factor for was refined. Crystal data and refinement parameters are provided as supplementary material.

2.3. DFT Calculations. Calculations were carried out using the B3LYP hybrid functional^{4,5,6,7} with the 6-31++G(d,p) 5d basis set for C, H, N, and O atoms and CEP effective core potential with CEP-121G basis for Re^{8,9,10} as implemented by the Gaussian 09 suite of programs.¹¹ The CPCM solvent model was used,^{12,13,14} and all geometry optimizations and vibrational frequency calculations were carried out in this model of the solvent with UAHF radii. Free energies of non-gas solutes were corrected for conversion of an ideal gas at 1 atm to 1 M standard state,¹⁵ and an additional correction to adjust the standard state of DMF to a pure liquid was applied.¹⁶ Standard reduction potentials were calculated vs. NHE in DMF (4.17 V) which was obtained using the calculated absolute free energy of H₂ gas, the free energy of the gas-phase electron¹⁷ and the absolute free energy of the proton solvated in DMF. This last value (−273.3 kcal/mol) was determined as that which gave the correct pK_a value (18.4) of phenol in DMF using calculated absolute free energies of phenol and its conjugate base in DMF solution. IR spectra were visualized using GaussSum with fwhm = 8 cm^{−1}.¹⁸ UV-vis spectra in aqueous solution were calculated using the TD-B3LYP method and the CPCM solvation model with water solvent and UAHF radii.

2.4. Cyclic Voltammetry of $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ under Argon.

The reductive CV of $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ (Figure S9) exhibits features similar to $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$, with irreversible reduction peaks at $E_p^c = -1.53$ and -1.75 V followed by a poorly resolved reduction wave which acquires a peak shape with $E_p^c = -2.0$ V at higher scan rates. The first reduction becomes quasi-reversible at higher scan rates and the diffusion coefficient is estimated as $8.6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. For $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$, higher scan rates were needed to observe the anodic counterpart of R1, and R3 was only present for higher scan rates indicating a faster k_t , but simulation was not performed since the absence of an isopotential point in Figure S9 shows the first reduction couple was not isolated from following electrochemical steps.

The anodic CV after reduction shows a small wave O1 at 0.76 V associated with re-oxidation followed by irreversible waves at 1.25 and 1.45 V analogous to O3 in $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ (Figures S10). After electrolysis at -1.6 V, reductive waves are absent and new oxidations O4 (0.50 V) and O5 (1.04 V) appeared. Peak O5 is chloride oxidation while O4 is analogous to O4 in $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$. The CV of the chemically deprotonated complex is identical to the electrochemically reduced complex. An irreversible reduction, R3 was observed at -2.43 V.

Table S2. Comparison of bond lengths [Å] and angles [deg] to [Re(bpy)(CO)₃Cl].

	[Re(4DHBP)(CO) ₃ Cl]•2DMSO	[Re(bpy)(CO) ₃ Cl]
Re(1)-N(111)	2.177(3)	2.176(6)
Re(1)-N(211)	2.163(3)	2.173(6)
Re(1)-C(131)	1.916(4)	1.919(7)
Re(1)-C(141)	1.911(4)	1.932(7)
Re(1)-C(151)	1.906(4)	1.938(9)
Re(1)-Cl(1)	2.5058(8)	2.460(2)
N(121)-Re(1)-N(111)	74.41(9)	74.9(2)
N(111)-Re(1)-Cl(1)	86.09(7)	85.7(2)
N(121)-Re(1)-Cl(1)	83.00(7)	83.5(2)
C(131)-Re(1)-Cl(1)	92.67(11)	92.1(2)
C(141)-Re(1)-Cl(1)	91.00(10)	93.8(2)
C(151)-Re(1)-Cl(1)	176.31(10)	171.3(3)
C(131)-Re(1)-N(111)	97.09(12)	97.8(3)
C(141)-Re(1)-N(111)	173.34(12)	172.5(3)
C(151)-Re(1)-N(111)	95.00(12)	91.0(3)
C(131)-Re(1)-N(121)	170.65(12)	172.4(3)
C(141)-Re(1)-N(121)	99.31(12)	97.3(3)
C(151)-Re(1)-N(121)	93.89(13)	92.8(3)
C(141)-Re(1)-C(131)	89.02(14)	89.5(3)
C(151)-Re(1)-C(131)	90.69(15)	90.8(4)
C(141)-Re(1)-C(151)	87.54(14)	89.4(4)

Table S3. Hydrogen bonds details for [Re(4DHBP)(CO)₃Cl]•2DMSO [Å and deg.].

D-H	d(D-H)	d(H...A)	<DHA	d(D...A)	A
O114-H114	0.968	1.509	156.68	2.429	O21A_b
O114-H114	0.968	1.649	164.06	2.594	O21_a
O114-H114	0.968	2.618	159.11	3.540	S21A_b
O114-H114	0.968	2.737	166.57	3.686	S21_a
O124-H124	0.844	1.785	155.92	2.578	O11 [x+1, y, z]

Table S4. Cl⁻H distances in [Re(4DHBP)(CO)₃Cl]•2DMSO [Å].

Cl(1)···H125	2.864	x-1, y, z
Cl(1)···H126	2.893	x-1, y, z
Cl(1)···H12A	3.069	1-x, 1-y, 2-z
Cl(1)···H12B	2.917	2-x, -y, 2-z
Cl(1)···H12C	2.981	
Cl(1)···H13A	3.209	
Cl(1)···H23E	2.947	1+x, y-1, z

Figure S2. ^1H NMR spectra of isolated (A) $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ and (B) $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$. (a): the isolated complex, (b): the *in-situ* chemically deprotonated complex generated by treatment of with 2 eq. Bu_4NOH (1M solution in methanol), and (c): the electrochemically reduced complex in CD_3CN . *DMF contamination from the Vycor-tipped glass tube separating the reference electrode from the electrolysis solution. **Residual toluene co-crystallized during synthesis which can be removed by dissolution in CH_3CN and precipitation with ether. See experimental details in the text for sample preparation.

Table S5. Calculated lowest energy optical transitions for $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ in water. Only transitions with pure orbital character are listed. Higher energy transitions include states with significant orbital mixing.

		Wavelength	Oscillator Strength	Orbital Character
$[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$	1	398	0.0014	HOMO→LUMO (99%)
	2	380	0.074	H-1→LUMO (99%)
	3	355	0.0003	H-3→LUMO (98%)
	4	337	0.3709	H-2→LUMO (96%)
$[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$	1	375	0.0024	HOMO→LUMO (98%)
	2	362	0.0904	H-1→LUMO (98%)
	3	330	0.001	H-2→LUMO (96%)

$[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$

$[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$

Figure S3. Frontier molecular orbitals of $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ showing orbitals contributing to the lowest energy electronic transitions (Table S1).

Figure S4. A: Spectrophotometric pH titration of [Re(4DHBP)(CO)₃Cl] in Britton-Robinson buffer with 1% CH₃CN co-solvent. Inset: ϵ as a function of pH and sigmoidal fits used to determine the average pK_a of 5.6. **B:** Spectrophotometric pH titration of [Re(6DHBP)(CO)₃Cl] in Britton-Robinson buffer. Inset: ϵ as a function of pH and sigmoidal fits used to determine the average pK_a of 4.5.

Figure S5. Spectrophotometric pH titration of [Re(6DHBP)(CO)₃Cl] in CH₃CN using Et₃N as the base. **A:** 0, 0.25, 0.5, 0.75, 1.0, 1.5 eq. Et₃N. **B:** 1.5, 2.4, 4.8, 7.0, 9.1, 13, 30 eq. Et₃N. **C:** Plots of ϵ vs. eq. Et₃N at 395, 345, and 442 nm.

Figure S6. (A) Cyclic voltammograms showing scan rate dependence of the two-electron reduction of $[\text{Re}(\text{tBu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ (1 mM) in DMF with $v =$ (a) 0.1 V s^{-1} ; (b) 0.5 V s^{-1} ; (c) 1 V s^{-1} and (d) 3 V s^{-1} . (B) Cyclic voltammograms showing the effect of cathodic switching potential on the re-oxidation processes ($v = 0.5 \text{ V s}^{-1}$). The diffusion coefficient in DMF was calculated as $3.0 \times 10^{-6} \text{ cm}^2/\text{s}$ from a plot of i_p^c vs $v^{1/2}$. Potentials are referenced to Ag/AgCl (3M KCl).

Figure S7. Cyclic voltammograms showing the effect of (A) scan rate ($v = 0.1, 0.25, 0.5, 0.75$, and 1 V s^{-1}) and (B) switching potential ($v = 0.1 \text{ V s}^{-1}$) on the two-electron reduction and re-oxidation of $[\text{Re}(4\text{DHBP})(\text{CO})_3\text{Cl}]$ (2 mM) in DMF. Potentials are referenced to Ag/AgCl (3M KCl). C: Multi-scan reductive CVs comparing $[\text{Re}(4\text{DHBP})(\text{CO})_3\text{Cl}]$ (a) and $[\text{Re}(\text{tBu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ (b)

Figure S8. Experimental (A) and simulated (B) cyclic voltammograms for a 2.0 mM $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$ solution in DMF showing only the first reduction according to the mechanism and parameters given in Scheme 3. Bottom to top: 0.05, 0.1, 0.25, 0.75, and 1 V s^{-1} .

Figure S9. Reductive cyclic voltammograms showing the scan rate dependence of: **A:** the one-electron and **B:** the two-electron reduction with $\nu = 0.1, 0.25, 0.5, 0.75, 1, 2 \text{ V s}^{-1}$, $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ (1 mM) in DMF. The inset of (A) shows the dependence of i_p^c for the first reduction on $\nu^{1/2}$. These data were used to calculate the diffusion coefficient, D , from the Randles-Sevcik equation, $i_p = 0.4463nFA[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}](nF\nu D/RT)^{1/2}$, as $8.6 \times 10^{-7} \text{ cm}^2/\text{s}$. Potentials are referenced to Ag/AgCl (3M KCl).

Figure S10. Cyclic voltammetry of 2 mM $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ in DMF with $\nu = 0.1 \text{ V s}^{-1}$ (a), after exhaustive 2e^- reduction (b), and in the presence of 2eq. Bu_4NOH (c,d). Waves R1 and R2 are the two-electron oxidation according to the proposed mechanism (text **Scheme X**), O1 is re-oxidation of the doubly reduced species, O2 and O3 are Re oxidations, O5 is the $2\text{Cl}^-/\text{Cl}_2$ couple, O4 is oxidation of the phenolate form of the ligand formed after reduction or deprotonation. Potentials are referenced to Ag/AgCl (3M KCl).

Figure S11. Solution IR in CH_3CN of $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ during electrochemical reduction (a) and re-oxidation (b) and upon oxidation of the chemically deprotonated species (c). In (a), the black trace is the initial complex, blue traces are the singly deprotonated complex which is poorly soluble in CH_3CN , and there red trace is $[\text{Re}(\text{6DHBP}-2\text{H}^+)(\text{CO})_3]^-$. In traces b and c, the black spectrum is a mixture of $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{6DHBP})(\text{CO})_3(\text{CH}_3\text{CN})]^+$.

Figure S12. Solution IR in DMF of $[\text{Re}(' \text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ (bold, black spectrum) during electrochemical reduction. The bold blue spectrum is $[\text{Re}(' \text{Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]^-$. The bold red spectrum contains a mixture of neutral $[\text{Re}(' \text{Bu}_2\text{bpy})(\text{CO})_3]$ and the doubly reduced species $[\text{Re}(' \text{Bu}_2\text{bpy})(\text{CO})_3]^-$ (1934, 1832 cm^{-1}).

Figure S13. Calculated IR spectra in DMF for species derived from $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$. Scaling factor = 0.981.

Figure S14. Calculated IR data ($\nu(\text{CO})$ in DMF) for species derived from $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$. Scaling factor = 0.981.

Table S6. Two-electron reduction free-energy pathway to doubly deprotonated species of $[\text{Re}^{\text{I}}(4\text{DHBP})(\text{CO})_3(\text{DMF})]^+$.

Species	G^*_{species}	Reservoir	$G^*_{\text{reservoir}}$	G^*_{total}	Rel. $\Delta G^*_{\text{total}}$ (eV)	Rel. $\Delta G^*_{\text{total}}$ vs. NHE (eV)	$\Delta G^*_{\text{step vs. NHE}}$ (eV)
$[\text{Re}^{\text{I}}(4\text{DHBP})(\text{CO})_3(\text{S})]^+$	-1313.141971	$2\text{H}^+, 2\text{e}^-$	-0.873700	-1314.014246	0.000000	0.000000	2.434711
$[\text{Re}^{\text{I}}(4\text{DHBP})(\text{CO})_3]^-$	-1064.900773	$2\text{H}^+, \text{S}$	-249.332063	-1314.231411	-5.909360	2.434711	-0.968807
$[\text{Re}^{\text{I}}(4\text{DHBP}+2\text{H}^+)(\text{CO})_3]^+$	-1065.807310	S	-248.461129	-1314.267014	-6.878167	1.465904	-0.687196
$[\text{Re}^{\text{I}}(4\text{DHBP}-2\text{H}^+)(\text{CO})_3]^-$	-1063.781291	$2\text{H}^+, \text{H}_2, \text{S}$	-250.512402	-1314.292268	-7.565363	0.778708	

Table S7. One-electron reduction free-energy pathway to singly deprotonated species of $[\text{Re}^{\text{I}}(4\text{DHBP})(\text{CO})_3(\text{DMF})]^+$.

Species	G^*_{species}	Reservoir	$G^*_{\text{reservoir}}$	G^*_{total}	Rel. $\Delta G^*_{\text{total}}$ (eV)	Rel. $\Delta G^*_{\text{total}}$ vs NHE (eV)	$\Delta G^*_{\text{step vs NHE}}$ (eV)
$[\text{Re}^{\text{I}}(4\text{DHBP})(\text{CO})_3(\text{S})]^+$	-1313.385071	H^+, e^-	-0.436850	-1313.821778	0.000000	0.000000	1.392137
$^2[\text{Re}^{\text{I}}(4\text{DHBP})(\text{CO})_3(\text{S})]^0$	-1313.488613	2H^+	-0.435467	-1313.923937	-2.779899	1.392137	-0.511669
$^2[\text{Re}^{\text{I}}(4\text{DHBP}+\text{H}^+)(\text{CO})_3(\text{S})]^+$	-1313.942883	--	-0.000000	-1313.942741	-3.291568	0.880468	-0.116099
$[\text{Re}^{\text{I}}(4\text{DHBP}-\text{H}^+)(\text{CO})_3(\text{S})]^0$	-1312.921514	$\text{H}^+, \frac{1}{2}\text{H}_2$	-1.025637	-1313.947008	-3.407667	0.764369

Figure S13. Free-energy profiles for two-electron reduction pathway from $[\text{Re}^{\text{I}}(4\text{DHBP})(\text{CO})_3(\text{DMF})]^+$ to the doubly deprotonated intermediate $[\text{Re}^{\text{I}}(4\text{DHBP}-2\text{H}^+)(\text{CO})_3]^-$ (top), and to the one-electron reduction pathway to $[\text{Re}^{\text{I}}(4\text{DHBP}-\text{H}^+)(\text{CO})_3(\text{DMF})]^0$ (bottom) in DMF. The latter pathway involves the disproportionation of the $[\text{Re}^{\text{I}}(4\text{DHBP}+\text{H}^+)(\text{CO})_3(\text{DMF})]^+$ intermediate.

Figure S13. Cyclic voltammograms of chemically deprotonated $[\text{Re}(\text{6DHBP})(\text{CO})_3\text{Cl}]$ under Ar, CO_2 , or a 30% CO_2 in N_2 mixture. The peak current independence on $[\text{CO}_2]$ illustrates that this is not a catalytic current.

Table S8. Calculated structure of $[\text{Re}(\text{4DHBP})(\text{CO})_3\text{Cl}]$.

Energy: -957108.4405093

C	-1.79620	-0.74103	0.05040
N	-0.57116	-1.33487	0.08019
C	-0.51454	-2.68297	0.09549
C	-1.63734	-3.49536	0.07906
C	-2.89993	-2.88525	0.04427
C	-2.97115	-1.48592	0.03105
Re	1.19440	-0.00001	0.05192
N	-0.57115	1.33487	0.08017
C	-0.51451	2.68297	0.09545
C	-1.63731	3.49538	0.07901
C	-2.89990	2.88528	0.04423
C	-2.97113	1.48595	0.03103
C	-1.79619	0.74104	0.05039
C	2.56319	1.35570	-0.08662
O	3.37995	2.18320	-0.17428
C	1.34842	-0.00003	1.95539
O	1.44661	0.00018	3.12082
C	2.56317	-1.35574	-0.08661
O	3.37992	-2.18325	-0.17420
H	-1.53267	4.58387	0.09279
H	-3.94985	1.00328	0.00682
H	-3.94986	-1.00324	0.00683
H	-1.53272	-4.58385	0.09285
Cl	0.84618	-0.00005	-2.49418
H	0.47864	-3.12653	0.12199
H	0.47868	3.12652	0.12194
O	-4.05470	3.57236	0.02473
H	-3.87849	4.56843	0.03584
O	-4.05474	-3.57232	0.02477
H	-3.87854	-4.56839	0.03590

Table S9. Calculated structure of [Re(6DHBP)(CO)₃Cl].

Energy: -957105.7030055

C	-2.14797	-0.70672	0.03962
N	-0.93749	-1.33357	0.13924
C	-0.91337	-2.67802	0.21805
C	-2.07929	-3.46096	0.16490
C	-3.29916	-2.82099	0.03505
C	-3.34023	-1.42459	-0.02194
Re	0.87579	-0.01399	0.01721
N	-0.89541	1.36162	0.13559
C	-0.82772	2.70453	0.21387
C	-1.96689	3.52657	0.16326
C	-3.20688	2.92472	0.03729
C	-3.29304	1.53012	-0.01861
C	-2.12479	0.77356	0.03941
C	2.27695	1.28713	-0.21853
O	3.15305	2.03996	-0.37345
C	1.15545	-0.01199	1.90531
O	1.33440	-0.00980	3.06177
C	2.23741	-1.35763	-0.21059
O	3.09141	-2.13661	-0.35990
H	-1.84697	4.61142	0.22450
H	-4.26415	1.05081	-0.10016
H	-4.29481	-0.91382	-0.10708
H	-1.99409	-4.54911	0.22705
H	-4.22162	-3.39937	-0.01331
H	-4.11119	3.53133	-0.00871
Cl	0.36617	-0.01139	-2.50126
O	0.40243	3.21429	0.34710
H	0.36634	4.22544	0.37875
O	0.29836	-3.23089	0.35404
H	0.22728	-4.23990	0.38696

Table S10. Calculated structure of $[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3]^-$.

Energy: -667617.1127964			
C	1.78445	0.74316	-0.05287
N	0.53912	1.32259	-0.06356
C	0.48300	2.68497	-0.04831
C	1.58984	3.49979	-0.03046
C	2.91239	2.93420	-0.02693
C	2.94304	1.49571	-0.03712
Re	-1.17762	0.00186	-0.15627
N	0.53840	-1.32200	-0.07371
C	0.48162	-2.68426	-0.05973
C	1.58811	-3.49952	-0.03376
C	2.91085	-2.93454	-0.01927
C	2.94216	-1.49616	-0.02899
C	1.78386	-0.74326	-0.05360
C	-2.52123	-1.35683	-0.50613
O	-3.32433	-2.17493	-0.71798
C	-1.67622	-0.01957	1.64671
O	-1.94838	-0.03270	2.78713
C	-2.51923	1.37023	-0.47030
O	-3.32206	2.19493	-0.65638
H	1.46184	-4.58510	-0.02367
H	3.91711	-1.00573	-0.01461
H	3.91799	1.00511	-0.03176
H	1.46380	4.58539	-0.01926
H	-0.51606	3.11729	-0.04865
H	-0.51773	-3.11596	-0.06808
O	3.97367	-3.64405	0.00261
O	3.97562	3.64318	-0.01393

Table S11. Calculated structure of $[\text{Re}(\text{4DHBP}-1\text{H}^+)(\text{CO})_3\text{Cl}]^-$.

Energy: -956815.6609188

C	-1.86114	-0.59183	0.05564
N	-0.67938	-1.26814	0.10426
C	-0.70940	-2.61740	0.13678
C	-1.88088	-3.35495	0.11409
C	-3.10071	-2.66420	0.04826
C	-3.08137	-1.26469	0.02450
Re	1.17195	-0.06060	0.05463
N	-0.48600	1.38665	0.07335
C	-0.34514	2.73578	0.08779
C	-1.40204	3.62212	0.07371
C	-2.75025	3.14062	0.04187
C	-2.87398	1.71285	0.03067
C	-1.75938	0.88965	0.04805
C	2.63108	1.19210	-0.11366
O	3.50550	1.95752	-0.21962
C	1.34374	-0.04830	1.95327
O	1.45468	-0.04231	3.11883
C	2.43772	-1.51465	-0.07994
O	3.19136	-2.40220	-0.16433
H	-1.20703	4.69670	0.08753
H	-3.87760	1.28571	0.01203
H	-4.02471	-0.71830	-0.01979
H	-1.84844	-4.44754	0.14111
Cl	0.82102	-0.08267	-2.50456
H	0.25301	-3.12273	0.18164
H	0.67821	3.10587	0.11222
O	-3.77707	3.91665	0.02785
O	-4.29683	-3.28172	0.00795
H	-4.18014	-4.28507	0.03061

Table S12. Calculated structure of $[\text{Re}(\text{4DHBP}-1\text{H}^+)(\text{CO})_3(\text{DMF})]$.

Energy: -823887.5998571			
C	2.02809	-0.64058	0.20118
N	0.91202	-1.27979	-0.25057
C	0.91034	-2.63006	-0.28424
C	1.98629	-3.40385	0.11492
C	3.13997	-2.75064	0.57696
C	3.15132	-1.35099	0.61853
Re	-0.79197	-0.01251	-0.86077
N	0.79784	1.37715	-0.26812
C	0.70200	2.73241	-0.29555
C	1.69740	3.58471	0.12840
C	2.93492	3.06624	0.64223
C	3.01294	1.62963	0.65325
C	1.96588	0.84297	0.20643
C	-2.16533	1.29164	-1.24225
O	-2.98513	2.08732	-1.47817
C	-0.28853	-0.01859	-2.70238
O	0.02151	-0.02190	-3.82909
C	-2.07163	-1.42232	-1.20891
O	-2.83202	-2.28070	-1.42660
H	1.54339	4.66476	0.07458
H	3.92940	1.17066	1.02730
H	4.04371	-0.83486	0.97587
H	1.93304	-4.49488	0.06562
O	-1.15687	0.01401	1.34390
C	-2.27199	-0.11742	1.92625
H	-3.19923	-0.26095	1.34931
N	-2.42335	-0.09406	3.24230
C	-3.74901	-0.25380	3.84651
H	-4.50033	-0.38142	3.05799
H	-3.75006	-1.13670	4.50131
H	-3.99041	0.63729	4.44314
C	-1.29797	0.08833	4.16149
H	-0.37120	0.19921	3.59285
H	-1.22691	-0.78603	4.82428
H	-1.47127	0.98667	4.77113
H	0.00288	-3.10487	-0.65145
H	-0.23288	3.13361	-0.68273
O	4.24436	-3.40298	0.98337
O	3.89019	3.80912	1.05429
H	4.11754	-4.40282	0.90443

Table S13. Calculated structure of $[\text{Re}(\text{4DHBP}-1\text{H}^+)(\text{CO})_3]$.

Energy: -667909.8629315

C	-1.82112	-0.56796	-0.05554
N	-0.64738	-1.26618	-0.03755
C	-0.70044	-2.61812	-0.01977
C	-1.88452	-3.33248	-0.02206
C	-3.09410	-2.61898	-0.04610
C	-3.05085	-1.21813	-0.05911
Re	1.19834	-0.09362	-0.16542
N	-0.39875	1.37418	-0.14794
C	-0.22292	2.72602	-0.14695
C	-1.25130	3.63517	-0.07582
C	-2.61681	3.19115	0.00887
C	-2.77569	1.75822	0.00268
C	-1.68862	0.91032	-0.07032
C	2.65767	1.13610	-0.52296
O	3.52831	1.87767	-0.73887
C	1.64410	-0.05260	1.65268
O	1.88866	-0.01976	2.79716
C	2.43616	-1.57672	-0.39094
O	3.17624	-2.46653	-0.52105
H	-1.02899	4.70461	-0.07622
H	-3.78821	1.35662	0.06942
H	-3.98533	-0.65466	-0.07933
H	-1.87178	-4.42588	-0.01008
H	0.25349	-3.14077	-0.00148
H	0.80850	3.06879	-0.20259
O	-3.60884	3.98740	0.08739
O	-4.29968	-3.21088	-0.05891
H	-4.20731	-4.21840	-0.04893

Table S14. Calculated structure of $[\text{Re}(\text{6DHBP}-2\text{H}^+)(\text{CO})_3]^-$.

Energy: -667616.8372193			
C	2.10608	0.74240	-0.08268
N	0.86925	1.33724	-0.02347
C	0.75699	2.72733	0.06660
C	1.97168	3.50236	0.02081
C	3.19741	2.88816	-0.06514
C	3.27939	1.48102	-0.11089
Re	-0.85343	-0.00034	-0.15510
N	0.87023	-1.33665	-0.02351
C	0.75902	-2.72683	0.06654
C	1.97432	-3.50094	0.02090
C	3.19958	-2.88582	-0.06499
C	3.28050	-1.47862	-0.11079
C	2.10663	-0.74088	-0.08267
C	-2.18980	-1.34808	-0.56546
O	-3.03962	-2.10192	-0.83250
C	-1.47387	-0.00032	1.60693
O	-1.83481	-0.00043	2.72581
C	-2.19071	1.34643	-0.56569
O	-3.04101	2.09978	-0.83259
H	1.87685	-4.58727	0.07267
H	4.24778	-0.98833	-0.15927
H	4.24705	0.99148	-0.15943
H	1.87340	4.58863	0.07253
H	4.11181	3.48312	-0.08799
H	4.11443	-3.48009	-0.08772
O	-0.37256	-3.27524	0.18899
O	-0.37501	3.27489	0.18905

Table S15. Calculated structure of $^1[\text{Re}(\text{4DHBP})(\text{CO})_3(\text{DMF})]^{1+}$.

C	1.994571	-0.725277	0.229943
N	0.855206	-1.343714	-0.187315
C	0.804438	-2.690064	-0.154678
C	1.853269	-3.481108	0.285504
C	3.022382	-2.846550	0.720309
C	3.090241	-1.449367	0.689149
Re	-0.811390	-0.052989	-0.847473
N	0.838368	1.315896	-0.317983
C	0.770059	2.658162	-0.415678
C	1.811776	3.501370	-0.064150
C	2.994138	2.926650	0.415744
C	3.078060	1.534227	0.524405
C	1.987009	0.755620	0.152004
C	-2.154382	1.266046	-1.281108
O	-2.964578	2.059213	-1.548147
C	-0.306024	-0.144456	-2.690623
O	0.004441	-0.200750	-3.813075
C	-2.138567	-1.425890	-1.145311
O	-2.939429	-2.252494	-1.325150
H	1.697931	4.576176	-0.166096
H	3.993256	1.089784	0.893572
H	3.994527	-0.958983	1.026118
H	1.755343	-4.562272	0.287260
O	-1.162870	0.072999	1.333087
C	-2.288958	0.080199	1.908583
H	-3.216700	-0.000602	1.334435
N	-2.437963	0.182833	3.220346
C	-3.767815	0.175935	3.830034
H	-4.531445	0.084604	3.055632
H	-3.851192	-0.668645	4.521455
H	-3.923035	1.106738	4.384553
C	-1.297966	0.307910	4.127211
H	-0.370651	0.286559	3.557206
H	-1.310103	-0.519715	4.843628
H	-1.372613	1.252142	4.676232
H	-0.113568	-3.150522	-0.498232
H	-0.157507	3.071843	-0.790960
O	4.102867	-3.514231	1.172834
O	4.072790	3.647410	0.783886
H	3.946854	-4.474046	1.147576
H	3.904705	4.598386	0.667230

Table S16. Calculated structure of $^1[\text{Re}(\text{4DHBP}^{2-})(\text{CO})_3]^{1-}$.

C	-1.769810	0.703373	-0.065073
N	-0.497680	1.303318	-0.103707
C	-0.460009	2.677326	-0.091949
C	-1.565058	3.483536	-0.061170
C	-2.859098	2.874976	-0.032397
C	-2.952014	1.509357	-0.031518
Re	1.215822	0.023277	-0.077958
N	-0.485529	-1.288324	-0.118120
C	-0.420591	-2.657019	-0.106728
C	-1.511915	-3.484350	-0.060870
C	-2.812777	-2.895108	-0.012958
C	-2.929552	-1.530396	-0.013933
C	-1.760829	-0.705904	-0.066424
C	1.810538	-0.228974	1.699014
O	2.229261	-0.392628	2.792540
C	2.461947	-1.253702	-0.813174
O	3.223057	-2.037453	-1.260181
C	2.499546	1.431977	-0.392356
O	3.285182	2.294604	-0.565994
H	-1.378436	-4.562239	-0.058970
H	-3.913065	-1.076549	0.033729
H	-3.928486	1.038462	-0.005898
H	-1.448728	4.563508	-0.061326
H	0.529248	3.119594	-0.111470
H	0.577720	-3.079027	-0.135416
O	-3.943220	-3.670830	0.039178
H	-3.694320	-4.607937	0.040574
O	-4.002217	3.634764	-0.004899
H	-3.766931	4.575287	-0.009556

Table S17. Calculated structure of $^1[\text{Re}(\text{4DHBP}+2\text{H}^+)(\text{CO})_3]^{1+}$.

C	-1.756716	-0.689860	-0.060762
N	-0.494304	-1.337943	0.021203
C	-0.422679	-2.626317	0.128391
C	-2.881525	-2.848910	-0.040356
C	-2.949369	-1.504606	-0.138401
Re	1.260369	-0.003815	-0.218687
N	-0.493167	1.337367	0.009380
C	-0.419124	2.626842	0.099278
C	-2.880775	2.849362	-0.027314
C	-2.951013	1.503937	-0.107198
C	-1.756712	0.689709	-0.055964
C	2.623797	1.343446	-0.492385
O	3.449378	2.152091	-0.625656
C	1.669399	0.018367	1.613627
O	1.896864	0.033466	2.759002
C	2.628444	-1.352392	-0.459929
O	3.458929	-2.159003	-0.573963
H	-3.919679	1.031208	-0.211231
H	-3.912585	-1.033214	-0.289493
H	0.566366	-3.069284	0.190452
H	0.570921	3.069211	0.147167
C	-1.585136	-3.559485	0.178351
H	-1.429044	-4.349242	-0.574056
H	-1.578185	-4.083899	1.148895
C	-1.579217	3.563050	0.144348
H	-1.552347	4.114519	1.099361
H	-1.436431	4.331343	-0.632722
O	-4.010970	-3.594914	-0.131976
H	-3.803173	-4.540531	-0.055605
O	-4.013309	3.593526	-0.089868
H	-3.804596	4.539852	-0.025747

Table S18. Calculated structure of $^1[\text{Re}(\text{4DHBP}-2\text{H}^+)(\text{CO})_3]^{1-}$.

C	-1.776021	0.744735	-0.097592
N	-0.531230	1.322159	-0.205843
C	-0.474397	2.685077	-0.218694
C	-1.572371	3.503278	-0.129585
C	-2.900624	2.948286	0.000143
C	-2.925611	1.501831	0.003155
Re	1.189018	-0.000037	-0.182964
N	-0.531189	-1.322157	-0.205044
C	-0.474421	-2.685085	-0.217698
C	-1.572473	-3.503228	-0.129065
C	-2.900793	-2.948187	-0.000225
C	-2.925712	-1.501731	0.002622
C	-1.776034	-0.744691	-0.097508
C	1.482869	0.000112	1.665410
O	1.630938	0.000241	2.827697
C	2.558087	-1.363020	-0.354729
O	3.385780	-2.178750	-0.457438
C	2.558202	1.362836	-0.355093
O	3.385912	2.178534	-0.457767
H	-1.442772	-4.581528	-0.146959
H	-3.893847	-1.021801	0.091533
H	-3.893710	1.021973	0.092861
H	-1.442657	4.581572	-0.147651
H	0.518195	3.113260	-0.306908
H	0.518193	-3.113333	-0.305368
O	-3.945632	-3.652071	0.099119
O	-3.945374	3.652216	0.100158

Table S19. Calculated structure of $^2[\text{Re}(\text{4DHBP}^-)(\text{CO})_3(\text{DMF})]^0$.

C	1.989204	-0.728285	0.191523
N	0.828554	-1.316673	-0.313473
C	0.775022	-2.660526	-0.413733
C	1.800537	-3.510959	-0.043239
C	2.989184	-2.924301	0.468941
C	3.084016	-1.555148	0.584269
Re	-0.776381	0.055988	-0.870066
N	0.843933	1.345088	-0.172637
C	0.809551	2.692990	-0.139878
C	1.844088	3.487821	0.318396
C	3.018920	2.836023	0.781112
C	3.096178	1.461156	0.756846
C	1.995960	0.693200	0.270599
C	-2.099795	1.436814	-1.162754
O	-2.901548	2.267906	-1.341860
C	-0.259542	0.152530	-2.699114
O	0.059756	0.211875	-3.822576
C	-2.111872	-1.272221	-1.308203
O	-2.920542	-2.071747	-1.576665
H	1.750571	4.569158	0.319780
H	3.996780	0.973210	1.110070
H	3.995881	-1.116389	0.971344
H	1.689897	-4.585675	-0.146832
O	-1.203799	-0.076452	1.334606
C	-2.345032	-0.074797	1.867816
H	-3.253533	0.023197	1.264063
N	-2.546521	-0.187926	3.175923
C	-3.896046	-0.165751	3.736837
H	-4.629728	-0.060706	2.935524
H	-4.087103	-1.096656	4.280577
H	-3.995805	0.676514	4.429477
C	-1.441145	-0.333932	4.120430
H	-0.495832	-0.326346	3.580179
H	-1.547229	-1.278412	4.664370
H	-1.461503	0.491809	4.839294
H	-0.144657	-3.073797	-0.813109
H	-0.100928	3.156364	-0.504146
O	4.053261	-3.688653	0.852377
O	4.086536	3.543452	1.253202
H	3.849758	-4.627375	0.714459
H	3.895536	4.493841	1.209456

Table S20. Calculated structure of $^2[\text{Re}(\text{4DHBP}+\text{H}^+)(\text{CO})_3(\text{DMF})]^{1+}$.

C	2.026195	-0.612587	0.229050
N	0.891414	-1.316964	-0.174016
C	0.875429	-2.622208	-0.132924
C	3.186543	-2.670053	0.747499
C	3.175215	-1.306692	0.693090
Re	-0.822993	-0.081367	-0.843884
N	0.768351	1.351586	-0.340844
C	0.648110	2.687685	-0.450684
C	1.652331	3.579536	-0.109604
C	2.861239	3.056412	0.373398
C	3.008059	1.675665	0.494334
C	1.946548	0.831705	0.132497
C	-2.212870	1.178620	-1.299308
O	-3.053219	1.932775	-1.585924
C	-0.314988	-0.179653	-2.685496
O	-0.001994	-0.239260	-3.807199
C	-2.104134	-1.504468	-1.114778
O	-2.880978	-2.356774	-1.280160
H	1.491813	4.647238	-0.220407
H	3.943054	1.276548	0.865478
H	4.056294	-0.762390	1.009484
O	-1.170002	0.047557	1.336839
C	-2.296098	0.041975	1.912121
H	-3.221842	-0.062498	1.338557
N	-2.447834	0.158937	3.222408
C	-1.310647	0.316442	4.127828
H	-0.383121	0.308222	3.557801
H	-1.404388	1.264604	4.667090
H	-1.306255	-0.504004	4.852584
C	-3.777836	0.137036	3.831536
H	-4.538421	0.008455	3.059464
H	-3.955577	1.077428	4.362777
H	-3.842220	-0.691790	4.543682
O	3.906778	3.834135	0.732550
H	3.690651	4.773290	0.603828
H	-0.027675	-3.124263	-0.462213
H	-0.296370	3.059117	-0.829031
O	4.289373	-3.307969	1.190901
H	4.160797	-4.271686	1.175189
C	2.006680	-3.480533	0.326360
H	1.657539	-4.126425	1.150987
H	2.278379	-4.181235	-0.482361

Table S21. Calculated structure of $^1[\text{Re}(\text{4DHBP-H}^+)(\text{CO})_3(\text{DMF})]^0$.

C	1.952048	-0.889705	0.126900
N	0.769754	-1.353785	-0.387961
C	0.642894	-2.699662	-0.530728
C	1.616689	-3.607767	-0.186940
C	2.876783	-3.171648	0.367348
C	2.980912	-1.734153	0.498102
Re	-0.787427	0.109120	-0.848032
N	0.940716	1.285035	-0.144994
C	0.962599	2.631612	-0.074131
C	2.052160	3.351319	0.385578
C	3.185517	2.638165	0.797689
C	3.176257	1.243129	0.726352
C	2.042553	0.587478	0.249727
C	-2.048703	1.560526	-1.055894
O	-2.813300	2.432269	-1.186909
C	-0.293678	0.265510	-2.685596
O	0.010492	0.361079	-3.808852
C	-2.194234	-1.118085	-1.337832
O	-3.044539	-1.852536	-1.650354
H	2.014229	4.435677	0.418646
H	4.053404	0.692042	1.040157
H	3.904954	-1.337291	0.903071
H	1.435314	-4.668895	-0.332269
O	-1.143112	-0.080985	1.338501
C	-2.264017	-0.058969	1.918523
H	-3.191415	0.073550	1.352578
N	-2.413138	-0.192048	3.229390
C	-1.274638	-0.384560	4.126025
H	-0.351805	-0.403032	3.548577
H	-1.239399	0.434187	4.852190
H	-1.391331	-1.330586	4.664671
C	-3.738824	-0.152240	3.845688
H	-4.499727	0.015190	3.081380
H	-3.779327	0.659965	4.578652
H	-3.939367	-1.100454	4.354825
O	4.303581	3.235898	1.265003
H	4.196891	4.202387	1.265356
O	3.805438	-3.958680	0.707829
H	-0.300235	-3.041991	-0.944089
H	0.069115	3.148788	-0.403025

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