A DFT Study on the Electrocatalytic Reduction of CO₂ to CO by a Molecular Chromium Complex

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Abstract

A variety of molecular transition metal-based electrocatalysts for the reduction of carbon dioxide (CO₂) have been developed to explore the viability of utilization strategies for addressing its rising atmospheric concentrations and the corresponding effects of global warming. Concomitantly, this approach could also meet steadily increasing global energy demands for value-added carbon-based chemical feedstocks as non-renewable petrochemical resources are consumed. Reports on the molecular electrocatalytic reduction of CO₂ mediated by chromium (Cr) complexes are scarce relative to other earth-abundant transition metals. Recently, our group reported a Cr complex that can efficiently catalyze the reduction of CO₂ to carbon monoxide (CO) at low overpotentials. Here, we present new mechanistic insight through a computational (DFT) study, exploring the origin of kinetic selectivity, relative energetic positioning of the intermediates, speciation with respect to solvent coordination and spin state, as well as the role of the redox-active bipyridine moiety. Importantly, these studies suggest that under certain reducing conditions, the formation of bicarbonate could become a competitive reaction pathway, informing new areas of interest for future experimental studies.

Introduction

Anthropogenic carbon dioxide (CO₂) emissions continue to be a primary contributor to climate change, but the displacement of petrochemicals from energy production is made more difficult by increasing global demand in the absence of a suitable replacement. The prospect of redefining CO₂ from combustion byproduct to a renewable feedstock for the production of fuels and commodity chemicals is therefore particularly attractive, as a sustainable CO₂-based energy strategy could both mitigate negative environmental effects and offer energy independence from depleting fossil fuel reserves.¹ The efficient electrochemical reduction of CO₂ would also help to overcome the geographic and temporal limitations of renewable energy sources, resulting in transformative changes in energy usage.

While Fe²⁺ and Mn³⁺ complexes are ubiquitous in recent breakthroughs related to molecular electrocatalytic CO₂ reduction with earth-abundant transition metal complexes (Co and Ni have

also shown relevant activity and selectivity⁴), reports employing effective molecular Cr species are scarce.⁵ Recently, our group reported the first molecular chromium electrocatalyst $\text{Cr}(\text{t}^{\text{bu}}\text{dhbpy})\text{Cl}(\text{H}_2\text{O})$, where 6,6'-di(3,5-di-*tert*-butyl-2-phenolate)-2,2'-bipyridine = $[\text{t}^{\text{bu}}\text{dhbpy}]^{2-} = \text{L}$, for the selective reduction of CO_2 to CO and H_2O with quantitative efficiencies under protic conditions.⁶ Under CO_2 saturation conditions with phenol (PhOH) as an added proton donor, the Cr catalyst was able to achieve turnover frequencies of $5.7 \pm 0.1 \text{ s}^{-1}$ with a high Faradaic efficiency for CO ($\text{FE}_{\text{CO}} = 96 \pm 8\%$) at an overpotential of 110 mV. Kinetic studies using variable concentration electrochemical analyses experimentally determined the reaction to be first order with respect to PhOH, CO_2 , and the catalyst. These studies, complemented by cyclic voltammetry simulations, suggested that C–OH bond cleavage was the rate-determining step of the process.

However, to the best of our knowledge, the intermediates involved in the catalytic mechanism for CO_2 reduction by $\text{Cr}(\text{t}^{\text{bu}}\text{dhbpy})\text{Cl}(\text{H}_2\text{O})$ have not been directly identified and/or quantified to date. Given the scarcity of molecular Cr catalysts for CO_2 reduction, we sought to computationally explore the mechanism of the $\text{Cr}(\text{t}^{\text{bu}}\text{dhbpy})\text{Cl}(\text{H}_2\text{O})$ catalyst to provide insight into the future optimization of efficient and selective molecular electrocatalysts for CO_2 reduction based on a Cr active site. In this work, a complete Density Functional Theory (DFT) study of the reaction mechanism is presented (**Figure 1**), which is both consistent with our reported mechanistic proposal⁶ and provides additional insight on catalyst activation, CO_2 binding, C–OH bond cleavage and the origin of the selectivity for CO_2 over H^+ at the Cr center.

Figure 1. Overview of the mechanistic components examined by DFT in this work.

Methods

Unrestricted geometry optimizations were performed without geometry constraints at the DFT level with the Gaussian 16 program, Rev B.01,⁷ employing the hybrid functional B3LYP⁸ and the 6-31+G(d,p) basis set for all atoms.⁹ Dispersion and bulk solvent effects (*N,N*-dimethylformamide = DMF) were accounted for at the optimization stage, by using Grimme's D3 parameter set with Becke-Johnson (BJ) damping¹⁰ and the SMD continuum model¹¹, respectively. The stationary points and their nature as minima or saddle points (TS) were characterized by vibrational analysis, which also produced enthalpy (H), entropy (S) and Gibbs energy (G) data at 298.15 K. The minima connected by a given transition state were determined by perturbing the transition states along the TS coordinate and optimizing to the nearest minimum. Free energies were corrected (ΔG_{qh}) to account for concentration effects and for errors associated with the harmonic oscillator approximation. Thus, according to Truhlers's quasi-harmonic approximation, all vibrational frequencies below 100 cm⁻¹ were set to this value.¹² These anharmonic and concentration corrections were calculated with the Goodvibes code.¹³ Energies were refined by means of single point calculations with the 6-311+G(2d,p) basis set. The stability of the wavefunction was studied at the double and triple zeta levels of theory. Redox potentials were computed relative to the PHNZ⁻/PHNZ pair (PHNZ = phenazine, see page S2) and referenced to Fc⁺/Fc values from experimental data ($E_{PHNZ^-/PHNZ} = -1.63$ V in DMF, **Figure S1**). Analysis of the electron density was performed within the Atoms In Molecules (AIM) theory of R. F. W. Bader¹⁴ using the Multiwfn program.¹⁵ Kohn-Sham orbital projections and spin densities were plotted in ChemCraft with contour values of 0.045 and 0.005, respectively. The color scheme used for atoms is C = black, O = red, N = blue, H = grey, Cl = green and Cr = maroon. For added clarity, select figures were generated with truncated structures and omitted H atoms as indicated in the respective captions; all calculations were performed using the complete structural model from the original publication. The labelling scheme for minima is $\frac{\text{multiplicity}}{\# \text{ bound DMF}} \text{Cr}(\text{axial ligand})^{\text{charge}}$ and $\frac{\text{multiplicity}}{\# \text{ bound DMF}} \text{TSN}^{\text{charge}}$ for transition states; the [^{tbu}dhbpy]²⁻ ligand framework is a common feature of all Cr species and does not change its coordination mode during the reaction, so it has been omitted in the notation for clarity.

Results and Discussion

Chloride-Displacement Equilibrium

Cyclic voltammetry obtained of the Cr(III) precatalyst, Cr(L)Cl(H₂O), in a DMF solution (0.1 M tetrabutylammonium hexafluorophosphate, TBAPF₆, electrolyte) exhibits chemically related reduction features at -1.66 and -1.78 V vs Fc⁺/Fc that correspond to an overall one-electron process.⁶ The addition of tetrabutylammonium chloride, TBACl, shifts the first wave to more

negative potentials, resulting in a coalescence with the second reduction feature which is consistent with the two redox waves corresponding to the ‘end-states’ of a chloride-displacement equilibrium reaction. The corresponding neutral Cr(L)Cl(DMF) , ${}^4_1\text{Cr(Cl)}^0$, and cationic solvento species $[\text{Cr(L)(DMF)}_2]^+$, ${}^4_2\text{Cr}^{+1}$, that are presumed to undergo a one-electron reduction at these potentials were subsequently examined via computational methods to assess the thermodynamic and kinetic feasibility of this equilibrium (**Figure 2**). *Nota bene*, in solution DMF was assumed to replace the crystallographically determined bound H_2O .

Figure 2. Chloride/DMF exchange equilibrium. S = *N,N*-DMF, tBu = *tert*-butyl.

In agreement with experimental data, ${}^4_1\text{Cr(Cl)}^0$, the calculated lowest energy solvento analogue of the crystallographically observed Cr(III) aquo complex has a high-spin d^3 manifold (see **Table S1** for details on alternative spin state energetics). The κ^1 -O coordination of the explicit DMF molecule *trans* to the chloride ligand renders the octahedral geometry 7.2 kcal/mol more stable than the solvento-free, 5-coordinate species ${}^4_0\text{Cr(Cl)}^0$. In the absence of applied potential, net displacement of chloride from ${}^4_1\text{Cr(Cl)}^0$ by a second equivalent of DMF produces a cationic Cr(III) complex, $[\text{Cr(L)(DMF)}_2]^+$, ${}^4_2\text{Cr}^{+1}$, that maintains an octahedral coordination environment with two κ^1 -O DMF molecules at the axial positions (the ground state remains a quartet, **Table S2**). This species is predicted to be either +2.9 or +0.7 kcal/mol more stable than ${}^4_1\text{Cr(Cl)}^0$, depending whether the outer-sphere reaction components (chloride and second DMF molecule) are explicitly included in the calculations (**Table S3**).¹⁶ Overall, these values are consistent with the assumption that these presumptive ‘end-state’ species from the chloride-displacement equilibrium are close in energy. In agreement with the existence of a dynamic equilibrium, the transition state (${}^4_1\text{TS1}^0$) for the dissociation of the chloride ligand in ${}^4_1\text{Cr(Cl)}^0$ (**Figure S2**) presents a barrier of +15.0 kcal/mol, further supporting the existence of the room-temperature equilibrium proposed from experimental results (**Figure 2**).

Reduction Pathways to CO₂ Binding

The first redox feature, experimentally observed at $E_p = -1.66$ V vs Fc^+/Fc , is ascribed to the one-electron reduction of the most electrophilic species that participates in the equilibrium, the cationic $\frac{4}{2}\text{Cr}^{+1}$. The corresponding neutral species produced from one-electron reduction, $\text{Cr}(\text{L})(\text{DMF})_n$ ($n = 0-2$), presents three energetically close solvento configurations: $\frac{3}{2}\text{Cr}^0$ and $\frac{5}{1}\text{Cr}^0$ lie 3.8 and 1.2 kcal/mol above $\frac{5}{0}\text{Cr}^0$, respectively, which makes the 4-coordinate quintet species the ground state (**Figure 3**, **Table S4**). Accounting for the effects of solvent relaxation on the primary coordination sphere, the calculated redox potential for this process is -1.69 V relative to Fc^+/Fc (**Eq. S1**), in good agreement with experiment (**Table 1**).

Figure 3. Lowest-energy configurations for the one-electron reduced, $[\text{Cr}(\text{L})(\text{DMF})_n]^0$ ($n = 0-2$) species; free energy values relative to $\frac{5}{0}\text{Cr}^0$. S = DMF.

Table 1. Experimental, calculated and predicted values after calibration of the redox features of the Cr catalyst (V vs. Fc^+/Fc).

	Experimental	Calculated	Calibrated
1st Redox Feature	−1.66	−1.69	−1.67
2nd Redox Feature	−1.78	−1.84	−1.77
3rd Redox Feature	−1.95	−2.12	−1.95

It is informative to later mechanistic discussion to elaborate on the distribution of added charge between these three species at this point. The lowest unoccupied molecular orbital (LUMO) of ${}^4_2\text{Cr}^{+1}$ is centered on the bipyridine (bpy) moiety of the ligand, but contains some overlap with the metal d_{yz} orbital (see **Figure S3A**). The highest energy singly occupied molecular orbital (SOMO) of the corresponding one-electron reduction product ${}^3_2\text{Cr}^0$ (**Figure S3B**) is similar to the LUMO of ${}^4_2\text{Cr}^{+1}$ and is localized primarily on the bpy moiety of the ligand. The spin-density plot (**Figure 4A**) suggests that the electronic structure of ${}^3_2\text{Cr}^0$ is best described as a high-spin Cr center which is antiferromagnetically coupled to a bpy-centered electron, resulting in an overall triplet species with a $d^3\text{-bpy}^{\cdot-}$ configuration.

Figure 4. (A) Spin density plot of ${}^3_2\text{Cr}^0$, (B) spin density plot of ${}^5_0\text{Cr}^0$. For clarity, tBu groups and H atoms have been omitted.

However, thermodynamically favorable DMF release results in a stabilization of the d_z^2 orbital for the quintet spin manifold. The high-spin, d^4 configuration of the mono- and non-

solvated species, ${}^5_1\text{Cr}^0$ and ${}^5_0\text{Cr}^0$, is evident in the analysis of the corresponding spin density plots (**Figures S4** and **4B**, respectively). This means that with axial ligand loss, the locus of added charge density shifts from the redox-active bpy fragment to the Cr center. A similar interplay between the occupation of the bpy π^* and the metal d_z^2 orbitals and the coordination of axial ligands has previously been reported for Mn and Re.^{3b}

The second redox feature, experimentally determined at $E_p = -1.78$ V vs Fc^+/Fc , is expected to correspond to the one-electron reduction of the neutral ${}^4_1\text{Cr}(\text{Cl})^0$. The LUMO of the neutral ${}^4_1\text{Cr}(\text{Cl})^0$ is predominantly bpy-based with some metal character (**Figures S5A**), similar to that of ${}^4_2\text{Cr}^{+1}$ (**Figure S3**). As was the case previously, good correlation was found between this empty orbital and the highest SOMO of the triplet species generated by one-electron reduction, $[\text{Cr}(\text{L})(\text{Cl})(\text{DMF})]^-$ (${}^3_1\text{Cr}(\text{Cl})^{-1}$, **Figure S5B** and **5A**). However, the overall ground state for the chloride-bound anion lies 4.4 kcal/mol below this on a quintet manifold as a solvent-free complex, ${}^5_0\text{Cr}(\text{Cl})^{-1}$; d_z^2 stabilization resulting from solvent loss to generate a slightly distorted square pyramidal geometry again promotes a high-spin, d^4 configuration (**Figure 5B**). Considering solvent relaxation in the inner coordination sphere (**Table S5**), the calculated redox potential for this process is -1.84 V relative to Fc^+/Fc (**Eq. S2**), which is in good agreement with experiment (**Table 1**).

Figure 5. (A) Spin density plot of ${}^3_1\text{Cr}(\text{Cl})^{-1}$, (B) spin density plot of ${}^5_0\text{Cr}(\text{Cl})^{-1}$. For clarity, tBu groups and H atoms have been omitted.

After reduction, chloride release to generate ${}^5_0\text{Cr}^0$ occurs within the quintet surface (Table S6), through ${}^5_0\text{TS2}^{-1}$ (Figure S6) located +3.5 kcal/mol above ${}^5_0\text{Cr}(\text{Cl})^{-1}$. The overall chloride-loss reaction from the five-coordinate anion is exergonic by 6.4 kcal/mol (Eq. S3). This means that the most stable one-electron reduced species *in all cases* is the neutral four-coordinate complex, $[\text{Cr}(\text{L})]^0$, ${}^5_0\text{Cr}^0$.

The third redox feature, from which catalysis occurs, is observed by cyclic voltammetry at $E_{1/2} = -1.95$ V and should correspond to the one-electron reduction of ${}^5_0\text{Cr}^0$. The LUMO of ${}^5_0\text{Cr}^0$ is bpy-centered with a small degree of metal-mixing (Figure S7A), which is again in good agreement with the structure of the highest energy SOMO (Figure S7B) of the anionic four-coordinate product of the one-electron reduction, ${}^4_0\text{Cr}^{-1}$ (the quartet is the lowest energy spin configuration, Table S7). As was the case for ${}^5_0\text{Cr}^0$, ${}^4_0\text{Cr}^{-1}$ is also most stable in the absence of axial DMF ligands, yielding a calculated reduction potential for ${}^5_0\text{Cr}^0$ of -2.12 V relative to Fc^+/Fc (Eq. S4), in fair agreement with the experimentally determined value (Table 1). The electronic structure of the distorted square-planar anionic complex is best described as a high-spin Cr(II) center antiferromagnetically coupled to a $\text{bpy}^{\cdot-}$ radical anion, based on the nature of the highest SOMO (Figure S7B) and the spin density population (Figure 6). The proposal of formal bpy reduction at the working potential of this Cr catalyst is in agreement with precedent from mechanistic proposals for Group VII electrocatalysts for CO_2 reduction with bipyridyl-based ligands.¹⁷

Figure 6. Spin density plot of ${}^4_0\text{Cr}^{-1}$. For clarity, tBu groups and H atoms have been omitted.

In order to address the possible systematic errors in the method used for redox potential determination, a regression analysis between calculated and experimental data was carried out. A linear fit (Figure S8) was used to obtain the calibrated results reported in Table 1; calibrated values from this analysis are given for all the redox processes discussed below and were used to summarize the catalyst activation steps in Figure 7.

Figure 7. Free energy profile of the lowest-energy pathways for the formation of the active catalyst species, ${}^4\text{Cr}^{-1}$. Potentials, including a working potential of -1.97 V (corresponding to the thermodynamic potential of catalysis observed experimentally, $E_{\text{cat}/2}$), are relative to Fc^+/Fc . S = DMF.

It is important to note that ${}^4\text{Cr}^{-1}$ and ${}^6\text{Cr}^{-1}$ (Table S7, Figure S9) lie just 1.5 and 3.8 kcal/mol above the ground state, ${}^4\text{Cr}^{-1}$, respectively, showing that solvent binding and alternative spin states have to be considered to properly model the reactivity of ${}^4\text{Cr}^{-1}$ towards CO_2 at the DFT level of theory, as Curtin-Hammett conditions can be met in subsequent reaction steps.¹⁸ It is worth emphasizing that all three of these species (${}^4\text{Cr}^{-1}$, ${}^4\text{Cr}^{-1}$ and ${}^6\text{Cr}^{-1}$) are best described by a $\text{Cr(II)}\text{-bpy}^{\cdot-}$ configuration (Figures 6 and S9).¹⁹ Finally, the corresponding minima of the low-spin, doublet configuration ${}^2_n\text{Cr}^{-1}$ ($n = 0\text{-}2$) presented large spin contamination values and much higher energies than the quartet ground state and are therefore considered not to be catalytically relevant.

CO₂ binding

The selective coordination and activation of CO_2 is a key determinant of reaction efficiency during electrocatalysis.²⁰ Understanding how preferential reactivity towards CO_2 rather than protons occurs at specific active sites offers crucial insight into the design of better electrocatalysts. The

slight curving of the ^{tbu}dhbpy framework in [Cr(^{tbu}dhbpy)]⁻ provides two distinct vacant sites for CO₂ binding and activation, which we define as the concave and convex sites. The former presents a lower free energy barrier for the formation of the Cr–C bond (**Figure 8**) and gives a more stable CO₂ adduct, it is therefore the only stereoisomer discussed throughout the study. The lowest energy TS for CO₂ binding at Cr was located at the quartet surface 10.0 kcal/mol above $^4_0\text{Cr}^{-1}$ ($^4_0\text{TS3}^{-1}$, **Table S8**), and the formation of the CO₂ adduct was endergonic at +4.7 kcal/mol relative to $^4_0\text{Cr}^{-1}$ (**Table S9**). These values suggest that CO₂ binding is a fast and highly reversible process, in good agreement our previously reported electrochemical studies.⁶

To assess if the asymmetric disposition of CO₂ relative to Cr at $^4_0\text{TS3}^{-1}$ (**Figure 8**; Cr–C distance of 2.65 Å, Cr–O distances of 2.87 and 3.36 Å, Cr–C–O angles of 88.0 and 116.5°) resulted from a π -symmetric η^2 binding interaction with CO₂ (observed in structurally characterized η^2 -CO₂ adducts of heavier Group 6 transition metal complexes²¹), a topological analysis of the electron density was carried out at the TS geometry using Atoms in Molecules (AIM): no evidence of discrete Cr–O interactions was apparent (**Figure S10**). Based on this result, we propose that the asymmetric disposition of CO₂ results from the nature of the orbitals involved in the formation of the Cr–C bond, as analysis of the transition state electronic structure indicates that the bpy-centered highest SOMO of $^4_0\text{Cr}^{-1}$ (**Figure S7B**) directly participates in the Cr–C bond formation through mixing with a polarized d_{yz} orbital (**Figure 8B**). This proposal of charge transfer from the ligand is supported by analysis of the β spin density distribution in the bpy fragment in $^4_0\text{TS3}^{-1}$ (**Figure S11A**), which lies in between the formally one-electron reduced bpy moiety in $^4_0\text{Cr}^{-1}$ (**Figure 6**) and the neutral bpy moiety in $^4_0\text{Cr}(\text{CO}_2)^{-1}$ (**Figure S11B**).

Figure 8. Molecular geometry (A), highest SOMO (B, β) and SOMO-2 (C, α) of the lowest energy transition state (${}^4\text{TS3}^{-1}$) for CO₂ binding (convex site), showing direct participation of the bpy-centered, metal-mixed π^* molecular orbital and the d_z^2 orbital in Cr-C bond formation. For clarity, tBu groups and H atoms have been omitted.

The product of CO₂ binding ${}^4\text{Cr}(\text{CO}_2)^{-1}$ is formulated as an η^1 -CO₂ adduct, featuring a Cr-C bond distance of 2.09 Å and Cr-O distances of 2.77 and 2.95 Å. The spin density plot of the CO₂ adduct reveals that the formally reduced bpy in ${}^4\text{Cr}^{-1}$ (**Figure 6**) has transferred its electron density to the Cr-C bond (**Figure S11B**). The dative σ covalent Cr-CO₂ bond is a two-electron interaction according to analysis of the electron distribution in the relevant molecular orbitals (**Figure S12B** and C). An additional π interaction between the d_{yz} atomic orbital of Cr and the p orbitals of the oxygen atoms on CO₂ was located, in agreement with a previous report (**Figure S12D**).^{17b} However, the topological analysis of the electron density on the optimized geometry of the CO₂ adduct, ${}^4\text{Cr}(\text{CO}_2)^{-1}$, only revealed a bond critical point (bcp) between the Cr and C atoms (no bcp was identified connecting the Cr center and the proximal O), further

supporting the η^1 -C nature of the Cr–CO₂ interaction and suggesting that minimal quantifiable interaction exists between the Cr center and the O atoms of the bound CO₂ (**Figure S13**).

Slightly higher barriers (+12.9 kcal/mol, **Table S8**) and less stable CO₂ adducts (+8.8 kcal/mol, **Table S9**) were found in the calculations when an explicit DMF molecule was coordinated *trans* to the site of CO₂ binding for the quartet spin manifold. However, the landscape for CO₂ binding at the low-lying sextet presented larger differences. In the absence of explicit DMF, optimizations of the CO₂ adduct as a sextet led to spontaneous CO₂ release; in the presence of a DMF molecule, a minimum was identified but was very high in energy (+20.2 kcal/mol, **Table S9**). It is clear from these results that the electron pairing that accompanies the Cr–C bond formation step cannot sustain a sextet configuration during the catalytic cycle.

Due to the well-recognized behavior of CO₂ to bind to redox-active ligands²², we computed the free energy profile for plausible bond formation events taking place at several positions of the formally reduced bpy backbone, which could lead to off-cycle species, thus limiting the long-term performance of the electrocatalyst. These studies suggest that CO₂ binding at the bpy backbone is not a viable competitive pathway in the thermodynamically accessible spin manifolds (**Tables S10 and S11**).

Comparing Protonation- and Reduction-First Pathways

We continued our mechanistic investigation by studying the thermodynamic profile of protonation and reduction of ${}^4_0\text{Cr}(\text{CO}_2)^{-1}$, to give the active species for C–OH bond cleavage. Experimentally, no evidence of a multi-electron wave at the reduction potential of CO₂ binding is observed, precluding the possibility of a reduction-first pathway within the characterized potential window.⁶

First Protonation

The transition state for the first protonation step, ${}^4_1\text{TS4}^{-1}$, is found at –2.0 kcal/mol relative to the free energy of the CO₂ adduct, ${}^4_0\text{Cr}(\text{CO}_2)^{-1}$, and independently computed PhOH and DMF (**Table S12**). This is due to the formation of a hydrogen-bonding interaction between PhOH and ${}^4_0\text{Cr}(\text{CO}_2)^{-1}$ that generates a low energy non-covalent assembly with a bound DMF molecule, ${}^4_1\text{Cr}(\text{CO}_2)^{-1}\cdot\text{PhOH}$, at –1.4 kcal/mol relative to the free energy of the CO₂ adduct (**Figure S14**). The ${}^4_1\text{TS4}^{-1}$ (**Figure S15A**) lies just 1.4 kcal/mol above this non-covalent adduct in the potential energy surface, reflecting a very flat profile for the initial protonation step. Based on the spin

density plots of ${}^4_0\text{Cr}(\text{CO}_2)^{-1}$ (**Figure S11B**), ${}^4_1\text{TS4}^{-1}$ (**Figure S15A**) and ${}^4_1\text{Cr}(\text{CO}_2\text{H})^0$ (**Figure S15B**), the bpy moiety remains neutral during this process.

The protonation of ${}^4_0\text{Cr}(\text{CO}_2)^{-1}$ by PhOH is accompanied by coordination of DMF, as expected for the more electrophilic, formally Cr(III) neutral species. The solvento adduct, ${}^4_1\text{Cr}(\text{CO}_2\text{H})^0$ is 3.8 kcal/mol more stable than the 5-coordinate species, ${}^4_0\text{Cr}(\text{CO}_2\text{H})^0$, and both show a strong preference (~ 21.0 kcal/mol) for a quartet configuration (**Table S13**). The overall protonation and solvent coordination process is exergonic (-6.4 kcal/mol, **Eq. 1**):

$$\text{Eq. 1: } \Delta[\text{qG}] = -6.4 \text{ kcal/mol}$$

However, this equation does not consider PhOH homoconjugation in DMF, which has a reported²³ equilibrium constant of $\log K_f ([(\text{A})_2\text{H}]^-) = 3.8$ and should not be neglected in any rigorous thermodynamic analysis. **Eq. 2** takes this into account and provides a free energy gain of 11.5 kcal/mol for the protonation step.

$$\text{Eq. 2: } \Delta[\text{qG}] = -11.5 \text{ kcal/mol.}$$

The subsequent protonation of ${}^4_1\text{Cr}(\text{CO}_2\text{H})^0$ to give a cationic carbonyl complex, ${}^4_1\text{Cr}(\text{CO})^{+1}$, is not thermodynamically favorable (**Eqs. S5 and S6**), suggesting that an additional reduction is required for C–OH bond cleavage to occur.

Reduction Following First Protonation

The one-electron reduction of ${}^4_1\text{Cr}(\text{CO}_2\text{H})^0$ gives ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$, with a calculated potential of -1.89 V vs Fc^+/Fc . This reduction is therefore approximately 1.9 kcal/mol exergonic at the working potential ($E_{\text{cat}/2} = -1.97$ V).⁶ The reduction event is primarily bpy-centered with some contribution from the Cr atom, according to a combined analysis of KS orbitals (**Figure S16B**) and the spin density plot (**Figure 9**), in good agreement with the predicted LUMO of the parent neutral species ${}^4_1\text{Cr}(\text{CO}_2\text{H})^0$ (**Figure S16A**).

Figure 9. Spin density plot of ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$. For clarity, tBu groups and most H atoms have been omitted.

The ground state for this triplet species, ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$, is best described as a high-spin quartet Cr(III) center antiferromagnetically paired with a formally reduced doublet bpy. In contrast to the spin state change that occurs for $[\text{Cr}(\text{Cl})(\text{DMF})]^{-}$, ${}^3_1\text{Cr}(\text{Cl})^{-1}$ with DMF ligand loss (*vide supra*), the lowest energy configuration for the solvent-free species, ${}^3_0\text{Cr}(\text{CO}_2\text{H})^{-1}$, remains in the triplet surface, 0.6 kcal/mol higher than ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$ and features an analogous electronic structure (**Figure S17A**). This can be ascribed to a stronger ligand field effect for the $-\text{CO}_2\text{H}$ moiety in comparison to Cl.²⁴ At the quintet spin surface, the lowest energy species is the solvento adduct ${}^5_1\text{Cr}(\text{CO}_2\text{H})^{-1}$, which lies 4.4 kcal/mol above the triplet ground state, ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$; the solvent-free ${}^5_0\text{Cr}(\text{CO}_2\text{H})^{-1}$ lies at +5.0 kcal/mol (**Table S15**). For both quintet species, the Cr(III)-bpy^{•−} formulation still applies to the electronic structure description, where the electron spin on the bpy is parallel with the unpaired spin localized on the Cr center (**Figure S17B and C**). The lowest energy pathway for CO₂ binding and protonation is summarized in **Figure 10**.

Figure 10. Free energy profile of the lowest-energy pathways for CO₂ binding and protonation. Potentials, including a working potential of -1.97 V , are relative to Fc^+/Fc . S = DMF. PhOH homoconjugation was taken into account for all proton transfer steps. *Potential energy difference was used instead of free energy.

C–OH Bond Cleavage

Cleaving the C–OH bond of a metal-bound hydroxycarbonyl, $\text{M}-\text{CO}_2\text{H}$, frequently represents the rate determining step for many CO₂ reduction electrocatalysts, including the widely studied Fe porphyrins and Mn bpy carbonyls.^{2a,25} Increases in proton activity aimed to accelerate this step can be accompanied by an increase of dihydrogen production, therefore diminishing efficiency.²⁶ The following section discussed possible pathways for C–OH bond cleavage by reaction with PhOH or a second CO₂ molecule, taking into account accessible spin states and solvent species.

Monoanionic pathway

The kinetic reaction parameters of this process were evaluated both in the triplet and quintet surfaces, due to the low-lying nature of the latter for the anionic hydroxycarbonyl complex $^3\text{Cr}(\text{CO}_2\text{H})^{-1}$ (see Reduction Following First Protonation). This species forms a weak non-

covalent assembly with PhOH, ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}\cdot\text{PhOH}$, which lies at +0.6 kcal/mol relative to ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$. The lowest energy transition state (${}^3_1\text{TS5}^{-1}$, **Figure 11**) was found in the triplet surface at +10.5 kcal/mol relative to ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$, with a DMF molecule bound *trans* to the CO_2H group (**Table S16**). The nature of the highest energy SOMO of this TS (**Figure 11A**) and the comparison of the spin density plots of ${}^3_1\text{TS5}^{-1}$ (**Figure 11B**) and ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$ (**Figure 9**) are consistent with electron delocalization from the bpy to the forming Cr–CO π -backbonding scaffold (**Figure 11A**).

Figure 11. Molecular geometry, highest SOMO (A) and spin density (B) of the lowest energy transition state (${}^3_1\text{TS5}^{-1}$) for PhOH-mediated C–OH bond cleavage. For clarity, tBu groups and most H atoms have been omitted.

In the quintet spin surface, the solvent-free transition state, ${}^5_0\text{TS5}^{-1}$, lies 11.1 kcal/mol higher than ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$, only 0.6 kcal/mol higher than ${}^3_1\text{TS5}^{-1}$ (**Table S16**). Spin density and KS plots reveal that for the quintet the electron density is primarily located in the metal center and not in the bpy (**Figure S18**). At the quintet spin manifold, the TS presents a much larger Cr–C bond distance, consistent with the formation of a bent carbonyl complex ${}^5_0\text{Cr}(\text{CO})^0$ as a product (*vide infra*); a larger C–OH distance for the cleaving bond but an also much larger O–H distance for the forming bond in H_2O compared to the triplet. Metrical parameters for relevant bond distances at the lowest-energy configurations for **TS5** at the triplet and quintet spin states are collected in **Table 2**.

Table 2. Relevant bond distances (Å) of the triplet and quintet TSs for C–OH bond cleavage.

	Cr–C	C–OH	HO–H
$^3_1\text{TS5}^{-1}$	2.070	1.938	1.156
$^5_0\text{TS5}^{-1}$	2.349	2.009	1.385

These data suggest that at the triplet surface, the TS has stronger protonation character and bond cleavage is concerted with the proton transfer reaction. By comparison, for the quintet manifold it is better described as a proton donor-assisted, C–OH bond cleavage. In other words, the quintet TS occurs earlier in the H–OH bond formation process but later in the C–OH bond cleavage. This proposal is in good agreement with the imaginary frequency found for these transition states, as evidenced by the overlap of the displaced geometries along the imaginary frequency (**Figure S19**). **Figure S19A** suggests that proton transfer occurs first for the triplet TS, and **Figure S19B** indicates that at the quintet spin manifold proton transfer and C–OH bond cleavage are synchronous. From these results, it can be postulated that in coordinating solvents, which favor a triplet spin configuration, a strong dependence on proton activity will be found, while in non-coordinating solvents a 5-coordinate quintet pathway should be expected, for which proton transfer is not as critical and thus the dependence on proton activity will be less pronounced.

Dianionic pathway

We also considered an alternative pathway, which starts with the reduction of the hydroxycarbonyl complex $^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$ to give a dianionic species, $^4_0\text{Cr}(\text{CO}_2\text{H})^{-2}$ (solvent loss accompanies the formation of the lowest energy dianionic product, **Table S17**). This reduction presents a calculated potential of –2.35 V vs Fc^+/Fc (**Eq. S8**), which translates into an 8.8 kcal/mol free energy barrier at the working potential. According to spin density and KS plots, the added electron is also located on the bpy, rendering a formally dianionic, singlet diradical bipyridine and a neutral, quartet Cr(II) metal center (**Figure S20**).

The dianionic species favorably forms a non-covalent assembly with PhOH, $^4_0\text{Cr}(\text{CO}_2\text{H})^{-2} \cdot \text{PhOH}$, which lies at –3.2 kcal/mol relative to $^4_0\text{Cr}(\text{CO}_2\text{H})^{-2}$, from which the lowest TS for C–OH bond cleavage, $^4_0\text{TS5}^{-2}$, is found at +1.1 kcal/mol relative to $^4_0\text{Cr}(\text{CO}_2\text{H})^{-2}$ and 9.9 kcal/mol relative to $^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$ (**Table S17**). At the $^4_0\text{TS5}^{-2}$ geometry the higher-energy bpy-based electron has been transferred to the metal center (**Figure**

S21). According to the imaginary frequency found, ${}^4_0\text{TS5}^{-2}$ displays synchronous proton transfer and C–OH bond cleavage steps alike ${}^5_0\text{TS5}^{-1}$, with comparable bond distances of 2.315 (Cr–C) and 1.450 Å (HO–H), but a significantly less elongated C–O bond (1.894 Å).

We note that the dianionic pathway presents a computed free energy of activation of comparable magnitude to those of the monoanionic mechanism en route to similar carbonyl products (**Figure 14**). Although the relative concentration of the ${}^4_0\text{Cr}(\text{CO}_2\text{H})^{-2}$ dianion generated in the electrode double-layer should be small from a Nernstian perspective (standard potential of –2.35 V vs Fc^+/Fc , compared to working potential of –1.97 V), the overall reaction energetics are similar enough to the pathway proceeding from the ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$ monoanion that both could feasibly contribute.

Carbonyl Complexes

The second protonation reaction at the monoanionic species yields a neutral carbonyl complex along with H_2O and PhO^- (or the non-covalent homoconjugation adduct $[\text{PhO}^-\cdots\text{HOPh}]$). The lowest energy configuration for this species $\text{Cr}(\text{L})(\text{CO})(\text{DMF})_n$ ($n = 0, 1$) is a solvento adduct in the triplet spin manifold, ${}^3_1\text{Cr}(\text{CO})^0$ (**Table S18** and **Figure 12**), which renders the C–OH bond cleavage step exergonic (–9.2 kcal/mol; –14.4 kcal/mol if homoconjugation is taken into account, **Eqs. S9** and **S10**, respectively). The highest SOMO of this spin configuration comprises a β electron (**Figure 12C**) delocalized through a molecular orbital with π -symmetric metal-carbonyl character (**Figure 12B**).

Figure 12. Molecular structure (A), highest SOMO (B), and spin density plot (C) of ${}^3_1\text{Cr}(\text{CO})^0$. For clarity, tBu groups and H atoms have been omitted.

A low-lying (+2.3 kcal/mol relative to ${}^3_1\text{Cr}(\text{CO})^0$, Table S18) quintet solvento analogue, ${}^5_1\text{Cr}(\text{CO})^0$ (Figure 13), features a bent carbonyl (Cr–C–O angle of 125.9°), in contrast with the more common linear geometry (Cr–C–O angle of 178.1°) found for the triplet ${}^3_1\text{Cr}(\text{CO})^0$ (Figure 12). The lack of a π -symmetric interaction between the carbonyl and Cr center weakens the Cr–C bond in the higher-energy quintet ${}^5_1\text{Cr}(\text{CO})^0$, which is elongated from 1.913 to 2.301 Å.

Figure 13. Molecular geometry (A), highest SOMO (B) and spin density plot (C) of ${}^5_1\text{Cr}(\text{CO})^0$. For clarity, tBu groups and H atoms have been omitted.

The five-coordinate, solvent-free carbonyl species are close in energy to the octahedral solvento ones, but the relative stability of the triplet and quintet spin manifolds is reversed (**Table S18**): the quintet, ${}^5_0\text{Cr}(\text{CO})^0$ is slightly more stable than ${}^3_0\text{Cr}(\text{CO})^0$ (+0.6 and +4.6 kcal/mol relative to the carbonyl ground state, ${}^3_1\text{Cr}(\text{CO})^0$, respectively). This is likely due to the strong d_z^2 character of the SOMO in the quintet species, which is stabilized by the dissociation of the axial DMF ligand, thus favoring the quintet configuration for the solvent-free species. The electronic structure of the solvent-free species is very similar to that of the solvento adduct and does not merit further discussion.

The one-electron reduction of the neutral carbonyl complex ${}^3_1\text{Cr}(\text{CO})^0$ gives a low spin species and loss of the axial DMF ligand, ${}^2_0\text{Cr}(\text{CO})^{-1}$ (**Table S19**), which is the carbonyl product of the dianionic C–OH bond cleavage pathway. A calculated potential (**Eq. S12**) of –2.02 V vs Fc^+/Fc renders the reduction process slightly endergonic (+1.1 kcal/mol) relative to $E_{\text{cat}/2}$.

CO Release

The release of the carbonyl ligand can be a limiting factor in electrocatalytic CO₂ reduction,^{2e} functioning as either the rate-determining step or instigating competitive degradation reactions.²⁷ Despite our continuous efforts, no TS could be located for this thermodynamically favorable step (−5.2 kcal/mol, **Eq. S11**). Relaxed potential energy scans for the Cr–C bond elongation suggest that this reaction is unlikely to occur in the triplet surface, both due to the stronger Cr–CO bond and the lower stability of the product, $^3_0\text{Cr}^0$. However, the low-lying quintet carbonyl configurations (0.6 and 2.3 kcal/mol above the ground state for $^5_0\text{Cr}(\text{CO})^0$ and $^5_1\text{Cr}(\text{CO})^0$, respectively, **Table S18**) present an almost flat potential energy surface for the Cr–C bond elongation ($\Delta E \sim 2$ kcal/mol). It is reasonable to consider this value as an approximate upper limit for the free energy of a dissociative process, which leads us to conclude that CO release does not present a free energy barrier significantly higher than +3 kcal/mol and is therefore fast. Consistent with these assumptions and analyses, no binding of CO was observed by cyclic voltammetry (**Figure S22**) and literature reports²⁸ provide further support to consider that the Cr(II)–CO interactions can be weak and the release of CO facile. From the $^2_1\text{Cr}(\text{CO})^{-1}$ monoanion, accessing bent carbonyl species from which CO release could be facile requires a larger thermodynamic penalty (**Table S19**) than the estimated kinetic barrier for CO loss at the neutral manifold, indicating that CO loss likely occurs at the neutral species. Overall, this suggests that the catalytic mechanism proceeds through the monoanionic $^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$ rather than the dianionic $^4_0\text{Cr}(\text{CO}_2\text{H})^{-2}$. The possible operating mechanisms for the C–OH bond cleavage and CO release are summarized in **Figure 14**.

Figure 14. Free energy profile of the lowest-energy pathways for C–OH bond cleavage and CO release. Potentials, including a working potential of -1.97 V , are relative to Fc^+/Fc . S = DMF. PhOH homoconjugation was taken into account for all proton transfer steps. *Estimated upper-limit barrier in the quintet spin manifold, calculated according to relaxed potential energy surface scans.

Competing Pathways:

-Bicarbonate Formation

Water (H_2O) is a commonly proposed byproduct in the CO_2 -to- CO reduction reaction under protic conditions. However, the production of bicarbonate, HCO_3^- , should not be overlooked,²⁹ as it is dependent on experimental conditions and its generation can modify proton activity in solution, cause complications under different solvents, enhance the rate of CO production,³⁰ or act as a substrate³¹; these features can be particularly relevant if the catalyst is heterogenized or used in a flow configuration. **Eq. 3** shows that the formation of HCO_3^- from $[\text{Cr}(\text{L})(\text{CO}_2\text{H})]^-$ ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$, is a thermodynamically favorable process, suggesting that the observed experimental selectivity towards water is the result of kinetic control.

$$\text{Eq. 3: } \Delta[qG] = -6.9 \text{ kcal/mol}$$

The kinetic parameters of bicarbonate formation were examined in both the triplet and quintet surfaces, with and without an explicit DMF molecule present. While the reaction pathway goes through analogous intermediates, the triplet surface is consistently ~ 6 kcal/mol lower in energy than the quintet one, and inclusion of a bound DMF molecule promotes a ~ 3 kcal/mol stabilization for both surfaces (**Table S20**). Therefore, the discussion will be limited to the mono-solvento in the triplet state for brevity, although we emphasize the positioning of intermediates is consistent across all energetically relevant possibilities for the spin manifold.

The lowest energy pathway for the formation of bicarbonate goes through three distinct transition states: binding of a second CO_2 molecule, proton transfer and C–O bond cleavage, which lie at +18.3, +16.7 and +16.0 kcal/mol above ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$ (**Figure 15**). These are connected by two high-energy intermediates, ${}^3_1\text{Cr}(\text{CO}_2\text{HCO}_2)^{-1}$ and ${}^3_1\text{Cr}(\text{CO}_2\text{CO}_2\text{H})^{-1}$ at +17.8 and +14.8 kcal/mol respectively, which makes the second CO_2 binding step the rate-determining step for the process. This is of particular relevance, as it implies that high concentrations of CO_2 will accelerate this process, while lower proton donor activity will slow water formation.

Figure 15. Free energy profile of the lowest energy pathway for the formation of bicarbonate. S = DMF. *Potential energy difference relative to the closest preceding minimum was used instead of free energy.

The upwards orientation of the covalent O–H bond of the metal-bound hydroxycarbonyl is critical to achieve a low-energy transition state (${}^3_1\text{TS6}^{-1}$, **Figure 16A**) *en route* to the formation of intermediate ${}^3_1\text{Cr}(\text{CO}_2\text{HCO}_2)^{-1}$, for which the CO_2HCO_2 sub-unit presents a conformation resembling a six-membered cycle, analogous to that proposed by the groups of Savéant and Kubiak in the presence of Mg^{2+} cations.^{3b,32} ${}^3_1\text{TS6}^{-1}$ and ${}^3_1\text{Cr}(\text{CO}_2\text{HCO}_2)^{-1}$ feature a hydrogen-bonding interaction between the H atom of the hydroxycarbonyl and an O atom of the incorporated CO_2 equivalent (**Figure 16A**). The KS orbital projection of the highest SOMO of ${}^3_1\text{TS6}^{-1}$ (**Figure 16B**) displays a burgeoning π interaction between the Cr and C atoms, which compensates for the decrease in formal carbon-oxygen bond order from double to single upon binding the second CO_2 molecule.

Figure 16. (A) Molecular geometry and (B) highest SOMO of ${}^3_1\text{TS6}^{-1}$, for the binding of a second CO_2 molecule to ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$ to form ${}^3_1\text{Cr}(\text{CO}_2\text{HCO}_2)^{-1}$. For clarity, tBu groups and most H atoms have been omitted.

The TS for H^+ transfer from the Cr-bound hydroxycarbonyl to the second CO_2 equivalent (${}^3_1\text{TS7}^{-1}$) is relatively symmetric and characterized by O–H bond distances of 1.146 and 1.261

Å for the breaking and forming bonds, respectively (**Figure S23A**). Analysis of the electronic structure suggests this TS presents a slightly less formally reduced bpy backbone (**Figure S24B**) than in the previous CO₂ binding ${}^3_1\text{TS6}^{-1}$ (**Figure S24A**), resulting from the fully established Cr–C π interaction in ${}^3_1\text{Cr}(\text{CO}_2\text{HCO}_2)^{-1}$ (**Figure S23B**). The final transition state ${}^3_1\text{TS8}^{-1}$ (**Figure S25A**) for the C–O bond cleavage that precedes bicarbonate formation presents a bent Cr–C–O angle of 141.0°, far from the almost linear (178.1°) geometry of the lowest energy product, ${}^3_1\text{Cr}(\text{CO})^0$. The Cr–C bond distance of 2.027 Å in ${}^3_1\text{TS8}^{-1}$ is also much closer to that of intermediate ${}^3_1\text{Cr}(\text{CO}_2\text{CO}_2\text{H})^{-1}$ (2.044 Å) than the presumptive carbonyl product ${}^3_1\text{Cr}(\text{CO})^0$ (1.913 Å). These metrical parameters and the distribution of significantly more electron density in the bpy backbone (**Figure S24C**) than in the final carbonyl product (**Figure 12C**) are consistent with an early transition state for the final step of bicarbonate formation. This stepwise transformation is summarized in **Figure 15**.

An alternative pathway for the formation of HCO₃[−] is the direct attack of the OH[−] group in the anionic hydroxycarbonyl intermediate ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$ towards free CO₂ (**Figure S26**). This concerted pathway presents a much larger energy barrier (+25.5 kcal/mol in the triplet surface (${}^3_0\text{TS9}^{-1}$), +25.9 in the quintet (${}^5_0\text{TS9}^{-1}$)) and was therefore excluded in our analysis.

-Hydride Formation

The formation of a metal hydride under reducing conditions in the presence of a proton donor can shift catalyst selectivity from CO to formate or H₂.³³ It is therefore key to understand the thermodynamic and kinetic parameters of the metal protonation reaction in order to design efficient electrocatalysts for CO₂ reduction. Due to the formally reduced character of the bpy backbone in the active species, ${}^4_0\text{Cr}^{-1}$, the kinetic and thermodynamic parameters for the protonation of the active species were evaluated both at the metal center and at the 5-position of the bpy, chosen as a representative example of the reactivity of the ligand backbone (**Tables S10 and S11; Figure 17**). The formation of a Cr(III) hydride, Cr(L)(H)(DMF) ${}^4_1\text{Cr}(\text{H})^0$ (**Table S21**) is thermodynamically favorable (−2.1 kcal/mol, −7.2 considering homoconjugation, **Eqs. S13 and S14**). However, the lowest energy transition state (${}^4_1\text{TS10}^{-1}$, **Figure 18A**) located for the formation of the hydride occurs in the quartet spin manifold and lies at +30.2 kcal/mol, rendering this process non-competitive with CO₂ binding (${}^4_1\text{TS3}^{-1} = 10.0$ kcal), in agreement with the quantitative selectivity the catalyst exhibits towards CO (**Figure 17**).

Figure 17. Free energy profile of the competing CO₂ binding and protonation of ${}^4_0\text{Cr}^{-1}$. S = DMF.

Based on the electronic structure analysis, a few notable differences are apparent for the transition state located for protonation, ${}^4_1\text{TS10}^{-1}$, in comparison to that for CO₂ binding (${}^4_1\text{TS3}^{-1}$): in ${}^4_1\text{TS10}^{-1}$ there is significantly less spin density on the bpy backbone (**Figure 18B**) and the metal-based atomic orbital participating in the SOMO (**Figure 18C**) has more d_z^2 character than d_{yz} . We hypothesize that since the harder and less polarizable H⁺ is unable to engage in π -symmetric interactions, the two electrons necessary to form the bond are required to be in orbitals with metal d_z^2 character to achieve the optimal degree of sigma symmetry at the transition state. The d_z^2 orbital presents minimal overlap with the bpy π^* system at the TS, forcing the electron density to be centered on the metal atom, populating orbitals of higher energy than the bpy π^* system. This hypothesis, formulated by Kubiak and co-workers for a related Re-bpy system^{17b} on the basis of orbital analysis of calculated reaction intermediates, is readily extended to this system by this determination of relevant transition states and the analysis of their electronic structure.

Figure 18. Molecular geometry (A), spin density (B), highest SOMO (C) and SOMO-1 (D) of the transition state (${}^4_1\text{TS10}^{-1}$) for the formation of a Cr hydride. For clarity, tBu groups and most H atoms have been omitted.

The protonation of the formally reduced bpy at a representative position for CO_2 binding (5, **Table S10**) was also studied. The barriers for the ligand-based protonation are slightly lower than those for the formation of the metal hydride (+24.7 and +25.2 kcal/mol for the quartet (**Figure S27**, ${}^4_1\text{TS11}^{-1}$) and sextet spin states, respectively (**Table S22**)) but not competitive with ${}^4_1\text{TS3}^{-1}$ (+8.0 kcal/mol). The reaction is also endergonic (+8.1 kcal/mol, +2.9 considering homoconjugation, **Eqs. S15 and S16**).

Conclusions

A complete DFT study of the mechanism of the first Cr-based, efficient CO_2 -to-CO reduction molecular electrocatalyst is reported, which takes into account the reactivity of low-lying spin states (with the limitations that a single-reference method presents) and includes explicit solvation, which affects, and even inverts, the relative stability of minima at different spin surfaces. In addition to the mechanism for the formation of H_2O and CO, the pathways for the thermodynamically accessible bicarbonate and metal hydride formation have been mapped. Our results on the possible formation of bicarbonate as a competitive co-product to CO instead of H_2O suggest that with appropriate relative substrate concentrations and proton activity, this pathway can be viable, which we intend to explore in future studies. This study highlights the non-innocent redox behavior of the bpy backbone, which is key to achieve activity and selectivity at low

overpotentials. The sharing of added electron density between bpy and the metal center in an extended molecular orbital ensures selectivity for CO₂ over H⁺ by preventing highly localized sigma character at the Cr center. This electronic delocalization is also an important component during Cr–C bond formation: the mixing of populated π^* ligand orbitals with a polarized d_{yz} orbital facilitates charge transfer from the redox-active bpy to the dative covalent bond. Indeed, the C–OH bond cleavage step relies on the same orbital pathway, with charge transfer from the reduced bpy to the metal center induced by intermolecular proton transfer; the extent of this charge transfer in the transition state is dependent on the spin and charge manifold. In ongoing studies, we are continuing to explore the consequences of perturbing the continuum of charge localization between ligand and metal center on the activity and selectivity of Cr-based molecular catalysts.

Associated Content

Supporting Information documents available online, including complete .xyz files, additional visualizations, redox potential calculation details and additional reaction equations.

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Notes

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TOC:

Bipyridine directs selectivity to CO!

Supporting Information

**A DFT Study on the Electrocatalytic Reduction of CO₂ to CO
by a Molecular Chromium Complex**

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Use of Fc^+/Fc as Computational Reference

In agreement with a previous report,¹ our computation of redox potentials relative to Fc^+/Fc with B3LYP gave an excellent correlation between calculated and experimental data ($R^2 = 0.996$), but computed values were systematically more positive (0.52 V in average, *cf.* the 0.48 V value found by Batista and coworkers with $R^2 = 0.96$). However, this underestimation does not occur when a different reference pair is considered: we employed the phenazine $\text{PHNZ}^-/\text{PHNZ}$ pair (PHNZ = phenazine) and referenced to Fc^+/Fc values from experimental data ($E_{\text{PHNZ}^-/\text{PHNZ}} = -1.63$ V in DMF, see **Table 1** and **Figure S8**).

Figure S1. CVs of 2.5 mM phenazine (PHNZ) under argon (Ar) saturation conditions. Conditions: 0.1 M $\text{TBAPF}_6/\text{DMF}$; glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode; 100 mV/s scan rate; referenced to internal ferrocene standard.

Chloride-Displacement Equilibrium

Table S1. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for Cr(L)Cl(DMF)_n ($n = 0, 1$) species, in kcal/mol.

Species	E	[qG] (DZ/TZ)
${}^2_0\text{Cr(Cl)}^0 + \text{DMF}$	+41.5	+29.4
${}^4_0\text{Cr(Cl)}^0 + \text{DMF}$	+19.8	+7.2
${}^2_1\text{Cr(Cl)}^0$	+21.6	+21.9
${}^4_1\text{Cr(Cl)}^0$	0.0	0.0

Table S2. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for $[\text{Cr(L)(DMF)}_2]^+$ species, in kcal/mol.

Species	E	[qG]
${}^2_2\text{Cr}^{+1}$	+24.4	+25.0
${}^4_2\text{Cr}^{+1}$	0.0	0.0

Table S3. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) comparing Cr(L)Cl(DMF) and $[\text{Cr(L)(DMF)}_2]^+$ species, in kcal/mol.

Species	E	[qG]
${}^4_0\text{Cr(Cl)}^0 + \text{DMF}$	+4.8	+2.9
${}^4_2\text{Cr}^{+1} + \text{Cl}^-$	0.0	0.0
${}^4_0\text{Cr(Cl)}^0 \cdot \text{DMF}$	-1.5	+7.7
${}^4_2\text{Cr}^{+1} \cdot \text{Cl}^-$	-3.6	+7.0

Figure S2. Molecular geometry of the transition state (${}^4_1\text{TS1}^0$, +15.0 kcal/mol) for the dissociation of chloride from ${}^4_1\text{Cr}(\text{Cl})^0$. H atoms and tBu groups omitted for clarity.

Reduction Pathways to CO₂ Binding

Table S4. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for Cr(L)(DMF)_n (n = 0-2) species, in kcal/mol. Entries in red presented large spin contamination.

Species	E	[qG]
$\begin{smallmatrix} 1 \\ 0 \end{smallmatrix} \text{Cr}^0 + 2 \text{ DMF}$	+37.5	+39.2
$\begin{smallmatrix} 3 \\ 0 \end{smallmatrix} \text{Cr}^0 + 2 \text{ DMF}$	+25.8	+26.4
$\begin{smallmatrix} 5 \\ 0 \end{smallmatrix} \text{Cr}^0 + 2 \text{ DMF}$	0.0	0.0
$\begin{smallmatrix} 1 \\ 1 \end{smallmatrix} \text{Cr}^0 + \text{DMF}$	+19.8	+33.6
$\begin{smallmatrix} 3 \\ 1 \end{smallmatrix} \text{Cr}^0 + \text{DMF}$	-2.3	+10.4
$\begin{smallmatrix} 5 \\ 1 \end{smallmatrix} \text{Cr}^0 + \text{DMF}$	-10.3	+1.2
$\begin{smallmatrix} 1 \\ 2 \end{smallmatrix} \text{Cr}^0$	+3.4	+29.1
$\begin{smallmatrix} 3 \\ 2 \end{smallmatrix} \text{Cr}^0$	-21.5	+3.8
$\begin{smallmatrix} 5 \\ 2 \end{smallmatrix} \text{Cr}^0$	-16.5	+7.9

Redox Potential Determination

$$\text{Eq S1: } \Delta[\text{qG}] = 1.6 \text{ kcal/mol}$$

$$V \text{ vs PHNZ}^-/\text{PHNZ} = -0.07. V \text{ vs Fc}^+/\text{Fc} = -1.69.$$

Figure S3. (A) LUMO of ${}^4_2\text{Cr}^{+1}$, (B) highest SOMO of ${}^3_2\text{Cr}^0$. H atoms and tBu groups omitted for clarity.

Figure S4. Spin density plot of ${}^5_1\text{Cr}^0$. H atoms and tBu groups omitted for clarity.

Table S5. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for Cr(L)(Cl)(DMF)_n (n = 0, 1) species, in kcal/mol. Entries in red presented large spin contamination.

Species	E	[qG]
${}^1_0\text{Cr}(\text{Cl})^{-1} + \text{DMF}$	+31.2	+33.1
${}^3_0\text{Cr}(\text{Cl})^{-1} + \text{DMF}$	+7.0	+7.6
${}^5_0\text{Cr}(\text{Cl})^{-1} + \text{DMF}$	0.0	0.0
${}^1_1\text{Cr}(\text{Cl})^{-1}$	+14.6	+28.4
${}^3_1\text{Cr}(\text{Cl})^{-1}$	-8.4	+4.4
${}^5_1\text{Cr}(\text{Cl})^{-1}$	-4.0	+8.3

Eq S2: $\Delta[\text{qG}] = 5.1$ kcal/mol

V vs PHNZ⁻/PHNZ = -0.22. V vs Fc⁺/Fc = -1.84.

Figure S5. (A) LUMO of ${}^4_1\text{Cr}(\text{Cl})^0$, (B) highest SOMO of ${}^3_1\text{Cr}(\text{Cl})^{-1}$. H atoms and tBu groups omitted for clarity.

Table S6. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the transition states for chloride dissociation from ${}^5_0\text{Cr}(\text{Cl})^{-1}$, in kcal/mol.

Species	E	[qG]
${}^3_0\text{TS2}^{-1} + \text{DMF}$	+27.9	+28.7
${}^5_0\text{TS2}^{-1} + \text{DMF}$	+2.9	+3.5
${}^3_1\text{TS2}^{-1}$	+0.9	+14.0
${}^5_1\text{TS2}^{-1}$	+0.6	+11.2

Figure S6. Molecular geometry of the transition state (${}^5_0\text{TS2}^{-1}$, +3.5 kcal/mol ([qG])) for the dissociation of chloride from ${}^5_0\text{Cr}(\text{Cl})^{-1}$. H atoms and tBu groups omitted for clarity.

Eq S3: $\Delta[\text{qG}] = -6.4$ kcal/mol

Figure S7. (A) LUMO of ${}^5\text{Cr}^0$, (B) highest SOMO of ${}^4\text{Cr}^{-1}$. H atoms and tBu groups omitted for clarity.

Table S7. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for $[\text{Cr}(\text{L})(\text{DMF})_n]^-$ ($n = 0-2$) species, in kcal/mol. ${}^6_2\text{Cr}^{-1}$ spontaneously releases a DMF molecule. Entries in red presented large spin contamination.

Species	E	[qG]
${}^2_0\text{Cr}^{-1} + 2 \text{ DMF}$	+24.8	+25.6
${}^4_0\text{Cr}^{-1} + 2 \text{ DMF}$	0.0	0.0
${}^6_0\text{Cr}^{-1} + 2 \text{ DMF}$	+4.3	+3.8
${}^2_1\text{Cr}^{-1} + \text{DMF}$	+15.7	+27.6
${}^4_1\text{Cr}^{-1} + \text{DMF}$	-9.7	+1.5
${}^6_1\text{Cr}^{-1} + \text{DMF}$	-5.6	+5.2
${}^2_2\text{Cr}^{-1}$	-0.3	+23.6
${}^4_2\text{Cr}^{-1}$	-7.1	+16.9

Eq. S4: $\Delta[\text{qG}] = 11.4 \text{ kcal/mol}$

V vs $\text{PHNZ}^-/\text{PHNZ} = -0.50$. V vs $\text{Fc}^+/\text{Fc} = -2.12$.

Figure S8. Plot of calculated versus experimental redox potentials.

Figure S9. (A) Spin density plot of ${}^4_1\text{Cr}^{-1}$, (B) spin density plot of ${}^6_0\text{Cr}^{-1}$. H atoms and tBu groups omitted for clarity.

CO₂ Binding at Cr

Table S8. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the transition states for CO₂ binding at Cr from ${}^4_0\text{Cr}^{-1}$, in kcal/mol. No TSs were located in the sextet spin state.

Species	E	[qG]
${}^4_0\text{TS3}^{-1} + \text{DMF}$	−0.1	+10.0
${}^4_1\text{TS3}^{-1}$	−8.3	+12.9

Table S9. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for $[\text{Cr}(\text{L})(\text{CO}_2)(\text{DMF})_n]^-$ (n = 0, 1) species, in kcal/mol. Optimizations to obtain ${}^6_0\text{Cr}(\text{CO}_2)^{-1}$ resulted in spontaneous release of CO₂.

Species	E	[qG]
${}^4_0\text{Cr}(\text{CO}_2)^{-1} + \text{DMF}$	−7.3	+4.7
${}^4_1\text{Cr}(\text{CO}_2)^{-1}$	−14.7	+8.8
${}^6_1\text{Cr}(\text{CO}_2)^{-1}$	−1.2	+20.2

Figure S10. Laplacian of the electron density, $\nabla^2\rho$, plots of the TS for CO_2 binding (${}^4_0\text{TS3}^{-1}$), showing a bcp between Cr and C and no bcps between Cr and O atoms.

Figure S11. (A) Spin density plot of ${}^4_0\text{TS3}^{-1}$, (B) spin density plot of ${}^4_0\text{Cr}(\text{CO}_2)^{-1}$. H atoms and tBu groups omitted for clarity.

Figure S12. Molecular geometry (A), Highest SOMO (B), SOMO-1 (C) and SOMO-10 (D) of ${}^4_0\text{Cr}(\text{CO}_2)^{-1}$. H atoms and tBu groups omitted for clarity.

Figure S13. Laplacian of the electron density, $\nabla^2\rho$, plot of ${}^4_0\text{Cr}(\text{CO}_2)^{-1}$, showing a bcp only between Cr and C.

CO₂ Binding at the bpy Moiety

While relaxed Potential Energy Surface scans revealed that CO₂ binding at the 1 and 2 positions of the bpy backbone is not feasible, transition states could be located for the formation of C–C bonds at the 3, 4 and 5 positions of the bipyridine framework in the quartet and sextet surfaces, with and without explicit DMF. A complete study is only reported for positions 5 (**TS12**) and 3 (**TS13**), similar values were obtained for CO₂ binding at the 4-position. All these barriers were at least 6.5 kcal/mol higher than the Cr–CO₂ bond formation one (**Table S10**), and the overall reactions were found to be highly endergonic, yielding products that were at least 10.8 kcal/mol less stable than the Cr–CO₂ adduct (**Table S11**). Based on these results, CO₂ binding at the bpy backbone can be ruled out as a viable competitive pathway.

Table S10. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the transition states for CO₂ binding at the bpy (positions 5 and 3) from ${}^4_0\text{Cr}^{-1}$, in kcal/mol.

Species	E	[qG]
${}^4_0\text{TS12}^{-1} + \text{DMF}$	+6.4	+17.2
${}^4_0\text{TS13}^{-1} + \text{DMF}$	+9.0	+19.6
${}^6_0\text{TS12}^{-1} + \text{DMF}$	+6.6	+16.7
${}^6_0\text{TS13}^{-1} + \text{DMF}$	+8.6	+18.5
${}^4_1\text{TS12}^{-1}$	−3.5	+18.7
${}^4_1\text{TS13}^{-1}$	−0.9	+22.2
${}^6_1\text{TS12}^{-1}$	−1.6	+19.6
${}^6_1\text{TS13}^{-1}$	+0.4	+21.5

Table S11. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the CO₂ binding adducts at the bpy (positions 5 and 3) from ${}^4_0\text{Cr}^{-1}$, in kcal/mol.

Species	E	[qG]
${}^4_0\text{bpyCO}_2\text{-5}^{-1} + \text{DMF}$	+3.5	+15.6
${}^4_0\text{bpyCO}_2\text{-3}^{-1} + \text{DMF}$	+5.6	+17.7
${}^6_0\text{bpyCO}_2\text{-5}^{-1} + \text{DMF}$	+3.1	+15.1
${}^6_0\text{bpyCO}_2\text{-3}^{-1} + \text{DMF}$	+4.8	+16.8
${}^4_1\text{bpyCO}_2\text{-5}^{-1}$	−6.5	+17.4
${}^4_1\text{bpyCO}_2\text{-3}^{-1}$	−4.2	+17.5
${}^6_1\text{bpyCO}_2\text{-5}^{-1}$	−5.5	+17.7
${}^6_1\text{bpyCO}_2\text{-3}^{-1}$	−5.1	+18.1

First Protonation

Table S12. Potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the PhOH adduct of ${}^4_1\text{Cr}(\text{CO}_2)^{-1}$ and the following protonation transition state (${}^4_1\text{TS4}^{-1}$) relative to ${}^4_1\text{Cr}(\text{CO}_2)^{-1}$ and independently computed PhOH and DMF, in kcal/mol.

Species	E	[qG]
${}^4_1\text{Cr}(\text{CO}_2)^{-1}\cdot\text{PhOH}$	-26.8	-1.4
${}^4_1\text{TS4}^{-1}$	-25.4	-2.0

Figure S14. Molecular geometry of ${}^4_1\text{Cr}(\text{CO}_2)^{-1}\cdot\text{PhOH}$. For clarity, tBu groups and most H atoms have been omitted.

Figure S15. (A) Spin density plot of ${}^4_1\text{TS4}^{-1}$, (B) spin density plot of ${}^4_1\text{Cr}(\text{CO}_2\text{H})^0$.

For clarity, tBu groups and most H atoms have been omitted.

Table S13. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the metal-bound hydroxycarbonyl $\text{Cr}(\text{L})(\text{CO}_2\text{H})(\text{DMF})_n$ ($n = 0, 1$), in kcal/mol.

Species	E	[qG]
${}^2_0\text{Cr}(\text{CO}_2\text{H})^0 + \text{DMF}$	+36.8	+25.1
${}^4_0\text{Cr}(\text{CO}_2\text{H})^0 + \text{DMF}$	+15.9	+3.8
${}^6_0\text{Cr}(\text{CO}_2\text{H})^0 + \text{DMF}$	+65.5	+50.5
${}^2_1\text{Cr}(\text{CO}_2\text{H})^0$	+21.3	+22.0
${}^4_1\text{Cr}(\text{CO}_2\text{H})^0$	0.0	+0.0
${}^6_1\text{Cr}(\text{CO}_2\text{H})^0$	+49.0	+46.8

$$\text{Eq S5: } \Delta[qG] = 10.2 \text{ kcal/mol}$$

$$\text{Eq S6: } \Delta[qG] = 5.1 \text{ kcal/mol}$$

Table S14. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the cationic carbonyl complex $[Cr(L)(CO)(DMF)]^+$, in kcal/mol.

Species	E	[qG]
${}^2_1Cr(CO)^{+1}$	+15.3	+15.9
${}^4_1Cr(CO)^{+1}$	0.0	0.0

Reduction

Table S15. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the reduced metal-bound hydroxycarbonyl $[\text{Cr}(\text{L})(\text{CO}_2\text{H})(\text{DMF})_n]^-$ ($n = 0, 1$), in kcal/mol. Entries in red presented large spin contamination.

Species	E	[qG]
${}^1_0\text{Cr}(\text{CO}_2\text{H})^{-1} + \text{DMF}$	+36.6	+26.4
${}^3_0\text{Cr}(\text{CO}_2\text{H})^{-1} + \text{DMF}$	+12.1	+0.6
${}^5_0\text{Cr}(\text{CO}_2\text{H})^{-1} + \text{DMF}$	+17.2	+5.0
${}^1_1\text{Cr}(\text{CO}_2\text{H})^{-1}$	+21.9	+23.9
${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$	0.0	+0.0
${}^5_1\text{Cr}(\text{CO}_2\text{H})^{-1}$	+4.9	+4.4

Eq S7: $\Delta[\text{qG}] = 9.2 \text{ kcal/mol}$

V vs $\text{PHNZ}^-/\text{PHNZ} = -0.40$. V vs $\text{Fc}^+/\text{Fc} = -2.03$. Calibrated V vs $\text{Fc}^+/\text{Fc} = -1.89$.

Figure S16. (A) LUMO of ${}^4_1\text{Cr}(\text{CO}_2\text{H})^0$, (B) highest SOMO of ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$. For clarity, tBu groups and most H atoms have been omitted.

Figure S17. Spin density plot of (A) ${}^3_0\text{Cr}(\text{CO}_2\text{H})^{-1}$, (B) ${}^5_1\text{Cr}(\text{CO}_2\text{H})^{-1}$ and (C) ${}^5_0\text{Cr}(\text{CO}_2\text{H})^{-1}$. For clarity, tBu groups and most H atoms have been omitted.

Second Protonation: Monoanionic Pathway

Table S16. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the transition states for the protonation of the metal-bound hydroxycarbonyl ${}^3_0\text{Cr}(\text{CO}_2\text{H})^{-1}$, in kcal/mol.

Species	E	[qG]
${}^3_0\text{Cr}(\text{CO}_2\text{H})^{-1} \cdot \text{PhOH} + \text{DMF}$	+0.8	+3.5
${}^3_0\text{TS5}^{-1} + \text{DMF}$	+15.4	+14.0
${}^5_0\text{Cr}(\text{CO}_2\text{H})^{-1} \cdot \text{PhOH} + \text{DMF}$	+4.5	+6.4
${}^5_0\text{TS5}^{-1} + \text{DMF}$	+12.9	+11.1
${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1} \cdot \text{PhOH}$	−13.8	+0.6
${}^3_1\text{TS5}^{-1}$	−1.2	+10.5
${}^5_1\text{Cr}(\text{CO}_2\text{H})^{-1} \cdot \text{PhOH}$	−8.9	+5.5
${}^5_1\text{TS5}^{-1}$	+6.9	+18.6

Figure S18. (A) Molecular geometry, (B) highest SOMO and (C) spin density plot of 5_0TS5^{-1} . For clarity, tBu groups and most H atoms have been omitted.

Figure S19. Overlapped displaced geometries along the imaginary frequency for ${}^3\text{TS5}^{-1}$ (A) and ${}^5\text{TS5}^{-1}$ (B). Scale displacement ± 0.35 . For clarity, tBu groups and most H atoms have been omitted.

Second Protonation: Dianionic Pathway

Table S17. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the doubly reduced metal-bound hydroxycarbonyl $[\text{Cr}(\text{L})(\text{CO}_2\text{H})(\text{DMF})_n]^{-2}$ ($n = 0, 1$) and transition states for their protonation, in kcal/mol. ${}^6_1\text{TS5}^{-2}$ could not be found, but relaxed potential energy surface scans suggest it is not the lowest energy for the dianionic pathway. Entries in red presented large spin contamination.

Species	E	[qG]
${}^2_0\text{Cr}(\text{CO}_2\text{H})^{-2} + \text{DMF}$	+6.7	+6.3
${}^4_0\text{Cr}(\text{CO}_2\text{H})^{-2} + \text{DMF}$	0.0	0.0
${}^6_0\text{Cr}(\text{CO}_2\text{H})^{-2} + \text{DMF}$	+15.8	+14.2
${}^2_1\text{Cr}(\text{CO}_2\text{H})^{-2}$	-4.4	+7.2
${}^4_1\text{Cr}(\text{CO}_2\text{H})^{-2}$	-7.2	+3.9
${}^6_1\text{Cr}(\text{CO}_2\text{H})^{-2}$	+4.0	+14.6
${}^2_0\text{TS5}^{-2}$	+8.5	+20.6
${}^4_0\text{Cr}(\text{CO}_2\text{H})^{-2} \cdot \text{PhOH}$	-14.3	-3.2
${}^4_0\text{TS5}^{-2}$	-9.8	+1.1
${}^6_0\text{TS5}^{-2}$	-4.3	+6.2
${}^2_1\text{TS5}^{-2}$	-9.1	+13.5
${}^4_1\text{Cr}(\text{CO}_2\text{H})^{-2} \cdot \text{PhOH}$	-21.9	+3.7
${}^4_1\text{TS5}^{-2}$	-12.5	+9.5

Eq S8: $\Delta[\text{qG}] = 25.0$ kcal/mol

V vs $\text{PHNZ}^{-}/\text{PHNZ} = -1.08$. V vs $\text{Fc}^{+}/\text{Fc} = -2.71$. Calibrated V vs $\text{Fc}^{+}/\text{Fc} = -2.35$.

Figure S20. (A) Spin density and (B) highest SOMOs of ${}^4_0\text{Cr}(\text{CO}_2\text{H})^{-2}$, presenting opposite spin. For clarity, tBu groups and most H atoms have been omitted.

Figure S21. (A) Highest SOMO and (B) spin density of ${}^4_0\text{TS5}^{-2}$. For clarity, tBu groups and most H atoms have been omitted.

Carbonyl Complexes

Table S18. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the neutral carbonyl complexes Cr(L)(CO)(DMF)_n (n = 0, 1), in kcal/mol.

Species	E	[qG]
${}^1_0\text{Cr}(\text{CO})^0 + \text{DMF}$	+26.7	+15.9
${}^3_0\text{Cr}(\text{CO})^0 + \text{DMF}$	+16.8	+4.6
${}^5_0\text{Cr}(\text{CO})^0 + \text{DMF}$	+15.3	+0.6
${}^1_1\text{Cr}(\text{CO})^0$	+13.3	+14.3
${}^3_1\text{Cr}(\text{CO})^0$	0.0	0.0
${}^5_1\text{Cr}(\text{CO})^0$	+5.4	+2.3

$$\text{Eq S9: } \Delta[\text{qG}] = -9.2 \text{ kcal/mol}$$

$$\text{Eq S10: } \Delta[\text{qG}] = -14.4 \text{ kcal/mol}$$

CO Release

$$\text{Eq S11: } \Delta[\text{qG}] = -5.2 \text{ kcal/mol}$$

Figure S22. CVs of 1.0 mM $\text{Cr}(\text{tbu_dhbpy})\text{Cl}(\text{H}_2\text{O})$ under Ar (black) and CO (red) saturation conditions. Conditions: 0.1 M $\text{TBAPF}_6/\text{DMF}$; glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode; 100 mV/s scan rate; referenced to internal ferrocene standard.²

Table S19. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the anionic carbonyl complexes $[\text{Cr}(\text{L})(\text{CO})(\text{DMF})_n]^-$ ($n = 0, 1$), in kcal/mol.

Species	E	[qG]
$\text{}^2_0\text{Cr}(\text{CO})^{-1} + \text{DMF}$	0.0	0.0
$\text{}^4_0\text{Cr}(\text{CO})^{-1} + \text{DMF}$	+5.2	+3.8
$\text{}^6_0\text{Cr}(\text{CO})^{-1} + \text{DMF}$	+4.6	+0.9
$\text{}^2_1\text{Cr}(\text{CO})^{-1}$	-9.6	+1.7
$\text{}^4_1\text{Cr}(\text{CO})^{-1}$	-6.4	+4.1
$\text{}^6_1\text{Cr}(\text{CO})^{-1}$	-3.6	+4.4

Eq S12: $\Delta[\text{qG}] = 13.6$ kcal/mol

V vs $\text{PHNZ}^-/\text{PHNZ} = -0.59$. V vs $\text{Fc}^+/\text{Fc} = -2.21$. Calibrated V vs $\text{Fc}^+/\text{Fc} = -2.02$.

Bicarbonate Formation

Table S20. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the transition states for HCO_3^- formation from ${}^3_1\text{Cr}(\text{CO}_2\text{H})^{-1}$ and CO_2 , in kcal/mol.

Species	E	[qG]
${}^3_0\text{TS6}^{-1} + \text{DMF}$	+19.5	+19.4
${}^3_0\text{TS7}^{-1} + \text{DMF}$	+19.2	+17.9
${}^3_0\text{TS8}^{-1} + \text{DMF}$	+17.8	+18.1
${}^5_0\text{TS6}^{-1} + \text{DMF}$	+27.2	+25.8
${}^5_0\text{TS7}^{-1} + \text{DMF}$	+28.0	+25.0
${}^5_0\text{TS8}^{-1} + \text{DMF}$	+23.3	+22.3
${}^3_1\text{TS6}^{-1}$	+6.6	+18.3
${}^3_1\text{TS7}^{-1}$	+6.0	+16.7
${}^3_1\text{TS8}^{-1}$	+3.5	+16.0
${}^5_1\text{TS6}^{-1}$	+13.5	+24.6
${}^5_1\text{TS7}^{-1}$	+13.6	+23.9
${}^5_1\text{TS8}^{-1}$	+11.9	+22.9

Figure S23. (A) Molecular geometry and (B) highest SOMO of ${}^3_1\text{TS7}^{-1}$ for the conversion of ${}^3_1\text{Cr}(\text{CO}_2\text{HCO}_2)^{-1}$ into ${}^3_1\text{Cr}(\text{CO}_2\text{CO}_2\text{H})^{-1}$. For clarity, tBu groups and most H atoms have been omitted.

Figure S24. Spin density plots of (A) ${}^3_1\text{TS6}^{-1}$, (B) ${}^3_1\text{TS7}^{-1}$ and (C) ${}^3_1\text{TS8}^{-1}$. For clarity, tBu groups and most H atoms have been omitted.

Figure S25. (A) Molecular geometry and (B) highest SOMO of ${}^3_1\text{TS8}^{-1}$ for the conversion of ${}^3_1\text{Cr}(\text{CO}_2\text{CO}_2\text{H})^{-1}$ into ${}^3_1\text{Cr}(\text{CO})^0$ and HCO_3^- . For clarity, tBu groups and most H atoms have been omitted.

Figure S26. Molecular geometry of the transition state for the concerted pathway for bicarbonate formation in the triplet spin manifold (${}^3_0\text{TS9}^{-1}$). For clarity, tBu groups and most H atoms have been omitted.

Hydride Formation

Table S21. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the Cr(L)(H)(DMF)_n ($n = 0, 1$) species, in kcal/mol.

Species	E	[qG]
$\text{}^2_0\text{Cr(H)}^0 + \text{DMF}$	+35.3	+23.7
$\text{}^4_0\text{Cr(H)}^0 + \text{DMF}$	+14.6	+2.6
$\text{}^4_1\text{Cr(H)}^0$	0.0	0.0

$$\text{Eq S13: } \Delta[\text{qG}] = -2.1 \text{ kcal/mol}$$

$$\text{Eq S14: } \Delta[\text{qG}] = -7.2 \text{ kcal/mol}$$

Ligand Protonation

Figure S27. Molecular geometry of the transition state for the protonation of the 5 position of the bpy backbone in the quartet spin state, ${}^4_1\text{TS11}^{-1}$. For clarity, tBu groups and most H atoms have been omitted.

Table S22. Relative potential (E) and corrected (concentration and quasiharmonic) triple zeta free energies ([qG]) for the products resulting from protonation of the bpy backbone at the 5 position, in kcal/mol.

Species	E	[qG]
${}^4_0\text{bpyH}^+-5^0 + \text{DMF}$	+14.2	+1.0
${}^6_0\text{bpyH}^+-5^0 + \text{DMF}$	+13.7	+0.5
${}^4_1\text{bpyH}^+-5^0$	0.0	0.0
${}^6_1\text{bpyH}^+-5^0$	2.9	+1.0

Eq S15: $\Delta[\text{qG}] = +8.1$ kcal/mol

Eq S16: $\Delta[\text{qG}] = +2.9$ kcal/mol

¹ Roy, L. E.; Jakubikova, E.; Guthrie, M. G.; Batista, E. R. *J. Phys. Chem. A* **2009**, *113*, 6745.

² Hooe, S. L.; Dressel, J. M.; Dickie, D. A.; Machan, C. W. *ACS Catal.* **2020**, *10*, 1146.